

## SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

# New Complex-Forming Organomineral Support Based on Aluminum Oxyhydroxide Modified with Nitrilotris(methylene phosphonic) Acid

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**Abstract**—A method for the surface chemical modification of aluminum oxyhydroxide (boehmite  $\gamma$ -AlO(OH)) by the nitrilotris(methylene phosphonic) acid (NTP) complexing ligand is proposed. The unmodified and NTP-modified boehmites are characterized using X-ray powder diffraction, XPS, and IR spectroscopy; the acid–base and complex-forming properties of surface-grafted NTP are studied. One of the three phosphonic groups of NTP is found to be involved in binding to the boehmite surface. The surface concentration and stepwise dissociation constants of grafted NTP are determined. A study of the nickel(II) sorption as a function of aqueous acidity shows that the modifying coating increases the sorption capacity of boehmite (causing  $\text{pH}_{50}$  to shift by one unit toward lower values). In terms of surface complexation theory, nickel(II) sorption from aqueous solutions may be described by models involving  $\equiv\text{Al}-\text{ONi}^+$  and  $\equiv\text{Al}-\text{ONi}(\text{OH})$  complexes in the case of boehmite and  $\equiv\text{Al}-\text{LH}_i \text{Ni}^{i-3}$  ( $i = 0, 1, 2, \text{ or } 3$ ) complexes in the case of NTP-modified boehmite (NTP-boehmite). NTP anchorage to the surface decreases the stability of nickel(II) complexes compared to their analogues in solutions. A mechanism of nickel(II) ion binding by NTP-boehmite is suggested. The prepared new organomineral support can be used to immobilize those metal ions that form stable complexes with phosphonic acids.

**Keywords:** chemical surface modification, aluminum oxyhydroxide, phosphonic complexones, surface complexation

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## INTRODUCTION

Mineral supports based on oxides, oxyhydroxides, and hydroxides of silicon ( $\text{SiO}_2$ ), iron ( $\text{Fe}_3\text{O}_4$ ,  $\gamma$ - $\text{Fe}_2\text{O}_3$ , and  $\alpha$ - $\text{FeO}(\text{OH})$ ), aluminum ( $\gamma$ - $\text{Al}_2\text{O}_3$ ,  $\gamma$ - $\text{AlO}(\text{OH})$ , and  $\alpha$ - $\text{Al}(\text{OH})_3$ ), manganese ( $\text{MnO}_2$ ), magnesium ( $\text{MgO}$ ), zinc ( $\text{ZnO}$ ), titanium ( $\text{TiO}_2$ ), or other metals serve for immobilizing various metal ions on their surfaces, including heavy, noble, and catalytically active metal ions. This is the basis for the use of (hydr)oxide supports in the sorption decontamination of waters, preconcentration and separation of metal ions, preparation of supported heterogeneous metal catalysts, synthesis of photo/electrochemically active materials, etc. For the more efficient retention of heavy-metal ions (Cu(II), Cd(II), Co(II), Ni(II), Pb(II), As(III), Cr(III), Zn(II), Mn(II), Hg(II), etc.), (hydr)oxides can be additionally surface-modified with compounds whose functional groups exhibit stronger or specific complexing properties compared to the surface OH groups of the unmodified supports [1, 2]. One new approach to the surface functionalization of (hydr)oxides involves the use phosphonic acids, with their anchoring phosphonic group  $\text{PO}(\text{OH})_2$ , as mod-

ifiers [3–7]. Along with various derivatives of alkyl/arylphosphonic acids containing one terminal complexing group ( $-\text{NH}_2$  or  $-\text{COOH}$ ) [8, 9], more promising modifiers to obtain complexing supports can be phosphonic complexones, which contain other coordinatively active sites ( $-\text{COOH}$ ,  $-\text{OH}$ ,  $-\text{PO}(\text{OH})_2$ , and N atoms) in addition to the anchor  $\text{PO}(\text{OH})_2$ - groups; these additional sites can bind to metal ions to form stable chelate rings. A wide range of commercially available phosphonic complexones (imino-*N*-acetic-*N*-methylene phosphonic acid/*N*-phosphonomethylglycine (PMG)/glyphosate, imino-*N,N*-diacetic-*N*-methylene phosphonic acid (IDAMP), 1-hydroxyethylidene diphosphonic acid (OEDP), iminodi(methylene phosphonic acid (IDP), *N*-hydroxyethylimino-*N,N*-di(methylene phosphonic acid (HEIDP) nitrilotris(methylene phosphonic acid (NTP), ethylenediamine-*N,N,N',N'*-tetra(methylene phosphonic acid (EDTP), diethylenetriamine *N,N,N',N'*-penta(methylene phosphonic acid (DTPP), etc.), greatly facilitates the synthesis of such chemically modified (hydr)oxides. In the literature there is very few information on the surface functionalization of (hydr)oxides ( $\text{SiO}_2$ ,  $\text{Fe}_3\text{O}_4$ ,  $\gamma$ - $\text{Fe}_2\text{O}_3$ ,

$\alpha$ -FeO(OH), and  $\gamma$ -AlO(OH)) by phosphonic complexones [10–15]. Moreover, there is no full understanding as to the structure of the formed phosphonic coating, the mechanism of binding of metal ions to the modified surface, and especially the relationship between the complexation of metal ions with the free and surface-immobilized phosphonic complexones. Of the metal (hydr)oxides, convenient objects for modification are aluminum compounds (oxide Al<sub>2</sub>O<sub>3</sub>, oxyhydroxide AlO(OH), and hydroxide Al(OH)<sub>3</sub>) due to their availability, non-toxicity, large specific surface area, chemical stability, and high concentrations of active surface centers involved in the binding of modifiers [16]. Therefore, the aim of this work was to study the conditions for the surface-modifying of one of the aluminum oxyhydroxides ( $\gamma$ -AlO(OH), boehmite) by nitrilotris(methylene phosphonic) acid (NTP) and to comprehensively study the physicochemical properties of the thus-obtained support (NTP-boehmite), including protolytic and sorption characteristics with respect to nickel(II) ions.

