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Tetrad effect in the distribution constants of the lanthanides in their adsorption on the zeolite A

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Abstract

In this study, the changes of the distribution constants K_d of the lanthanide nitrates in the system: zeolite A (solid phase)–sodium nitrate (aqueous phase) were investigated. The convex and concave tetrad effect in the run of the K_d values of the lanthanides was found. The explanation of the tetrad effect through the covalency in Ln–O lanthanide bond (where Ln is lanthanide, O– oxygen) is included. It is evident from the supplementary data of diffusive reflectance spectra of the zeolites and lanthanide oxides in the VIS and infrared region, that the Nd^{3+} ion forms more covalent complex with the negatively charged oxygen atoms of the zeolite framework than the rest of the lanthanide ions and that La^{3+}, Nd^{3+}, Sm^{3+} ions strongly hydrolyze in the zeolite phase, which results in the shift of T–O–T band (asymmetric stretching vibration band of –Si–O–Al-subunits) toward lower wavelengths.

Keywords: Adsorption; Diffusive reflectance spectra; T–O–T framework vibration; Zeolites

1. Introduction

The tetrad effect in the lanthanide chemistry discovered independently by Fidelis and Siekierski [1] on the one side and by Peppard [2] on the other, relies on the characteristic changes of the physical and chemical properties of the different lanthanide compounds with the division of the lanthanide series into four subgroups (tetrads): La–Nd, Pm–Gd, Gd–Ho, Er–Lu. The understanding of the effect is impossible taking into account only simple electrostatic forces considerations, i.e. the viewpoint of the bonding energy changes in lanthanide ions–ligands interaction, so the effect was explained from the viewpoint of the ligand field theory, which takes into account the interaction of the ligand electrons with f-orbitals of the lanthanide tripositive ions in their complexes and from the viewpoint of parameters of interelectronic repulsions (known as Racah parameters) in the lanthanide ion, or rather their changes during formation of the covalent complex species. Up till now the tetrad effect is still investigated by different researchers, especially geochemists [3–14]. The abundance of the lanthanides in different rocks shows the features of tetrad effect, which is convex or concave in nature depending on the covalency in the product and substrates of the complexation reaction.

The aim of this paper is to show that the adsorption of the lanthanides on the zeolite would be an effective tool in the investigation of the tetrad effect and that the existence of convex and concave character of the effect, however undisputed, is very complicated in nature and needs further explanation.

We decided to use the zeolite A in the investigation, because it is known in nuclear industry as a good material for the immobilization of the different radionuclides coming from the reprocessing of nuclear fuel [15–17], among them also lanthanides. Therefore, thorough understanding of rules governing the lanthanides adsorption on zeolite A is necessary. For comparison we enclosed also the data for the zeolite Y, which is not used in the decontamination in radioactive wastes; however, it is known from the broad application in the cracking processes in its lanthanide-loaded form [18].

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2. Experimental

2.1. Distribution experiment

The aqueous phases (100 ml volume) containing lanthanide nitrates (0.0005 M; 99.9% purity, Sigma Aldrich) dissolved in sodium nitrate with concentrations ranging from 0.001 to 2 M (pure, Sigma Aldrich) were equilibrated through 4 h with 100 mg samples of the sodium form of the zeolite A (PQ Corporation; chemical composition reported by supplier: Na_2O w/w 17%, Al_2O_3 28%, SiO_2 33%, H_2O 22%) in temperature 23 ± 1 °C. The aqueous phase was separated from the solid residue by filtration (paper filter Filtrak 390, Polskie Odczynniki Chemiczne), centrifugation at 10,000 *g* for 10 min. The procedure of centrifugation was used to be completely sure, that no traces of colloid are present in the aqueous phase. The concentration of the lanthanides was determined spectrophotometrically using Arsenazo III [19] according to the following procedure. To the solution containing no more than 40 μg of the lanthanides, 1 ml of 1% ascorbic acid solution was added. After a few minutes 1 ml of formate buffer ($pH = 3.5$) and 2 ml 0.05% arsenazo III were added. The whole volume was adjusted to 20 ml with water. The new pH value 2.6 was established through the addition of 0.1 M NaOH. The absorbance of the solution was measured at 650 nm in the presence of blank sample as the reference.

The concentration of the lanthanide in the solid phase c_Z was found as the relationship between the initial concentration c_{in} and the concentration in the equilibrium aqueous phase c_{aq} according to: $c_Z = (c_{in} - c_{aq})V/m$, where V and m refer to the volume and mass of the sample, respectively. In each run of the experiment the same 100 mg samples of the zeolite were used. The initial and equilibrium pH values were controlled using combined glass electrode (Sigma Chemical Co.) connected to the pH meter (CX-731 type, Elmetron Co.).

