



# INVESTIGATION OF THE EFFECT OF THE HALIDE ION ADDING ON EXTRACTION OF RARE EARTH IONS FROM NITRATE MEDIA APPLYING NAPHTHENIC ACID

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## ABSTRACT

Data were obtained on the influence of chloride and bromide ion impurities on the extraction of cerium (III) europium (III) and gadolinium (III) with a solution of naphthenic acid in o-xylene from nitrate media. The experiment showed a W-shaped dependence of the distribution coefficient on the Br<sup>-</sup> content. The nature of the dependence is explained by the formation of non-extractable MeBr<sup>2+</sup> and MeOH<sup>2+</sup> complexes; the local maximum is associated with an increase in the degree of dissociation of naphthenic acid. The non-monotonous nature of the dependence makes it possible to obtain the effect of anionic synergism and to increase the magnitude of the separation factor of lanthanides in comparison with a nitrate solution by 1.5 times.

**Keywords:** extraction, rare earth metals, lanthanides, carboxylic acids.

## INTRODUCTION

Rare-earth elements and their compounds are in demand in the production of a significant number of products in various fields: phosphors in television screens, monitors and mobile phones, hybrid engines based on NiMH batteries, NdFeB magnets, polishing powders, additives for changing color and strength during glass melting, catalysts in oil refining. Almost any modern device contains a certain amount of rare-earth metals. The growth of REM consumption in the world is growing annually, this requires the involvement of new sources, for example, secondary sources. In this case, the technological solutions will have a complex cationic composition, and at least anionic composition. The latter, obviously, will affect the efficiency of the processes of extraction and separation of lanthanides and requires a comprehensive study.

One of the widespread applications of rare earth metals is phosphors. Fluorescent lamps are a rich source of a heavy group of rare earth elements such as europium, yttrium and terbium. The main components of REE-containing fluorescent lamps are red phosphors Y<sub>2</sub>O<sub>3</sub>: Eu<sup>3+</sup> (YOX), green phosphors LaPO<sub>4</sub>: Ce<sup>3+</sup>, Tb<sup>3+</sup> (LAP), (Gd, Mg) B<sub>5</sub>O<sub>12</sub>: Ce<sup>3+</sup>, Tb<sup>3+</sup> (CBT), (Ce, Tb) MgAl<sub>11</sub>O<sub>19</sub> (CAT) and blue phosphors BaMgAl<sub>10</sub>O<sub>17</sub>: Eu<sup>2+</sup>, chlorapatite (Sr, Ca)<sub>10</sub>(PO<sub>4</sub>)<sub>2</sub>(Cl, F)<sub>2</sub>: Sb<sup>3+</sup>, Mn<sup>2+</sup> [1,2] is used somewhat less frequently as a blue phosphor. In total, La, Ce, Eu, Gd, Tb, Y can be obtained from fluorescent lamp powders (Innocenzi *et al.* 2018, Siziakova *et al.* 2019). Unlike other secondary sources of rare-earth metals, phosphors do not require complicated preliminary preparation. So, for example, when processing fluorescent lamps, it is enough to break the glass and separate it from the powder containing rare-earth metals, after which classical separation methods can be applied.

Both pyrometallurgical and hydrometallurgical processes are used, however hydrometallurgical are more preferable (Cheremisina *et al.* 2019, Siziakova *et al.* 2017, Dezhi *et al.* 2018). One of the main challenges in processing is the separation of mercury. The second factor

complicating the separation of rare earth metals is the presence of a large number of external ions; in different amounts, after leaching, the composition of the solutions may include: Al, Si, P, Ca and Mg, Mn, Sb, Cl, F, Br, Hg, Pb, Cd. Of these elements, non-metals F, Br, Cl can act as a complexing agent and influence the extraction processes. Extraction and separation of lanthanides is most often carried out by liquid extraction methods using various types of extractants (Cheremisina *et al.* 2015, Chirkst *et al.* 2006, Voropanova 2016), of which the carboxylic acids, including naphthenic acid (Voropanova *et al.* 2018), are the cheapest and most preferred for the processing of secondary raw materials.

Relatively little is known about the effect of the bromide anion on the processes of REM extraction. This work is devoted to the effect of the bromide anion as an impurity on the extraction of rare-earth metals from nitrate media.

## Experimental Part

Model solutions of rare-earth metals with a concentration of 0.01 mol/l, were prepared from their chemical grade nitrates. To add a bromide anion to the solution, a potassium bromide salt of the grade «chemically pure» was used.