## EXPERIMENTAL

Boehmite  $\gamma$ -AlO(OH) samples were prepared via alkali hydrolysis of aluminum salts as described elsewhere [17]. For this purpose, to aqueous solution of Al(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O (20.0 g in 50 mL water), NaOH solution (6.49 g in 30 mL water) was dropped under continuous stirring at ~3 mL/min. The thus-obtained amorphous precipitate was kept at 90°C for 4 h, thoroughly washed with distilled water until the reaction to NO<sub>3</sub><sup>-</sup> with diphenylamine became negative (the reaction sensitivity was 1–5  $\mu$ g NO<sub>3</sub><sup>-</sup> in the sample), filtered, air-dried at 20°C and then in a drying cabinet at 220°C for 4 h. Boehmite was produced by the following dehydration scheme: Al(OH)<sub>3</sub> · nH<sub>2</sub>O → bayerite  $\alpha$ -Al(OH)<sub>3</sub> → gibbsite  $\gamma$ -Al(OH)<sub>3</sub> → pseudoboehmite → boehmite  $\gamma$ -AlO(OH).

The NTP used was a commercially available sample (product AP 1, series Cublen®, Zschimmer and Schwarz). A complexone solution (0.1 mol/L) was prepared by dissolving a sample in distilled water, followed by standardization by potentiometric titration with an alkali solution. Boehmite surface modification was via immobilization, by treating boehmite (1.0 g) with an NTP solution (0.1 mol/L, 10 mL) at 60°C for 3 h. Then, the sorbent was filtered, thoroughly washed with distilled water to pH 7, and air-dried (60°C, 2 h). To determine the grafted NTP, the residual NTP concentration in the filtrate was determined after the NTP was oxidized to phosphate. For this, the resulting filtrate was diluted 10<sup>4</sup>-fold, to the solution (50 mL) added were 1 mL of 30% H<sub>2</sub>SO<sub>4</sub> and 0.4 g (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and then it was slowly concentrated to ~10 mL on a water bath. Afterwards, the solution was transferred into a 50-mL flask, and the phosphate ion

was determined spectrophotometrically as the phosphate–molybdenum blue formation reaction. The absorbance of colored solutions was measured on a UNICO 1201 spectrophotometer at  $\lambda = 882$  nm in a 5-cm cell. The calculated NTP concentration on the boehmite surface is 0.83 ( $\pm$ 0.02) mmol/g.

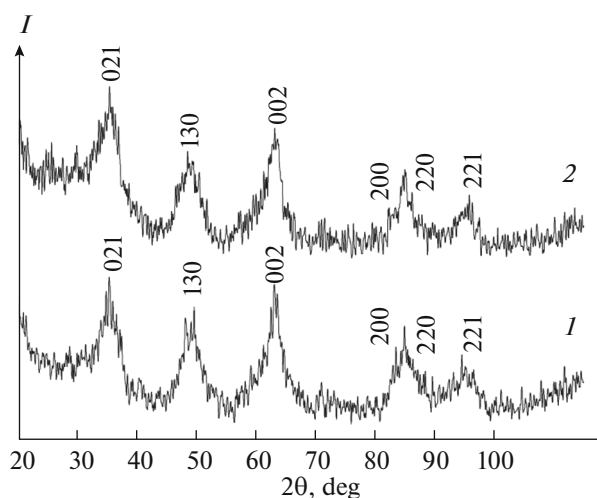
The hydroxo groups on the boehmite surface were determined using the fluoride ion substitution reaction:  $\equiv\text{Al}-\text{OH} + \text{F}^- \rightarrow \equiv\text{Al}-\text{F} + \text{OH}^-$ . For this purpose, a boehmite sample (0.05 g) was placed in a 50-mL portion of NaF solution (1 mmol/L; pH 5 adjusted with HNO<sub>3</sub> additions). The thus-prepared suspension was stirred for 24 h, then the sorbent was filtered and remnant fluoride ion was determined using an ELIT 221 fluoride-selective electrode by the multiple standard addition method. The calculated surface OH concentration on boehmite was 0.92  $\pm$  0.01 mmol/g.

The acid–base properties of boehmite/NTP-boehmite were studied by the potentiometric titration (with an I-160 MI ion meter) of the suspension (concentration 1 g/L) with a standard KOH solution at (20  $\pm$  1)°C and a constant ionic strength ( $I = 0.1$  mol/L, KCl). The potentiometric titration curves were processed in the Hyperquad 2008 program [18].

The nickel(II) sorption on boehmite/NTP-boehmite was studied as a function of acidity in the following manner: to NiCl<sub>2</sub> (0.1 mmol/L) solutions where the pH was adjusted (by HCl/KOH additions) in the presence of a background electrolyte (KCl) with the total ionic strength  $I = 0.1$  mol/L, weighed portions of the sorbent (1 g/L) were added. The suspension was shaken for 24 h at (20  $\pm$  1)°C, afterwards the sorbent was removed by centrifugation, pH in the centrifugate (equilibrium solution) was measured, and the remnant Ni(II) was measured spectrophotometrically as the formation of a colored dimethylglyoxime complex in an alkaline medium in the presence of an oxidizing agent (iodine). Absorbance was measured on a UNICO 1201 spectrophotometer at  $\lambda = 470$  nm in a 5-cm cell. The precision of determination was 10% [19]. The nickel(II) sorption was calculated as:  $\Gamma(\%) = 100(c_0 - c)/c_0$ , where  $c_0$  and  $c$  is, respectively, the initial and equilibrium concentration in solution. The modeling of sorption curve in terms of surface complex formation theory was carried out in Hyss and HypSpec software [18].

The static exchange capacity of NTP-boehmite in Ni(II) ions was derived from the sorption isotherm for the series of solutions with initial nickel(II) concentrations in the range 10<sup>-4</sup> to 10<sup>-3</sup> mol/L at pH 6.5.

X-ray diffraction spectra were measured on a DRON-3.0 diffractometer in monochromated FeK $\alpha$  radiation in the Bragg angle range 25°–115° in the step-by-step scan mode with a scan step of 0.1° and a time per point of 10 s. The average crystallite size was estimated using the Debye–Scherrer relationship.



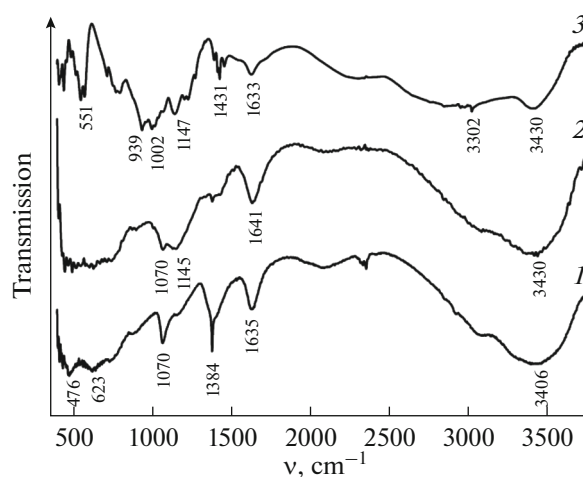
**Fig. 1.** Powder X-ray diffraction patterns of (1) boehmite and (2) NTP-boehmite.