The concentrations of Al in the solution from distribution experiment in the system: H_2O(100 ml)–zeolite A (100 mg) were determined according to the following procedure [19]. To the solution in diluted HCl with no more than 10 μg Al, 1 ml of ascorbic acid was added and the pH was adjusted to 2 through the addition of ammonium hydroxide. After 5 min, the volume of the solution was adjusted to about 15 ml with subsequent addition of 2.5 ml of 0.1% aqueous solution chromazurol S (Sigma Aldrich) and 1 ml of 20% CH_3COONa solution. The pH and the volume of the solution were adjusted to 6.0 (by ammonia hydroxide) and 25 ml, respectively, and the absorbance was measured at 545 nm in the presence of blank sample as the reference.

The concentration of Si in the solution was determined according to the following procedure [19]. The solution with no more than 0.2 μg Si was acidified to pH 1.5 by diluted H_2SO_4 and in the next step 3 ml ammonium molybdate (10%), 3 ml acetone and water were added to the volume of approximately 15 ml. The pH and the volume of the solution were adjusted to 1.4 (by 1 M H_2SO_4) and 25 ml (water) and after 5 min, the absorbance was measured at 400 nm in the presence of blank sample as the reference.

2.2. Samples preparation

Investigated samples were prepared by a 4 h equilibration of 500 mg A and Y zeolite separately (zeolite Y delivered by Zeolyst Inc.; chemical composition reported by supplier: Na_2O w/w 13%, SiO_2/Al_2O_3 molar ratio = 5.1, Na/Al molar ratio = 1) with 100 ml solution of appropriate metal nitrate (0.05 M, Sigma Aldrich 99.9% purity) in 0.1 M sodium nitrate (Sigma Aldrich 99.9% purity), filtration through the paper filter (Filtrak 390, Polskie Odczynniki Chemiczne). The lanthanide nitrates solutions (0.05 M) were prepared through the dissolution of respective lanthanide nitrates in water. Lanthanide nitrates were prepared from the respective lanthanide oxides (Sigma Aldrich 99.9% purity) in nitric acid.

2.3. VIS diffusive reflectance spectra of the lanthanide nitrates

The VIS diffusive reflectance spectra (region 300–800 nm) of the zeolite samples and oxides were recorded at room temperature on Specord M-50 (Medson Co.) spectrophotometer. The resolution of 0.5 nm was preserved during registering of spectra. The sodium forms of the zeolites A and Y were used as the references during the registering the spectra of zeolites A and Y modified with lanthanides. Zinc oxide and water were the references in the case of lanthanide oxides and 0.05 M nitrates solutions spectra, respectively. The path length of 1 cm was preserved for absorbance spectra of lanthanide nitrates.

2.4. Infrared diffusive reflectance spectra

The diffusive reflectance spectra in IR region (600–4000 cm^{-1}) of the zeolites samples were recorded at room temperature on 1725X Perkin Elmer instrument equipped with Varimax Horizontal ATR Plate-ZnSe (produced by International Crystal Laboratory). The reflection angle of 30° was preserved during measurements. The pure samples were used without the addition of any inert substances. All measurements were conducted at 23 °C and 1013 hPa conditions.

2.5. Scanning electron microscopy

Heterogeneity of the zeolite surfaces has been investigated by Scanning Electron Microscopy (SEM) method (microscope LEO SEM 1430 VP supplied with the EDX detector). Investigated samples were prepared by equilibration of 100 ml solution of 0.1 M $NaNO_3$ with the appropriate lanthanide nitrates solution (of the total concentration of 0.05 M), filtration through a paper filter (Filtrak 390, Polskie Odczynniki Chemiczne) and drying of the solid residue in the air. The concentration of Ln, Al, Si, Na and O were determined in 50-ty randomly selected points on the zeolite surface using the standardless version of SEM method. The electron beam has penetrated the samples for about 1 μm. The precision of O, Na and Ln determination was 10%, whereas of Si and Al was 5%. The example of the chemical composition of the zeolite A surface determination was given in previous paper [20].

3. Results and discussion

3.1. Equilibrium data

The change of the distribution constants of the lanthanides in the system $Ln(NO_3)_3$–$NaNO_3$–zeolite A with the nitrates concentrations is given in Fig. 1. The distribution constants K_d are defined as

$$K_d = (c_Z/c_{aq})V/m, \qquad (1)$$

where V and m denote the volume of aqueous phase and the mass of the adsorbent, respectively.

The values of K_d increase from La to Eu, Sm for the very low concentrations of nitrates (0.001, 0.01 M). For higher concentrations of nitrates the maximum of K_d values is shifted toward neodymium. It is known that the lanthanides from Nd–Tb range have the mixed coordination number (8–9) [21] and the equilibrium: $Ln(H_2O)_8^{3+} + H_2O \leftrightarrow Ln(H_2O)_9^{3+}$ depends strongly both on water activity and on the formation of outersphere complexes of the lanthanide tripositive ions with inorganic ligands like: chlorides, nitrates, acetates, thiocyanates. The coordination number in the aquoions changes from 9 to 8 and the hydration energy of the tripositive ions starts to predominate over the energy of complexation of these ions by the negative oxygen ions of the zeolite framework; as a result the decrease of K_d values is noticed beginning from Nd for the nitrates concentrations higher than 0.1 M.