As an extractant was used «chemically pure» grade naphthenic acid with a density of 0.92 g/cm<sup>3</sup> and an average dissociation constant pK<sub>d</sub> = 5,5 or K<sub>d</sub> = 3,16 · 10<sup>-6</sup>. An acid concentration of 0,5 mol/L was achieved by diluting the extractant in o-xylene of the grade «chemically pure» with a mass content of at least 99,7%. The phases were contacted using the HEL Parallel Auto-MATE® Reactor System with automatic pH adjustment and a temperature control sensor. Phase separation was carried out using a Koehler K61002 centrifuge.

The acidity of the medium in the system was maintained at pH = 5 ± 0,05, due to the fact that the maximum extraction of lanthanides occurs when the pH of the aqueous solution is slightly lower than the pH of



hydrate formation. Similar conditions for maximum recovery are characteristic of other unsubstituted carboxylic acids (Feng *et al.* 2014, Lobacheva *et al.* 2018).

The concentration of rare-earth metals in the aqueous phase before and after extraction was determined using x-ray fluorescence spectroscopy on a PANalytical Epsilon instrument. In addition, we used the photometric method for determining REM using arsenazo III.

The content of the rare-earth element in the organic phase was calculated by the difference in concentrations in the aqueous solution before and after extraction, taking into account the ratio of phase volumes:

$$C_{\text{org}} = (C_0 - C_{\text{aq}}) \cdot \alpha^{-1}, \quad (1)$$

where  $C_{\text{org}}$  and  $C_{\text{aq}}$  are the concentrations of rare-earth metals in the extract and in the equilibrium aqueous phase, respectively, mol/l;  $C_0$  - initial concentration of rare-earth metals in an aqueous solution, mol/l;  $\alpha$  - the ratio of the volumes of organic and aqueous phases, in the conditions of the experiment.

The distribution coefficient is calculated by the equation:

$$D = \frac{C_{\text{org}}}{C_{\text{aq}}}. \quad (2)$$

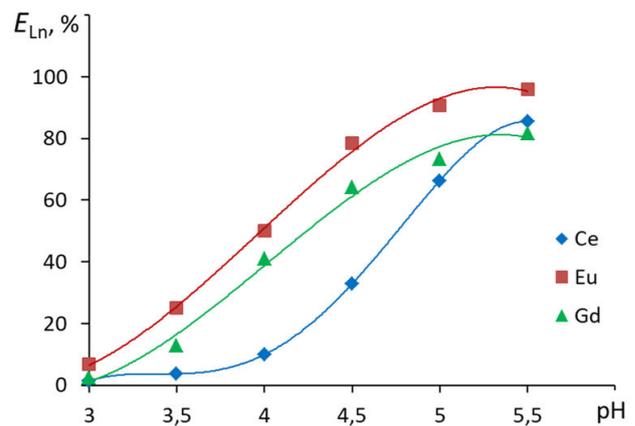
The separation coefficient of rare-earth metals is calculated by the equation:

$$\beta_{2/1} = \frac{D_2}{D_1}, \quad (3)$$

where index 2 is assigned better to the extracted element.

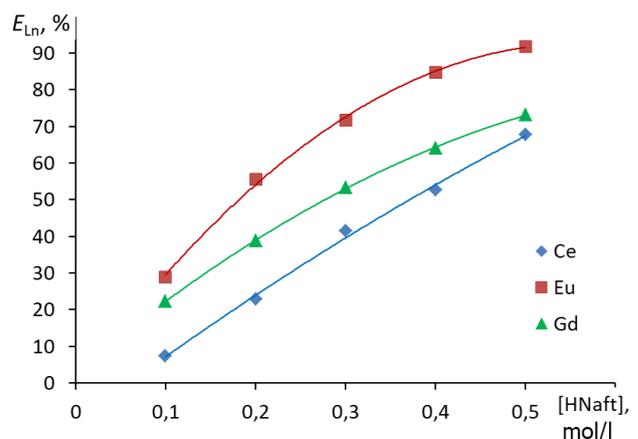
## RESULTS AND DISCUSSION

The experiment showed that at pH = 5 the best distribution of the metal in the organic phase is observed. At pH greater than 5, a significant amount of lanthanide hydroxides is formed and the extraction process is hampered by a sharp increase in the viscosity of the organic phase. At a pH value of less than 4, naphthenic acid exists in molecular and / or dimeric form and the extraction of metal cations into the organic phase is difficult.