X-ray photoelectron (XPE) spectra were measured on a SPECS electronic spectrometer using  $MgK_{\alpha}$  exciting radiation ( $h\nu = 1253.6$  eV) in the constant transmission energy (15 eV) mode of a Phoibos-150 energy analyzer. The measurements were performed at a residual pressure in the analyzer chamber maintained at  $2 \times 10^{-9}$  Torr by an oil free pump at 293 K. A test powder, without any preliminary treatment, was spread in a thin layer on the surface of pure indium and mounted on a molybdenum holder so that only the surface of the test powder fell into the zone of XPS analysis (the spot diameter was 5 mm). The binding energy scale of the spectrometer was calibrated against the  $Au4f_{7/2}$  line position ( $E_b = 84.0$  eV). The binding energy measurement error was  $\pm 0.1$  eV. The results were processed in CasaXPS software. The spectral lines in decomposition in components were fitted by a mixed Gaussian–Lorentzian function.

The Fourier-transform IR spectra of samples were recorded as KBr disks on an FSM-2201 IR spectrometer in the frequency range 400–4000  $cm^{-1}$  (in 2- $cm^{-1}$  steps). For this, 2.5 mg of the sample was pounded with an agate mortar and a pestle together with 250 mg KBr and pressed a disk by a hand hydraulic press.

## RESULTS AND DISCUSSION

The positions and relative intensities of lines in the diffraction pattern of the synthesized aluminum oxyhydroxide indicate that its crystal structure corresponds to boehmite  $\gamma$ -AlO(OH) (ICPDS card 3-65). Chemical modification of the boehmite surface with NTP does not alter the boehmite crystal lattice (Fig. 1). The crystallite sizes calculated from the Debye–Scherrer relation are the same for boehmite and NTP-boehmite:  $23 \pm 3$  nm.



**Fig. 2.** IR spectra of (1) boehmite, (2) NTP-boehmite, and (3) NTP.

The IR spectrum of the prepared boehmite (Fig. 2) features bands at 476 and 623  $cm^{-1}$  due to the Al–O stretching vibrations. Strong bands at 3600–3000 and 1635  $cm^{-1}$  relate, respectively, to the stretching and bending vibrations of O–H (boehmite OH groups and sorbate water). The spike at 1070  $cm^{-1}$ , typical of boehmite, arises from the bending vibrations of OH...OH hydrogen bonds of interplanar hydroxo groups [17]. The foreign peak at 1384  $cm^{-1}$  relates to chemisorbed  $NO_3^-$  ions, since the precursor in boehmite synthesis was  $Al(NO_3)_3$ . The IR spectra of unbound NTP in the range where the vibrations of phosphonic groups appear (900–1400  $cm^{-1}$ ) feature characteristic bands due to the stretching vibrations of a phosphoryl group P=O (1147  $cm^{-1}$ ) and the anti-symmetrical (1002  $cm^{-1}$ ) and symmetrical (939  $cm^{-1}$ ) stretching vibrations of P–O in protonated phosphonic groups ( $-H_2PO_3$  and  $-HPO_3^-$ ). The broad bands in the range 2100–2300  $cm^{-1}$  and 2600–2800  $cm^{-1}$  relate to the P–OH stretching vibrations [20]. The spectrum of NTP-modified boehmite, compared to the unmodified sample, features enhanced absorption in the range where phosphonic groups vibrate with a peak near 1145  $cm^{-1}$  (P=O and P–OAl vibrations [21]).

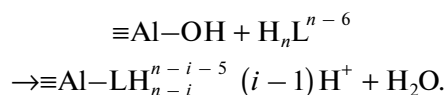
The XPE spectra of NTP, boehmite, and NTP-modified boehmite appear in Fig. 3. Comparing the survey spectra, one can clearly see that, when NTP is anchored to the boehmite surface, new characteristic lines appear due to carbon (C1s), phosphorus (P2p), and nitrogen (N1s). NTP binding to the boehmite surface is manifested in the Al2p spectrum by the appearance of a spectral component with the binding energy  $E_b = 75.1$  eV (Al–OP bond) in addition to the 74.3-eV component, which is characteristic of Al–O bonds in oxides [20]. For unbound NTP, the P2p spectrum is represented by a single line with  $E_b = 134.1$  eV, corresponding to an equivalent state of phosphorus atoms

in all three phosphonic groups of an NTP molecule. The phosphorus spectrum for the NTP anchored to the boehmite surface comprises two components with binding energies of 134.1 and 133.3 eV with roughly equal contributions. Two closely positioned peaks in the P2*p* spectrum were observed earlier for various sorbed phosphonic complexones (glycine-*N,N*-di(methylenephosphonic) acid on steel [22], imino-*N,N*-diacetic-*N*-methylenephosphonic acid on Fe<sub>3</sub>O<sub>4</sub> [12], and NTP on aluminum [23]). Presumably, the appearance of a low-energy component upon anchorage of NTP to the boehmite surface arises from the acquisition of a new state by phosphorus atoms upon the formation of P–OAl chemical bonds. The N1*s* spectrum for crystalline NTP consists of one component (402.5 eV) related to the protonated tertiary nitrogen atom of the betaine structure of the complexone. For NTP immobilized on the boehmite surface, the N1*s* spectrum features two components of similar intensities with  $E_b = 402.5$  and 400.1 eV. The appearance of an additional spectral component with  $E_b = 400.1$  eV can be associated with the formation of a donor–acceptor bond between the NTP nitrogen atom and the surface aluminum atoms, the latter being strong Lewis centers. Positionally similar spectral components in the N1*s* spectra were previously observed for surface-bound phosphonic complexones [12, 22, 23]. The N1*s* peak with  $E_b = 407.8$  eV in the spectrum of unmodified boehmite relates to the nitrogen of chemisorbed nitrate ions. The decomposition of the C1*s* carbon spectrum in NTP (free and surface-bound) gives several components; the major component (285.1 eV) corresponds to the methylene CH group of the NTP, and the 286.5 and 288.9 eV components are related to the C–O and C=O states (surface contamination with carbonaceous compounds). The O1*s* oxygen spectrum for unmodified boehmite can be fitted by two components: 531.0 eV (Al–O) and 532.8 eV (Al–OH) [20]. Two non-equivalent valence states of oxygen are observed for free NTP: 531.5 eV (P=O) and 533.0 eV (P–OH). The major component of the O1*s* spectrum for NTP-boehmite,  $E_b = 532.5$  eV, is likely related to the generation of new surface bond P–OAl; the other components correspond to P–OH (533.4 eV) and Al–O (531.2 eV) bonds.