The changes of the distribution constants are nonmonotous, so for the first tetrad of the lanthanides (La–Nd) the concave or convex deviation from the interpolation straightline in the run of K_d values is observed. This interpolation straightlines refer (pecked lines in Fig. 1) to idealized conditions, when the interaction between central ion and ligand would simply be coulombic in nature and no overlapping of central ion and ligand orbitals exists. Second tetrad (Pm–Gd) was not considered since we do not have the data for Pm. For the third tetrad (Gd–Ho) the positive deviation from the interpolation line is noticed for all nitrates concentrations. For the fourth tetrad (Er–Lu), similarly as in the case of the first tetrad, convex or concave deviations are evident. According to Kawabe [5–10,14], the concave tetrad is observed when the covalency in lanthanide ion–ligand in products of the complexation reaction is weaker, i.e. Racah parameters are higher, than in the substrates. Therefore for the ions: La^{3+}–Nd^{3+}, when the ion exchange-complexation reaction of the aquoions $Ln(H_2O)_9^{3+}$ with the sodium form NaZe of the zeolite is considered

$$Ln(H_2O)_9^{3+} + 3NaZ \leftrightarrow Ln(H_2O)_xZ_3 + 3Na^+ + (9-x)H_2O, \qquad (2)$$

covalency of the Ln–O bond in the $Ln(H_2O)_xZ_3$ species is weaker than in aquocomplex $Ln(H_2O)_9^{3+}$. For the convex tetrad effect, which appears for nitrates concentrations higher than 0.5 M, the reverse explanation should be justified: the covalency of Ln–O bond in $Ln(H_2O)_xZ_3$ is stronger (Racah parameters lower) than in aquocomplex. As it is visible from Fig. 1 the region of 0.2–0.5 M $NaNO_3$ concentration is transient and the fluent change from concave to convex tetrad effect is noticed for the light lanthanides (La–Nd), so there is probably a comparable extent of covalency in the products and substrates of the adsorption reaction or in the other words Racah parameters interelectronic repulsion are the same.

For the third and fourth tetrads the following reaction should be considered

$$Ln(H_2O)_8^{3+} + 3NaZ \leftrightarrow Ln(H_2O)_xZ_3 + 3Na^+ + (8-x)H_2O, \qquad (3)$$

and the covalency in the products of the reaction is stronger than in substrates for all nitrates concentrations for the third tetrad and for lower nitrates concentrations (0–0.5 M $NaNO_3$) for the fourth tetrad.

Apart from above-mentioned reactions the complexation of the lanthanide ions by nitrates should be taken into account, according to general reaction

$$Ln(H_2O)_n^{3+} + NO_3^- \leftrightarrow Ln(H_2O)_xNO_3^{2+} + (n-x)H_2O, \qquad (4)$$

where $n = 9$ and 8 for the light and heavy lanthanides. The formation of the lanthanide nitrato complexes was confirmed by several investigators [22], but its influence on the covalency in Ln–O bonds is not known. The light lanthanide ions (La^{3+}–Sm^{3+}) form stronger nitrato complexes than the rest of the lanthanide ions. The character of these complexes changes from outersphere, where the central ion is separated from ligand by water molecules, to innersphere with ligand in nearest environment of central ion. The shift from outer to innersphere nitrato complexes occurs during the increase of nitrate ion concentrations. Therefore in 2 M $NaNO_3$, as in our experimental conditions, one can expect formation of contact ionic pairs $LnNO_3^{2+}$ in aqueous phase with completely different covalency in Ln–O bond when compared with complexes $Ln(H_2O)_xNO_3^{2+}$.

The changes of pH of the aqueous phase during the adsorption of the lanthanides on the zeolite A are given on Fig. 2. These changes are defined as $\Delta pH = pH_{eq} - pH_{in}$, where indexes: eq, in denote equilibrium and initial pH's of