**Figure-1.** The dependence of the degree of extraction of rare-earth metals from nitrate media with naphthenic acid on the acidity of an aqueous solution.

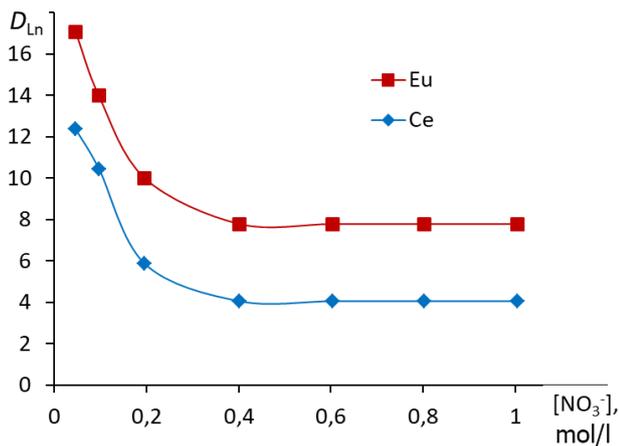
The results of extraction at various concentrations of extractant are presented in Figure-2.



**Figure-2.** Dependence of the degree of extraction on the concentration of extractant.

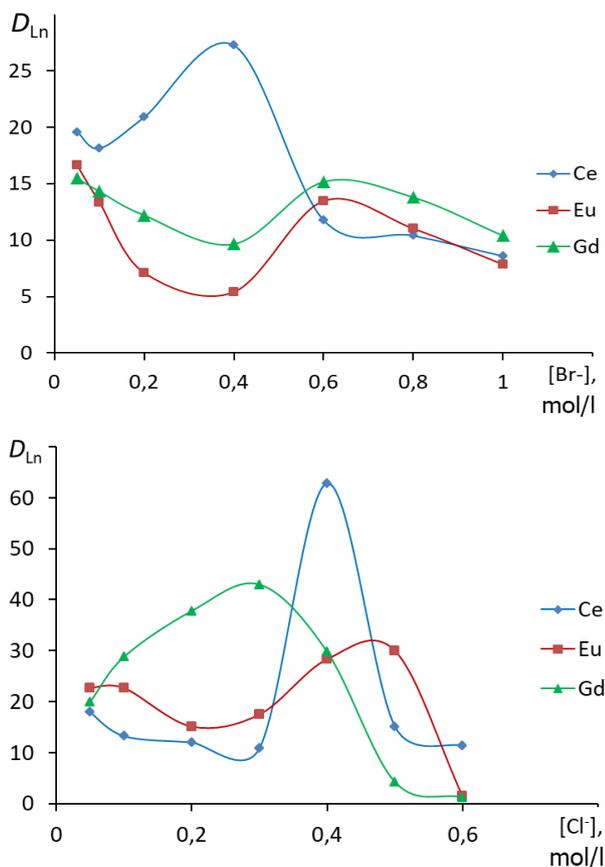
A natural increase in the degree of extraction is observed with an increase in the concentration of the extractant; however, it is impractical to carry out extraction at a concentration of the extractant above 0,5 mol/l, leads to an increase in the viscosity of the organic phase, a regular deterioration in the mixing of the phases and a decrease in the extractability.

It is known that the concentration of nitrate ion practically does not affect the lanthanide extraction performance (Cheremisina *et al.* 2015, Chirkst *et al.* 2006). According to the results of experimental studies, shown in Figure-3, with an increase in the concentration of nitrate ion, the distribution coefficient decreases slightly and reaches a constant value. This may be due to the formation of anionic nitrate complexes, the extraction of which is impossible.



**Figure-3.** The dependence of the distribution coefficient of cerium and europium on the concentration of nitrate ion.

A different picture is observed when a halide is introduced into the system. The dependences for the distribution coefficient of cerium (III), europium (III), and gadolinium (III) on the content of chloride and bromide anions in the solution are shown in Figure-4.



**Figure-4.** Dependences of the distribution coefficient of lanthanides on the concentration of chloride and bromide ions. A dependence on the concentration of chloride in an aqueous solution was obtained for a 0.5 M solution of oleic acid as an extractant [8].