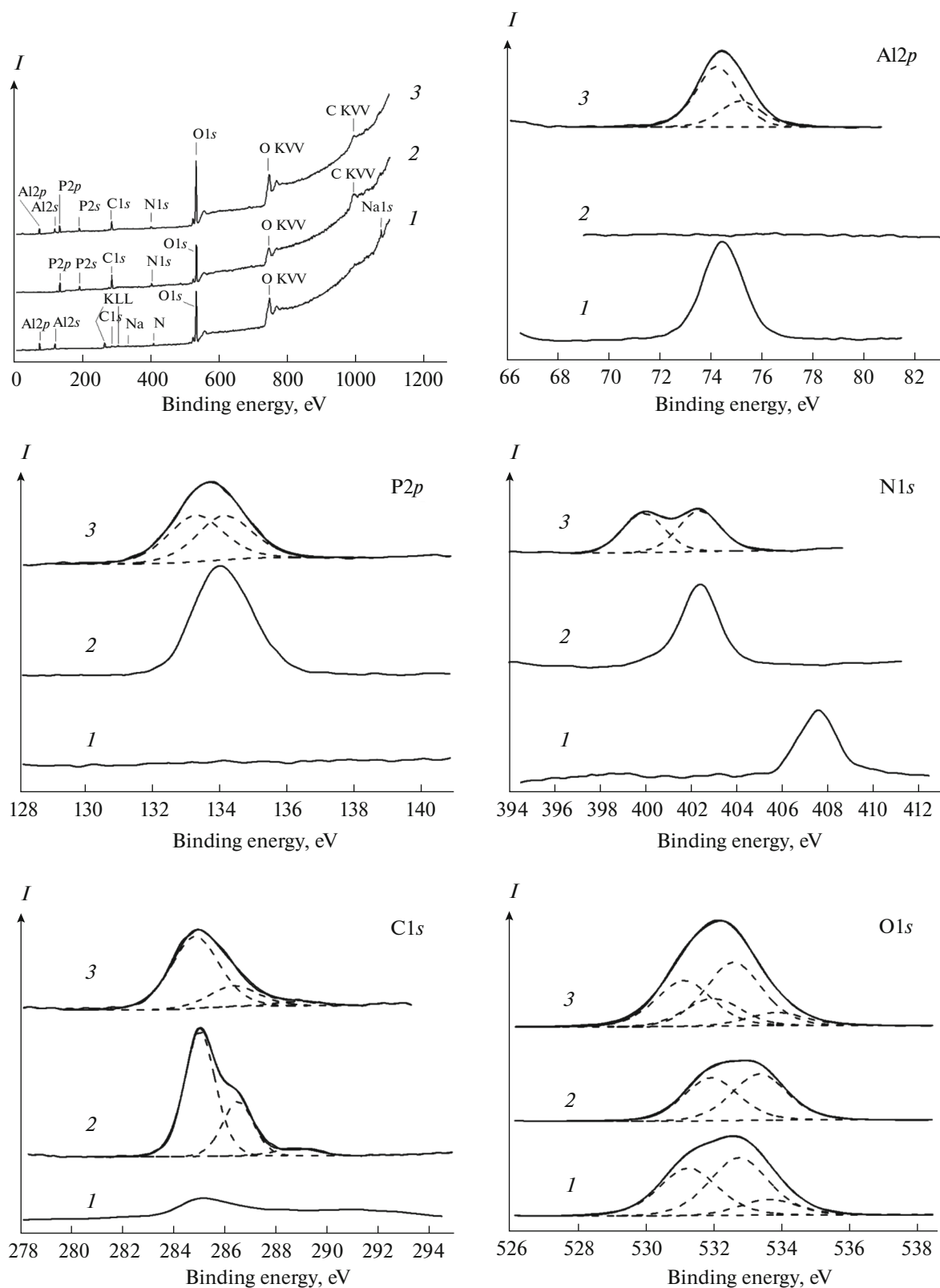
So, the results of IR and XPE spectroscopic studies of air-dry boehmite and NTP-boehmite samples show that the state of surface-immobilized NTP involves both surface-bound and unbound phosphonic groups. Further studies of the properties of the supports were carried out with samples that were in contact with an aqueous phase, which however did not rule out a change in the character of interaction of the modifier with the surface. Protolytic properties of grafted ligands are a very important characteristic of complexing supports; they are studied by titrimetric methods. The mathematical processing of the acid–base titration curves of supports that bear grafted compounds is

a difficult task, the solution of which should take into account the existence of a surface electric charge associated with the dissociation of grafted groups, as well as possible contributions of residual surface groups, the interaction between grafted groups, energy heterogeneity of the surface, etc. [3, 11]. Here, we used the simplest non-electrostatic model of the surface to model the acid–base titration curves for boehmite and NTP-boehmite at a constant ionic strength ( $I = 0.1$  mol/L) in solution; i.e., the electrostatic factor associated with the surface charge was ignored. Such a “pseudo-homogeneous” model is used in the literature to describe the protolytic properties of supports along with more complex models that take into account a double electric layer. When modeling the potentiometric titration curve of a boehmite suspension with a standard alkali solution (Fig. 4), we took into account the amphoteric properties of surface OH groups [16]:  $\equiv\text{AlOH} + \text{H}^+ \leftrightarrow \equiv\text{AlOH}_2^+$ ;  $\equiv\text{AlOH} \leftrightarrow \equiv\text{AlO}^- + \text{H}^+$ . The calculated equilibrium constants (Table 1) and the zero-charge point of the surface ( $\text{pH}_{zcp} 8.5 \pm 0.2$ ) fall within the ranges of values reported for boehmite [16].