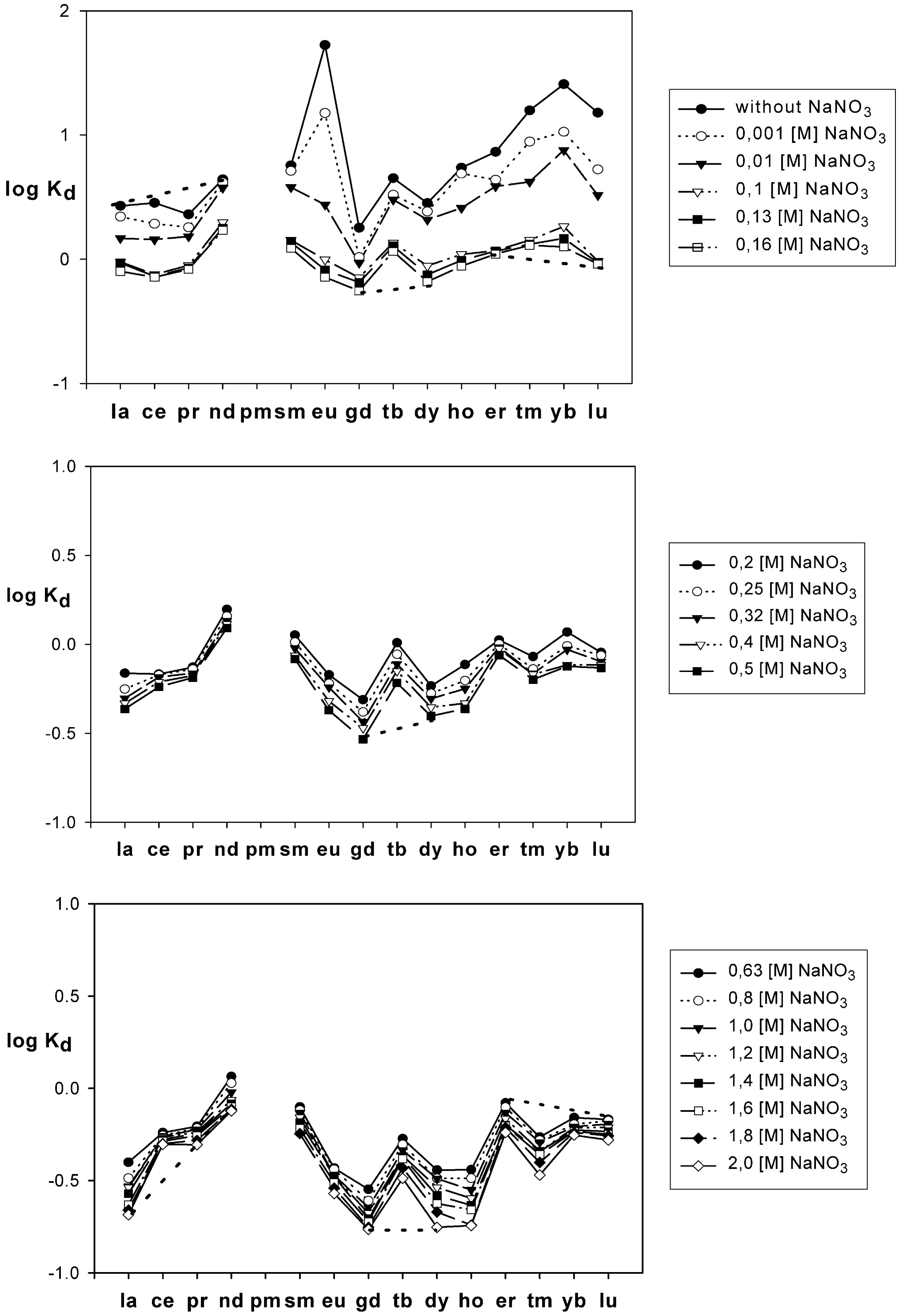

Fig. 1. The changes of distribution constants K_d of the lanthanides in the system $NaNO_3$–zeolite A with nitrate concentrations.

the aqueous phase. The example of the ΔpH change vs. pH_{eq} for La is given.

The minimum in ΔpH, marked as ΔpH_{min}, corresponds in our opinion with the completion of hydrolysis and to a smaller extent with the reaction of the lanthanide ions with surface hydroxyls [23]. Both of these reactions can be written as:

$$p\mathrm{LnNO_3Z_2} + q\mathrm{H_2O} \leftrightarrow \mathrm{Ln}_p(\mathrm{NO_3})_p(\mathrm{OH})_q\mathrm{Z}_{2p}^{-q} + q\mathrm{H}^+, \qquad (5)$$

$$3\mathrm{HOZ} + \mathrm{Ln}^{3+} \leftrightarrow \mathrm{Ln(OZ)_3} + 3\mathrm{H}^+. \qquad (6)$$

In the case of light lanthanides, especially La, Ce, Pr and Sm, the reaction (5) is very pronounced and as a result more negative ΔpH values are observed when compared with