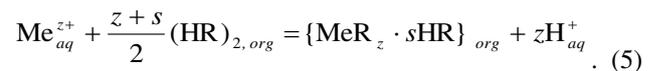
Attention is drawn to a similar course of dependencies for cerium and europium. With an increase in the concentration of the halide in the aqueous solution, the distribution coefficient of cerium reaches a maximum at a halogen concentration of about 0,4 mol/l. The behavior of cerium corresponds to the so-called anionic synergistic effect.

For europium, an increase in the concentration of the halide ion leads to a decrease in the distribution coefficient with a small subsequent increase in it as the halide in solution increases.

From the data presented in the graphs, we can conclude that the synergistic effect is positive, for example, cerium, or negative, for example, europium and gadolinium. In this case, the synergistic effect is considered positive provided that the distribution coefficient is exceeded for any chloride concentration of the distribution coefficient when the chloride concentration is wound to zero and vice versa.

The monitoring of the content of the halide ion in the system before and after extraction was performed using an ion-selective electrode, this made it possible to determine that the halide ions are not part of the extractable solvate. This fact is in good agreement with published data (Poullion *et al.* 1988, Glushko 2004).

The classic version of the description of the processes of extraction with carboxylic acids provides for the existence of an extractant molecule in the organic phase in the form of an undissociated dimer, a metal ion in the aqueous phase in the form of a simple hydrated cation (Poullion *et al.* 1988, Glushko 2004):



For which the equation of the effective equilibrium constant

$$K = \frac{\gamma_{\text{H}^+}^z [\text{MeR}_z \cdot s\text{HR}]_{org} [\text{H}_{aq}^+]}{\gamma_{\text{Me}^{z+}} [\text{Me}_{aq}^{z+}] [(\text{HR})_2]^{\frac{z+s}{2}}} \quad (6)$$

When using stoichiometric amounts of extractant, the volume of the organic phase is not more than 10% of the volume of the aqueous solution. With vigorous stirring, the surface area of the phase interface makes up the bulk of the reaction space. Given the high surface activity of carboxylic acids, their low solubility in water, it can be assumed that reaction (5) can proceed in the surface layer without the stage of distribution of the extracted complex between the organic and aqueous phases

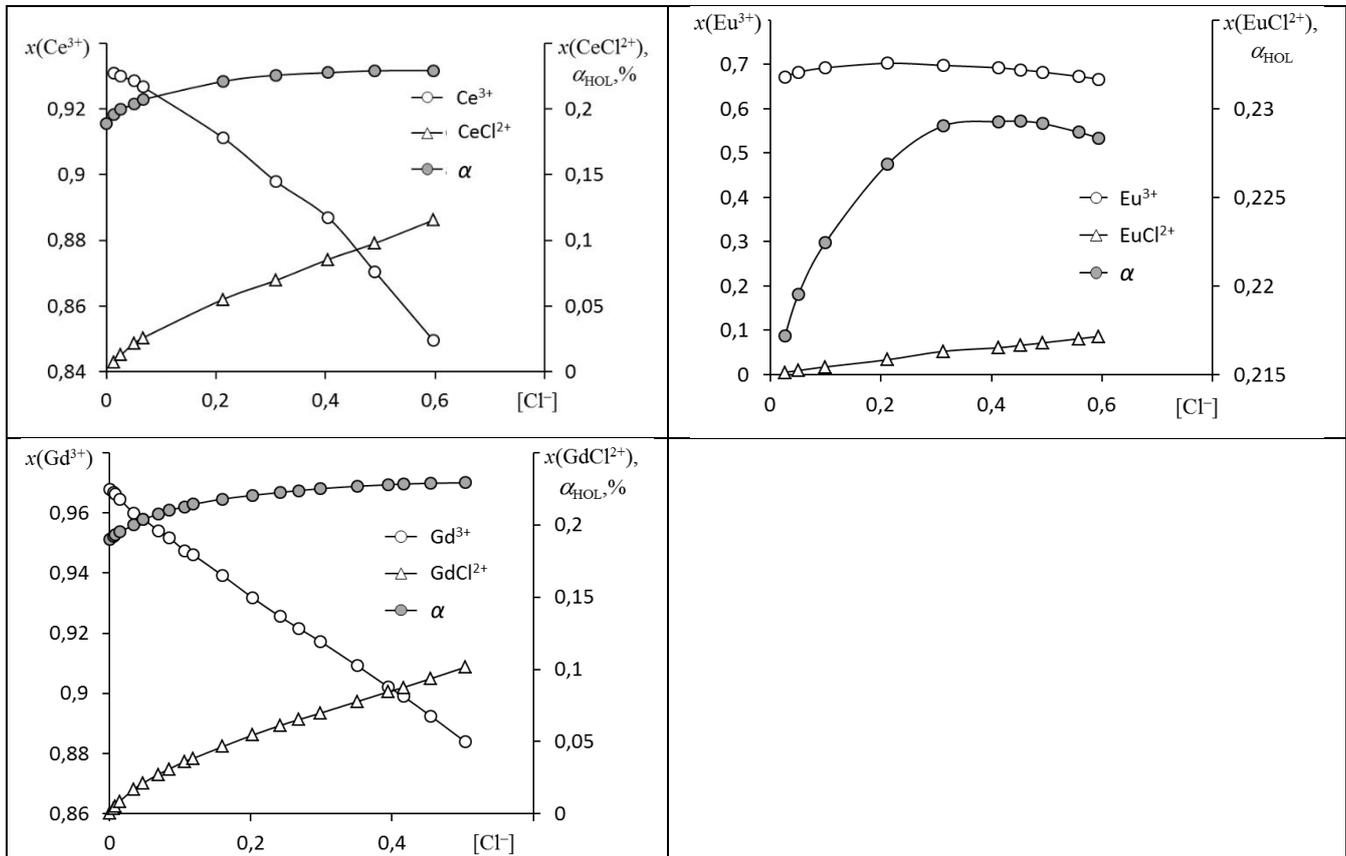
When using cation-exchange extractants, the anionic complexes of rare-earth metals are poorly extracted into the organic phase or are not extracted at all in the case of formation of anionic complexes. However, as follows from the obtained experimental data, the presence of a small amount of a "hard" Pearson base in the