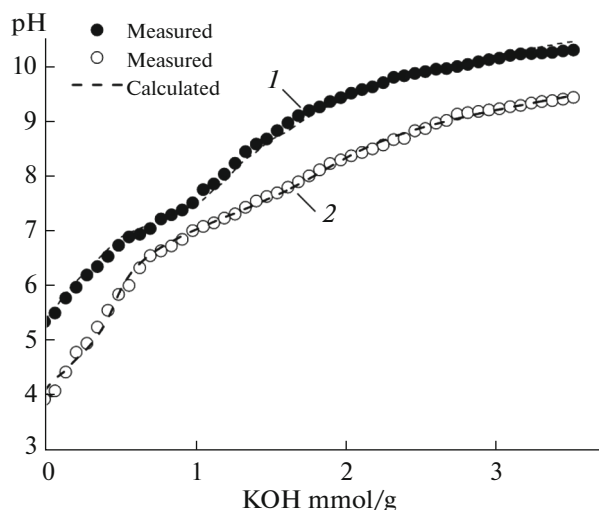
The chemical modification of boehmite by NTP, as the modification of other metal (hydr)oxides by phosphonic acids [4–6], occurs due to the ligand substitution reaction of surface OH groups. Since the content of grafted NTP on boehmite is found to be close to the concentration of surface OH groups of the unmodified boehmite (see above), it can be assumed that an NTP molecule, which is a hexaprotic acid ( $\text{H}_6\text{L}$ ) in an aqueous solution, is anchored to form only mononuclear (including one surface aluminum atom) complexes according to the scheme



The researchers who studied NTP adsorption on goethite [10, 24] and on boehmite [13] made a similar suggestion. The mathematical processing of titration curves for NTP-boehmite (Fig. 4) show that the acid basicity decreases when NTP is anchored to the surface; surface-grafted NTP behaves as a tetraprotic acid  $\equiv\text{Al}-\text{LH}_4^-$ , and this can be logically assigned to the involvement of one of the NTP phosphonic groups in surface interactions. A comparison of the dissociation constants of surface-grafted NTP groups with the respective constants for free NTP in solution (Table 1) shows that binding to the surface decreases the basicity of the nitrogen atom, as was previously observed for grafted amino groups on silica [3, 11]. The reason behind the lowered basicity of the nitrogen atom may lie in its coordination interaction with surface aluminum atoms, established according to the XPS. The acidity of the phosphonic groups in the NTP slightly decreases upon anchorage to the surface as compared to the acidity of its counterpart in solution, just as the



**Fig. 3.** XPS spectra and their decomposition into components for (1) boehmite, (2) NTP, and (3) NTP-boehmite.

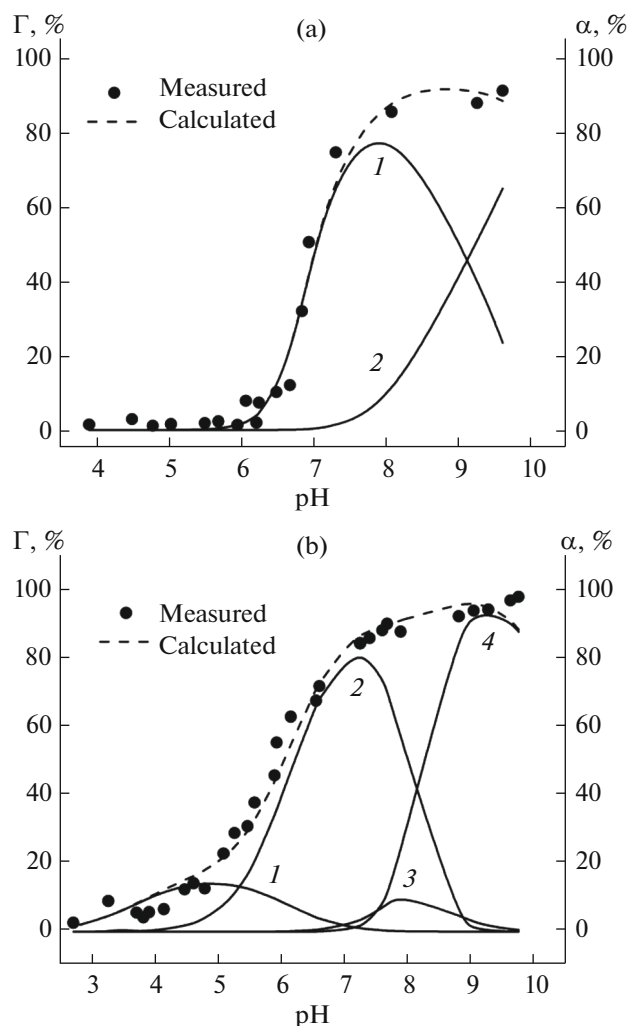


**Fig. 4.** Acid–base titration curves for (1) boehmite and (2) NTP-boehmite.

behavior of aminodi(methylenephosphonic) groups anchored to silica [11, 15].

So, on the basis of our data and literature data on possible mechanisms of interaction of the phosphonic group with oxide supports [4–6], we can suggest a structure of the grafted NTP layer on boehmite. The IR and XPE spectroscopic data relating to air-dry samples imply the existence of free and surface-bound phosphonic groups. The stoichiometry between the OH groups in unmodified boehmite and in grafted NTP (1.1 : 1.0) and the protolytic characteristics of the grafted NTP, which refer to a hydrated sample where the NTP is a tetraprotic acid, indicate that one phosphonic group of the NTP is involved in surface binding to one aluminum atom. A similar suggestion was made earlier in the study of NTP sorption on boehmite [13] and goethite [10]. With this, unbound phosphonic groups of the NTP and the nitrogen atom are functional active sites that can participate in coordination to metal ions.

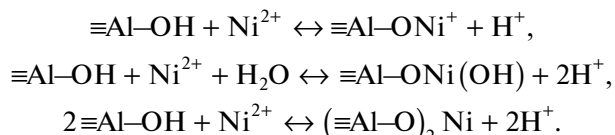
As a model cation for studying the complexing properties of NTP-boehmite, we chose a doubly charged nickel(II) cation, whose complexes with NTP were studied in aqueous solutions [25–27] and in a crystalline state [27, 28]. One very important parameter affecting the sorption of metal ions by complexing sorbents is the solution acidity. Nickel(II) sorption by boehmite increases with increasing solution pH (Fig. 5), as one can observe for various metal ions on aluminum (hydr)oxides [16]. The pH at which 50% of the nickel(II) is sorbed under the given conditions is  $\text{pH}_{50}$  7.0, and the complete nickel(II) binding by boehmite occurs in an alkaline environment. In general, the nickel(II) sorption capacity on aluminum (hydr)oxides is significantly lower than for doubly charged ions of other heavy metals, varying in the following order (for