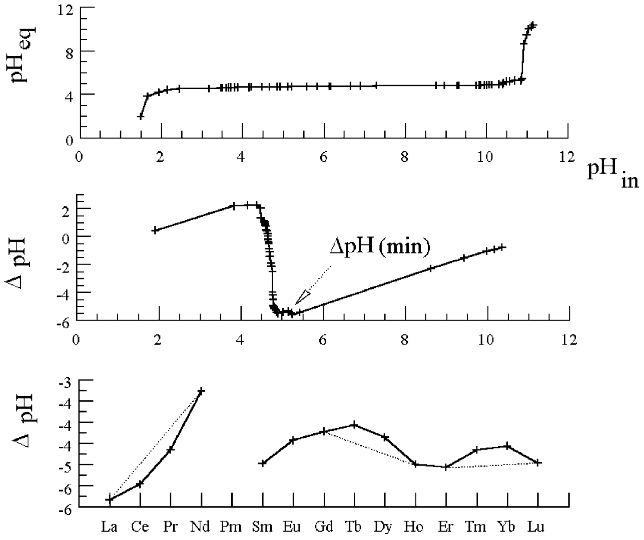

Fig. 2. The changes of pH of the aqueous phase during adsorption of the lanthanides on the zeolite A (initial concentration of $Ln(NO_3)_3$—0.0005 M).

analogous values for the rest of the lanthanides. The evident tetrad effect is observed for La–Nd, Gd–Ho and Er–Lu subgroups. In the first subgroup the destabilization of the f^1 (Ce^{3+}) and f^2 (Pr^{3+}) electrons in $Ln_p(NO_3)_p(OH)_qZ_{2p}^{-q}$ species occurs because the concave tetrad effect is observed. For Gd–Ho and Er–Lu subgroups the stabilization of electrons: f^8, f^9, f^{12}, f^{13} for Tb^{3+}, Dy^{3+}, Tm^{3+}, Yb^{3+} is evident since the convex tetrad effect is visible.

Of course we would question to what extent the hydrolysis of the zeolite A would affect above-mentioned equilibria. In connection with this, we decided to check the influence of the lanthanides presence in the zeolite phase on its chemical composition. The molar ratios Si/Al found for 50-ty randomly selected points on the zeolite surface by using SEM are given on Fig. 3. It is easy to notice, that for La, Nd, Sm and Eu the change of Si/Al ratio with the lanthanides concentrations can be neglected, because it is in the experimental error of the lanthanides concentration determination. Therefore we can conclude, that during equilibration of the zeolite samples with 0.05 M solutions of the lanthanide nitrates the release of Si and Al from the zeolite framework can be neglected. If so, then in our distribution experiments when we run with 0.0005 M lanthanide nitrates, the expected changes would be much lower. What is more important: in our previous work [20] we mentioned, that the zeolite A cubic structure is preserved during its contact with the solution of 0.05 M lanthanide nitrates. The unit cell constants of Ln-A zeolites (Ln = La,Ce,Pr,Nd,Sm) found from XRD patterns are almost identical with this found for Na-A form. Harjula mentioned in his work concerning the hydrolysis of the zeolites [24], that one should take into account the change of Na concentration in the aqueous phase during the equilibration of sodium form of the zeolite with the solution containing the trace concentration of sodium. We intentionally ran our experiments with the 0.1 M $NaNO_3$ as an aqueous phase, so the hydrolysis of the sodium form of the zeolite A was backed to the extent in which release of sodium to the aqueous phase was much lower than the concentration of sodium in the medium. Finally, it is worth to consider the influence of the pH on the release of Al and Si to the aqueous phase, which can be also understood as zeolite hydrolysis. It is evident from Fig. 4, that there is in practice no release of these elements in the pH range of 3–10, so therefore in our experimental conditions where we compare K_d values for the different nitrates concentrations (Fig. 1) with the pH values changing in 5–6 range, the release of Si and Al can be neglected.

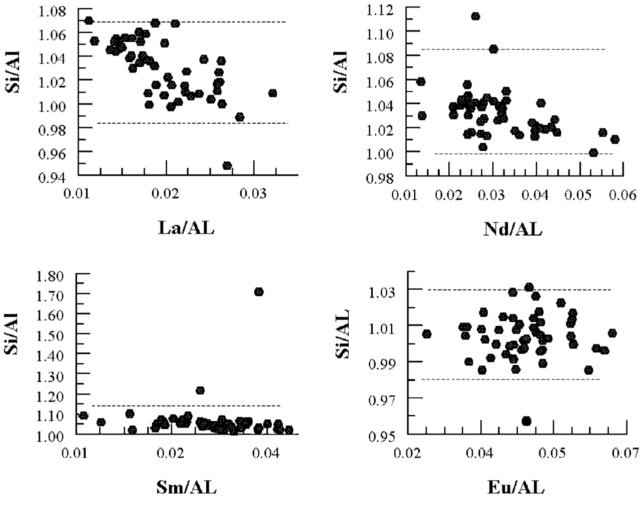

Fig. 3. The change of Si/Al molar ratio with the lanthanides concentrations.

3.2. Diffusive reflectance spectra

VIS Diffusive Reflectance spectra of the zeolites A and Y loaded with lanthanides and of lanthanide oxides are shown in Figs. 5–9 and compared with the VIS absorption spectra of the lanthanide nitrates solution. We intentionally selected lanthanide oxides for comparison, because the lanthanide

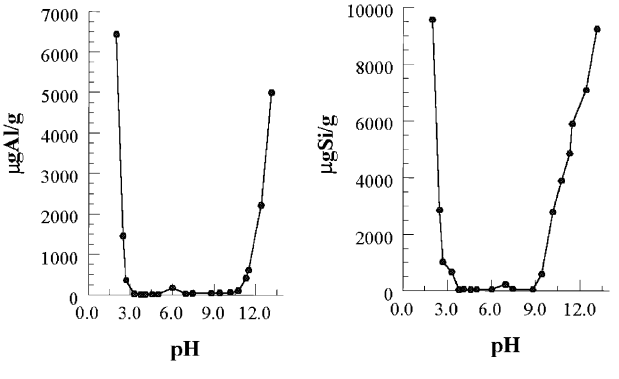

Fig. 4. The release of Al and Si from the zeolite A framework with pH increase (solid phase: 100 mg zeolite A, aqueous phase: 100 ml of 0.1 M $NaNO_3$).

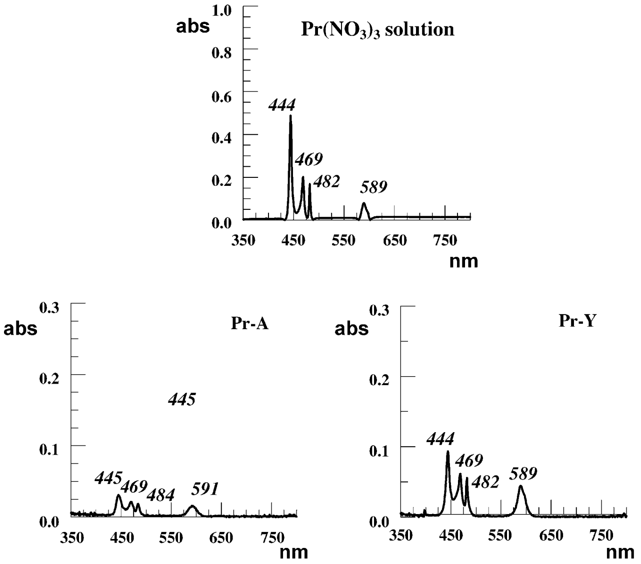

Fig. 5. VIS diffusive reflectance spectrum of the prazeodymium oxide and zeolites Y, A loaded with prazeodymium nitrate (absorption spectra of the aqueous 0.05 M lanthanide nitrates for comparison).

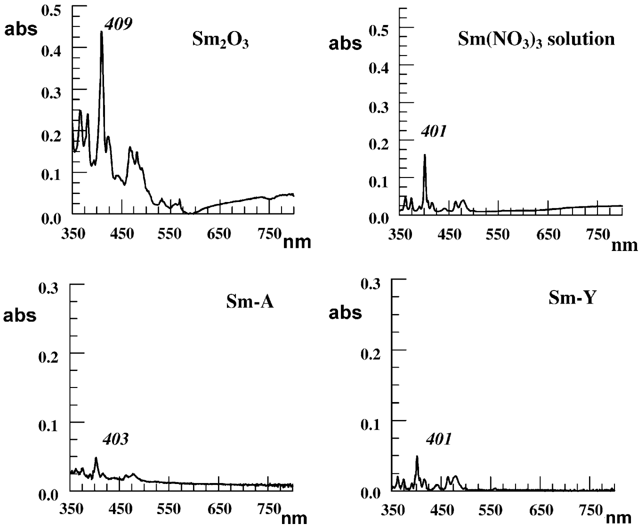

Fig. 7. VIS diffusive reflectance spectrum of the samarium oxide and zeolites Y, A loaded with samarium nitrate (absorption spectra of the aqueous 0.05 M lanthanide nitrates for comparison).

oxides are typical covalent compounds, so any similarity with the spectra of the zeolites would be the proof for covalency in Ln–O bond. In the case of praseodymium it was impossible to detect the Diffusive Reflectance VIS spectrum for Pr_6O_{11}, so we compared only the the Pr-loaded zeolites and aquoeus solution.

It is well known from classical coordination chemistry [25] that the UV–VIS absorption spectra of the lanthanide compounds are sensitive to the nature of complexes formed. The red shift of the bands is observed if the complexes of the lanthanides are more covalent. If we compare the spectra of the lanthanide oxides, zeolite A loaded with lanthanides and at last the zeolite Y, we can find the red shift of the bands in the order: solution of nitrates, zeolite Y $<$ zeolite A $<$ oxides. This sequence is evident only for the Nd, Pr and Sm, especially when we inspect the bands: 589, 591 for Pr, 795, 741, 581, 521 for Nd and 401 for Sm. Therefore, we can conclude that the Ln–O bond covalency is the greatest in the case of lanthanide oxides. We can conclude that the nearest environment of the lanthanide tripositive ion in the zeolite phase consists of H_2O molecules and OH^- ions and the participation of O^{2-} ions in the first coordination sphere of the lanthanide ion is rather minor. However, in the case of Nd^{3+} ion in zeolite A coordination through O^{2-} ions from the zeolite network is possible. The spectrum of zeolite A loaded with Nd is similar to the Nd_2O_3 spectrum in the sense of the bands positions; for example bands: 799, 744, 581,