**Fig. 5.** (a) Nickel(II) sorption on boehmite vs acidity ( $\Gamma$ , %) and the surface species distribution diagram ( $\alpha$ , %) (1)  $\equiv\text{Al}-\text{ONi}^{2+}$  and (2)  $\equiv\text{Al}-\text{ONi}(\text{OH})$ .  $c_{\text{Ni(II)}} = 10^{-4}$  mol/L,  $c_{\text{boehmite}} = 1$  g/L. (b) Nickel(II) sorption on NTP-modified boehmite vs acidity ( $\Gamma$ , %) and the surface species distribution diagram ( $\alpha$ , %): (1)  $\equiv\text{Al}-\text{LH}_3\text{Ni}^{2+}$ , (2)  $\equiv\text{Al}-\text{LH}_2\text{Ni}^+$ , (3)  $\equiv\text{Al}-\text{LHNi}^{2-}$ , and (4)  $\equiv\text{Al}-\text{LNi}^{3-}$ .  $c_{\text{Ni(II)}} = 10^{-4}$  mol/L,  $c_{\text{NTP-boehmite}} = 1$  g/L.

amorphous  $\text{Al}(\text{OH})_3$ ):  $\text{Cu(II)} > \text{Pb(II)} > \text{Zn(II)} > \text{Cd(II)} > \text{Ni(II)}$ ,  $\text{Co(II)}$  [29];  $\text{Cu(II)} > \text{Pb(II)} > \text{Zn(II)} > \text{Ni(II)} > \text{Co(II)} > \text{Cd(II)}$  [30].

The obtained experimental data on the binding of nickel(II) by boehmite were considered in terms of surface complexation modelling (SCM [31]) as applied to the interaction of metal ions with the surface of oxides. During the sorption of ions of doubly charged metals on aluminum (hydr)oxides, in particular, the following surface reactions are possible [16]:



**Table 1.** Protolytic properties of boehmite and NTP-modified boehmite (0.1 mol/L KCl, (20 ± 1°C))

Equilibrium	log <i>K</i>
Boehmite	
$\equiv\text{Al}-\text{OH}_2^+ \leftrightarrow \equiv\text{Al}-\text{OH} + \text{H}^+$	-7.2 ± 0.1
$\equiv\text{Al}-\text{OH} \leftrightarrow \equiv\text{Al}-\text{O}^- + \text{H}^+$	-9.8 ± 0.1
NTP anchored to boehmite	
$\equiv\text{Al}-\text{L}^{5-} + \text{H}^+ \leftrightarrow \equiv\text{Al}-\text{LH}^{4-}$	9.7 ± 0.1
$\equiv\text{Al}-\text{L}^{5-} + 2\text{H}^+ \leftrightarrow \equiv\text{Al}-\text{LH}_2^{3-}$	18.9 ± 0.1
$\equiv\text{Al}-\text{LH}^{4-} + \text{H}^+ \leftrightarrow \equiv\text{Al}-\text{LH}_2^{3-}$	9.2 ± 0.1
$\equiv\text{Al}-\text{L}^{5-} + 3\text{H}^+ \leftrightarrow \equiv\text{Al}-\text{LH}_3^{2-}$	26.2 ± 0.1
$\equiv\text{Al}-\text{LH}_2^{3-} + \text{H}^+ \leftrightarrow \equiv\text{Al}-\text{LH}_3^{2-}$	7.3 ± 0.1
$\equiv\text{Al}-\text{L}^{5-} + 4\text{H}^+ \leftrightarrow \equiv\text{Al}-\text{LH}_4^-$	30.0 ± 0.2
$\equiv\text{Al}-\text{LH}_3^{2-} + \text{H}^+ \leftrightarrow \equiv\text{Al}-\text{LH}_4^-$	3.8 ± 0.2
NTP in solution (0.1 mol/L KNO <sub>3</sub> , 25°C) [25, 26]	
$\text{L}^{6-} + \text{H}^+ \leftrightarrow \text{HL}^{5-}$	12.5
$\text{L}^{6-} + 2\text{H}^+ \leftrightarrow \text{H}_2\text{L}^{4-}$	19.72
$\text{HL}^{5-} + \text{H}^+ \leftrightarrow \text{H}_2\text{L}^{4-}$	7.22
$\text{L}^{6-} + 3\text{H}^+ \leftrightarrow \text{H}_3\text{L}^{3-}$	25.62
$\text{H}_2\text{L}^{4-} + \text{H}^+ \leftrightarrow \text{H}_3\text{L}^{3-}$	5.90
$\text{L}^{6-} + 4\text{H}^+ \leftrightarrow \text{H}_4\text{L}^{2-}$	30.21
$\text{H}_3\text{L}^{3-} + \text{H}^+ \leftrightarrow \text{H}_4\text{L}^{2-}$	4.59
$\text{L}^{6-} + 5\text{H}^+ \leftrightarrow \text{H}_5\text{L}^-$	31.8
$\text{H}_4\text{L}^{2-} + \text{H}^+ \leftrightarrow \text{H}_5\text{L}^-$	1.6
$\text{L}^{6-} + 6\text{H}^+ \leftrightarrow \text{H}_6\text{L}$	32.3
$\text{H}_5\text{L}^- + \text{H}^+ \leftrightarrow \text{H}_6\text{L}$	0.5

In the calculations we used the value we determined for the concentration of surface OH groups of boehmite ( $c_{\equiv\text{Al}-\text{OH}} = 0.92$  mmol/g) and their calculated protonation/dissociation constants (Table 1). The nickel(II) hydrolysis constants for  $I = 0.1$  mol/L ( $\log K_{\text{h1}} = -8.0$ ,  $\log K_{\text{h2}} = -16.76$ ) were taken from [25]. The modeling was in terms of the non-electrostatic surface model; along with electrostatic models, this model is used for the description of sorption processes where metal ions and oxides are involved [31]. It was found that the sorption curve for nickel(II) on boehmite can be described as the formation of two types of surface complexes; a sharp increase in sorption is associated with the formation of  $\equiv\text{Al}-\text{ONi}^+$  species, which are hydrolyzed in alkaline media to yield  $\equiv\text{Al}-\text{ONi}(\text{OH})$  (Fig. 5, Table 2). Compositionally similar surface complexes were used to describe nickel(II) sorption on amorphous  $\text{Al}(\text{OH})_3$  [29] and