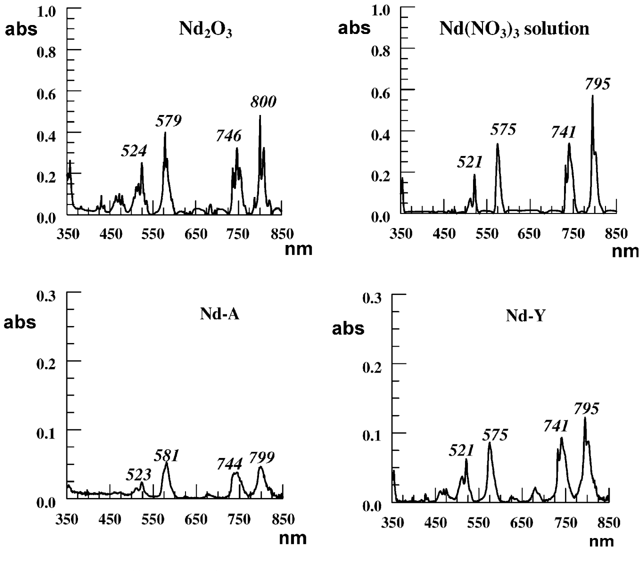

Fig. 6. VIS diffusive reflectance spectrum of the neodymium oxide and zeolites Y, A loaded with neodymium nitrate (absorption spectra of the aqueous 0.05 M lanthanide nitrates for comparison).

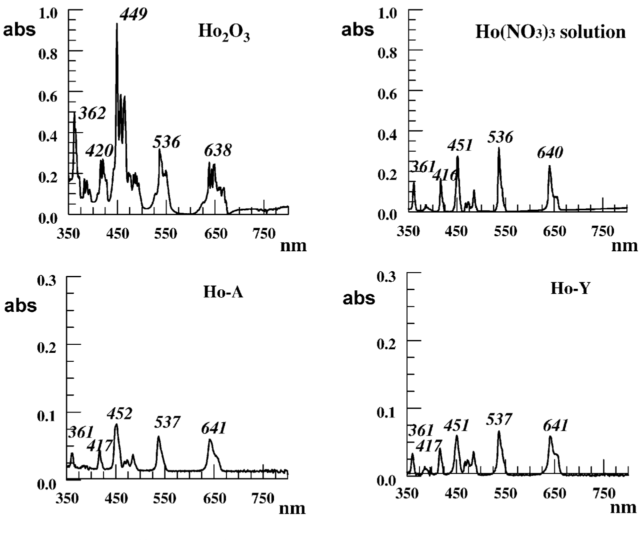

Fig. 8. VIS diffusive reflectance spectrum of the holmium oxide and zeolites Y, A loaded with holmium nitrate (absorption spectra of the aqueous 0.05 M lanthanide nitrates for comparison).

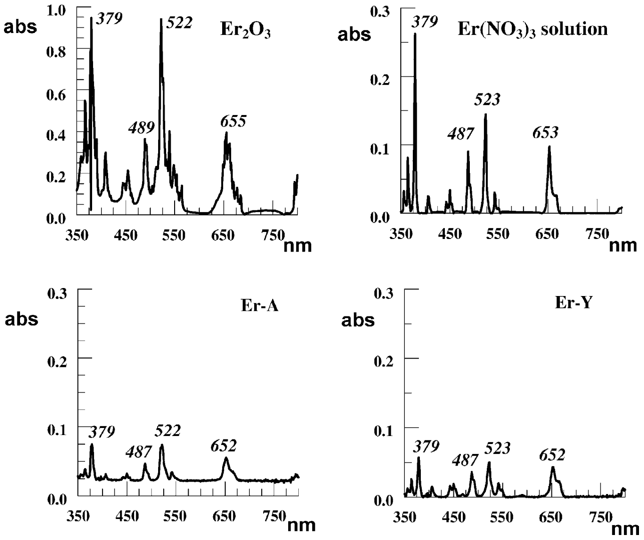

Fig. 9. VIS diffusive reflectance spectrum of the erbium oxide and zeolites Y, A loaded with erbium nitrate (absorption spectra of the aqueous 0.05 M lanthanide nitrates for comparison).