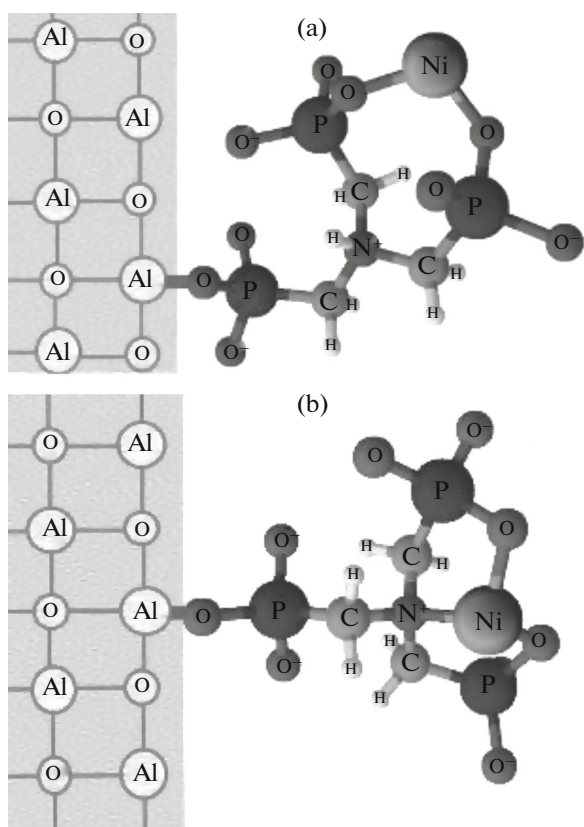
**Table 2.** Complexing properties of boehmite and NTP-modified boehmite (0.1 mol/L KCl, (20 ± 1°C))

Equilibrium	log <i>K</i>
Boehmite	
$\equiv\text{Al}-\text{OH} + \text{Ni}^{2+} \leftrightarrow \equiv\text{Al}-\text{ONi}^+ + \text{H}^+$	-3.6 ± 0.1
$\equiv\text{Al}-\text{OH} + \text{Ni}^{2+} + \text{H}_2\text{O} \leftrightarrow \equiv\text{Al}-\text{ONi}(\text{OH}) + 2\text{H}^+$	-12.8 ± 0.3
Ni(II)-NTP-boehmite	
$\equiv\text{Al}-\text{L}^{5-} + \text{Ni}^{2+} \leftrightarrow \equiv\text{Al}-\text{LNi}^{3-}$	7.0 ± 0.2
$\equiv\text{Al}-\text{L}^{5-} + \text{Ni}^{2+} + \text{H}^+ \leftrightarrow \equiv\text{Al}-\text{LHNi}^{2-}$	14.5 ± 0.3
$\equiv\text{Al}-\text{LNi}^{3-} + \text{H}^+ \leftrightarrow \equiv\text{Al}-\text{LHNi}^{2-}$	7.5 ± 0.3
$\equiv\text{Al}-\text{L}^{5-} + \text{Ni}^{2+} + 2\text{H}^+ \leftrightarrow \equiv\text{Al}-\text{LH}_2\text{Ni}^-$	23.1 ± 0.1
$\equiv\text{Al}-\text{LHNi}^{2-} + \text{H}^+ \leftrightarrow \equiv\text{Al}-\text{LH}_2\text{Ni}^-$	8.6 ± 0.3
$\equiv\text{Al}-\text{L}^{5-} + \text{Ni}^{2+} + 3\text{H}^+ \leftrightarrow \equiv\text{Al}-\text{LH}_3\text{Ni}$	28.5 ± 0.1
$\equiv\text{Al}-\text{LH}_2\text{Ni}^- + \text{H}^+ \leftrightarrow \equiv\text{Al}-\text{LH}_3\text{Ni}$	5.4 ± 0.2
Ni(II)-NTP in solution (0.1 mol/L KNO <sub>3</sub> , 25°C) [25, 26]	
$\text{Ni}^{2+} + \text{L}^{6-} \leftrightarrow \text{NiL}^{4-}$	11.3
$\text{Ni}^{2+} + \text{L}^{6-} + \text{H}^+ \leftrightarrow \text{NiHL}^{3-}$	19.6
$\text{NiL}^{4-} + \text{H}^+ \leftrightarrow \text{NiHL}^{3-}$	8.3
$\text{Ni}^{2+} + \text{L}^{6-} + 2\text{H}^+ \leftrightarrow \text{NiH}_2\text{L}^{2-}$	25.3
$\text{NiHL}^{3-} + \text{H}^+ \leftrightarrow \text{NiH}_2\text{L}^{2-}$	5.7
$\text{Ni}^{2+} + \text{L}^{6-} + 3\text{H}^+ \leftrightarrow \text{NiH}_3\text{L}^-$	28.5
$\text{NiH}_2\text{L}^{2-} + \text{H}^+ \leftrightarrow \text{NiH}_3\text{L}^-$	3.2

boehmite [32]. The values obtained for the equilibrium formation constants of the sorbed complexes were  $\log K = -4.0$  ( $\equiv\text{Al}-\text{ONi}^+$ ) and  $\log K = -13.8$  ( $\equiv\text{Al}-\text{ONi}(\text{OH})$ ) [32], close to our data.

The nickel(II) sorption versus aqueous acidity curve for NTP-modified boehmite shifts toward lower pH (pH<sub>50</sub> 6.0) relative to the curve for unmodified boehmite. From the literature it is known that 1 : 1 (mol/mol) complexes with various degrees of protonation ( $\text{NiH}_i\text{L}^{i-4}$  ( $i = 0, 1, 2, \text{ or } 3$ )) are formed in aqueous solutions in the Ni(II)-NTP system [25–27]. A similar set of complexes was used to model the interaction of nickel(II) with surface-immobilized NTP. The dissociation constants of surface-immobilized NTP determined previously (Table 1) and the nickel(II) hydrolysis constants taken from [25] were used in the calculations. The results show that the nickel(II) sorption curve on NTP-boehmite can be satisfactorily described by the formation of a set of  $\equiv\text{Al}-\text{LH}_i\text{Ni}^{i-3}$  ( $i = 0, 1, 2, \text{ or } 3$ ) complexes identical in composition to complexes in solutions. In earlier studies of equilibria involving NTP, metal ions (Cu(II), Cd(II), or Zn(II)), and boehmite, it was also





**Fig. 6.** Schematics of nickel(II) ion binding to the surface of NTP-modified boehmite: (a)  $\equiv\text{Al-LHNi}^{2-}$  complex and (b)  $\equiv\text{Al-LNi}^{3-}$  complex.