523 are rather near the bands: 800, 746, 579, 524 characteristic for oxide than near the bands: 795, 741, 575, 521 characteristic for the zeolite Y loaded with Nd and for neodymium nitrate solution. Therefore it is clear why the distribution constant K_d of Nd has a much higher value than the distribution constants of the remaining lanthanides. It results from the stronger attraction of the Nd^{3+} ion with O^{2-} ions. For Ho and Er there is essentially no difference between particular spectra of nitrates solution, zeolite Y, zeolite A. The spectra of Ho and Er oxides have features, which make them distinctly different from the spectra of zeolites. For example bands: 638, 536, 449 for Ho_2O_3 are split similarly as bands: 655, 379 for Er_2O_3. Therefore, the assumption about the full separation of Ho^{3+} and Er^{3+} ions from the negatively charged zeolite framework by water molecules is justified.

The change of the T–O–T band (in infrared region) of the zeolite A samples loaded with lanthanide nitrates is given on Fig. 10. The T–O–T band is responsible for asymmetric stretching vibration in Al–O–Si subunits and is very sensitive to metal presence in the zeolite structure. The red shift of this band, according to Sarkany [26–29], is responsible for the interaction of bare metal ions with negatively charged zeolite framework. We can notice the red shift of this band for the light lanthanides in zeolite A, especially for La^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Lu^{3+}. Therefore one can conclude about the strong interaction of the light lanthanide ions with the zeolite framework, much stronger than of the heavy ones, especially Gd^{3+}–Er^{3+} ions. It is interesting that the position of T–O–T band for Na^+ ion is nearly the same as that found for La^{3+}. One can presume that the lanthanides from La to Nd easily hydrolyze in the zeolitic phase with the formation of hydroxyspecies $Ln_p(NO_3)_p(OH)_qZ_{2p}^{-q}$ contrary to heavy lanthanides, where the separation of the lanthanide ions from the oxide ions O^{2-} of the zeolitic framework by water molecules occurs. Therefore, the evident parallelism between the red shift of the T–O–T for the light lanthanides and the low values of ΔpH (see Fig. 2) accompanying the process of their adsorption on the zeolite A is understood. On the other hand more general conclusion is, that the position of T–O–T band depends strongly on the dehydration of the ion, because weakly hydrated Na^+ ion is similar to the strongly hydrated La^{3+} ion, so one can presume that in the case of Na^+ weak interaction with the zeolite framework is counterbalanced by the ease dehydration.

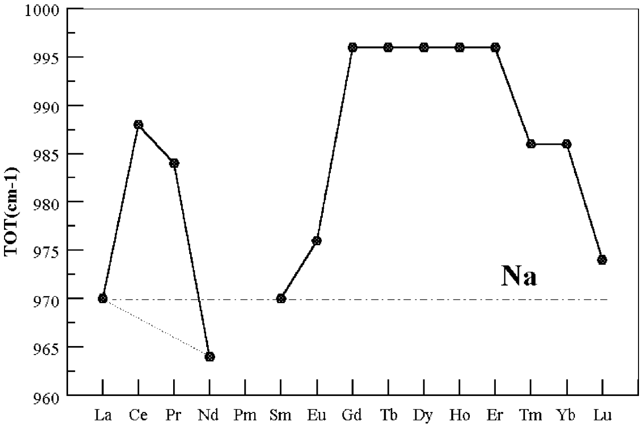

Fig. 10. The change of the T–O–T band position of the zeolite A samples loaded with lanthanide nitrates (horizontal dotted line refers to NaA form).

We can notice only the part of the tetrad effect for the light lanthanides (La–Nd) in the change of the position of TOT band, which is justified because one should remember that there are numerous facts supporting the delocalization of 4f orbitals of the light lanthanides; among them the most important are: the change of the crystallographic structure of the metallic lanthanides from La to Pm and the values of their melting points. In the case of salts and the complex compounds the decrease of nepheloauxetic ratio in the series PrF_3–$PrCl_3$–$PrBr_3$–PrI_3 is the evidence for the delocalization of 4f electrons [30].

4. Conclusions

1. Investigation of the distribution constants of the lanthanides on the zeolite A is a good tool for the study of tetrad effect in the formation of lanthanide complexes.
2. For 0–0.2 M nitrates concentrations the covalency in Ln–O for $Ln_p(NO_3)_p(OH)_qZ_{2p}^{-q}$ species in the zeolite phase is weaker, i.e. Racah parameters are lower, than for aquoions in La^{3+}–Nd^{3+} range, whereas for Gd^{3+}–Lu^{3+} ions the predominance of the covalency in the product of the adsorption reaction is evident.
3. For 0.5–2 M nitrates concentrations the covalency in Ln–O for $Ln_p(NO_3)_p(OH)_qZ_{2p}^{-q}$ species in the zeolite phase is stronger, i.e. Racah parameters are higher, than for aquoions in La^{3+}–Nd^{3+} range, whereas for

Gd^{3+}–Lu^{3+} ions the covalency in substrates of the adsorption reaction (in aquoions) is stronger than in products.

4. Further investigation is necessary to explain the connection between the covalency in Ln–O bond and the character of the nitrato lanthanide complexes formed, their inner or outersphere nature.

Acknowledgements

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