found that  $\equiv\text{Al-LH}_2\text{M}^-$ ,  $\equiv\text{Al-LHM}^{2-}$ , and  $\equiv\text{Al-LM}^{3-}$  complexes are formed on the surface [13]. Upon nickel(II) sorption on NTP-boehmite at pH 6–8,  $\equiv\text{Al-LH}_3\text{Ni}$  and  $\equiv\text{Al-LH}_2\text{Ni}^-$  protonated complexes are formed to convert to the monoprotonated complex  $\equiv\text{Al-LHNi}^{2-}$  or (at high alkalinities) to the normal complex  $\equiv\text{Al-LNi}^{3-}$ . The stability of surface nickel(II) complexes  $\equiv\text{Al-LH}_i\text{Ni}^{i-3}$  ( $i = 0, 1, \text{ or } 2$ ) is lower than that of the respective complexes in solution. So, the stability constants of  $\equiv\text{Al-LHNi}^{2-}$  and  $\equiv\text{Al-LNi}^{3-}$  are four to five orders of magnitude lower than for their homogeneous analogues  $\text{NiHL}^{3-}$  and  $-\text{NiL}^4$  (Table 2). This result differs from Kostenko et al.'s data [15], who found that  $\text{Cu(II)}$ ,  $\text{Pb(II)}$ ,  $\text{Zn(II)}$ , and  $\text{Cd(II)}$  complexes with amino-di(methylenephosphonic) acid immobilized on  $\text{SiO}_2$  ( $\text{SiO}_2-\text{H}_3\text{L}^-$ ) of composition  $\text{SiO}_2-\text{MH}_2\text{L}$  and  $\text{SiO}_2-\text{MHL}^-$  are more stable than their analogues in solutions.

Structural studies of nickel(II) complexes with NTP in solution [27] and in crystalline state [28] showed that the nitrogen atoms in  $\text{NiH}_i\text{L}$  ( $i = 1, 2, \text{ or } 3$ ) protonated complexes are not involved in coordination to nickel(II). Coordination is due to the oxygen atoms of two or three phosphonic groups with the clo-

sure of an unstable eight-membered ring(s). It can be assumed that the protonated surface nickel(II) complexes on NTP-boehmite have a similar structure with the only difference that only two phosphonic groups free of binding to the surface are involved in nickel(II) coordination (Fig. 6). A normal nickel(II) NTP complexonate of composition  $\text{NiL}^{4-}$  in solutions and in the crystalline state has a chelate structure with three five-membered rings involving a nitrogen atom [27, 28]. It is likely that the surface-anchored normal complex has a similar structure, and its lower stability can be explained by the presence of as few as two chelate metal rings.

It is of interest to compare the sorption properties of the prepared NTP-boehmite and other complex-forming sorbents containing grafted phosphonic groups, such as complexing ion exchangers based on polymers with amino-methylenephosphonic groups  $-\text{CH}_2-\text{NH}-\text{CH}_2-\text{PO}(\text{OH})_2$  [33] and silicas  $\text{SiO}_2$  bearing anchored amino-methylenephosphonic and amino-di(methylenephosphonic)  $-\text{N}(\text{CH}_2-\text{PO}(\text{OH})_2)_2$  acid groups [11, 15]. Polymeric phosphonic sorbents, represented by various industrial brands (Purolite S940 and S950, Lewatit TP260, and others), are widely used for binding various metal ions ( $\text{Cu(II)}$ ,  $\text{Zn(II)}$ ,  $\text{Ni(II)}$ ,  $\text{Cd(II)}$ , and  $\text{Fe(III)}$ ) along with other complexing polymers. Silicas with heterogenized phosphonic derivatives, in contrast, are poorly characterized, and are rarely used in practice. The advantages of all organomineral supports with grafted phosphonic acids and their derivatives are their nonswellability in solvents, mechanical strength, thermal stability, and high mass transfer rates. So, the results of this work show that the time to establish sorption equilibrium in the  $\text{Ni(II)}$ –NTP-boehmite system is 30–60 min against 24–48 h for phosphonic ion exchangers. The sorption properties of NTP-boehmite with respect to metal ions, including nickel(II), are not inferior to those provided by the phosphonic polymer sorbent, as can be seen when comparing the respective distribution ratios ( $D$ , mL/g):  $\log D = 3.4$  (amino-methylenephosphonic ion exchanger, pH 5.6) [34] against  $\log D = 3.0$  (NTP-boehmite, pH 5.6) and  $\log D = 4.0$  (NTP-boehmite, pH 7.5). A definite disadvantage of the phosphonic compounds heterogenized on oxide supports compared to polymer substrates consists in the lower concentration of grafted groups and, as a result, the lower sorption capacity for metal ions. For phosphonic polymer ion exchangers (Purolite S940), for example, it amounts to  $\sim 2$  mmol/g (in  $\text{Cu(II)}$  ions) against  $\sim 0.3$  mmol/g (in  $\text{Cu(II)}$  ions) for  $\text{SiO}_2-\text{ADPA}$  [15] and  $\sim 0.25$  mmol/g (in  $\text{Ni(II)}$  ions) for NTP-boehmite. The new organomineral support based on aluminum oxyhydroxide surface-modified with a phosphonic complexone, can be used to extract nickel(II) ions from the process solutions and wastewater of hydrometallurgical facilities, and to recover nickel-containing wastes in electroplating. Modified



boehmite, due to its improved complexing properties, can also be used as an efficient support for nickel(II)-based heterogeneous catalysts.

## CONCLUSIONS

The results of our work for the first time show the fundamental possibility of being chemically grafting to the aluminum oxyhydroxide surface not only for relatively simple derivatives of phosphonic acids [4], but also for structurally more complex polyphosphonic complexones, such as NTP. The body of the data obtained implies that the anchor function of NTP is carried out by only one phosphonic group of the complexone, making the remaining functional groups active in binding metal ions. The nickel(II) ion selected to study the complexing properties of the modified support, is a representative of the doubly charged heavy-metal cations (Co(II), Fe(II), Cu(II), Zn(II), Cd(II), and Pb(II)) that form complexes of similar composition with NTP in solutions, and this renders the results more general. It turned out that the stability of nickel(II) phosphonates formed on the boehmite surface with grafted NTP groups is lower than for their counterparts in solutions, probably, due to a decrease in NTP denticity upon anchorage. Further studies on the surface modification of aluminum (hydr)oxides by other phosphonic complexones will enable us to elucidate trends in the complexing properties of anchored complexones and to prepare new complexing organomineral supports for efficient/selective binding of various metal ions.

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## CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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