form of a chloride or bromide ion leads to a local increase in the distribution coefficient.

Figure-5 shows the results of calculating the ion-molecular composition of aqueous solutions in equilibrium

with the extract. Common to all the dependences is a regular increase in the proportion of chloride complexes of rare-earth metal cations with an increase in the concentration of chloride ion.



**Figure-5.** The dependence of the distribution of equilibrium forms of cerium on the concentration of chloride ion.

Simultaneously with an increase in the concentration of chloride, the degree of dissociation of the carboxylic acid increases, which, apparently, leads to an increase in the distribution coefficient. A marked increase in the degree of dissociation of carboxylic acid due to an increase in the ionic strength of the solution according to the equation

$$\alpha_{HR} = \frac{1}{\gamma'_{\pm}} \cdot \sqrt{\frac{K_{d(HR)}}{C_{(HR)}}} \quad (7)$$

To describe the effect of the bromide ion, we can assume a similar mechanism of action, weaker than for the chloride ion. Unfortunately, it is not possible to perform a detailed calculation of the ratio of the ionic forms of the existences of lanthanides in bromide solutions due to the lack of reliable data on the instability constants or Gibbs energy for the formation of bromide complexes. It can be assumed that the stability of bromide complexes should be less than that of chloride complexes, but greater than for mononitrate complexes, based on a comparison of the "stiffness" of the anion as the base according to Pearson. As an indirect confirmation of this assumption, we can cite the literature data (Glushko 2004) on the Gibbs energy of complex formation (Table-1).

**Table-1.** Comparison of the Gibbs energy of the formation of complex compounds of lanthanides.

Lanthanide	Gibbs free energy, kJ/mol			
	[LnCl] <sup>2+</sup>	[LnBr] <sup>2+</sup>	[LnNO <sub>3</sub> ] <sup>2+</sup>	[LnOH] <sup>2+</sup>
Ce	812,5	700,7	793,3	858,6
Eu	715,5		699,6	845,5
Gd	797,1		779,9	764,4



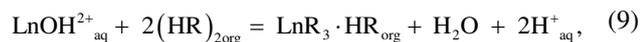
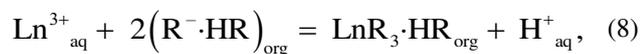
The occurrence of a positive or negative anionic synergistic effect is associated with the formation of lanthanide hydroxocomplexes. An analysis of the thermodynamic information given in Table-1 indicates that the gadolinium hydroxocomplex has the highest Gibbs

energy of formation. Indeed, the calculation of the content of the proportion of hydroxo compounds of the studied lanthanides for nitrate chloride and nitrate solutions at pH = 5 (Table-2).

**Table-2.** REM forms equilibrium in solution.

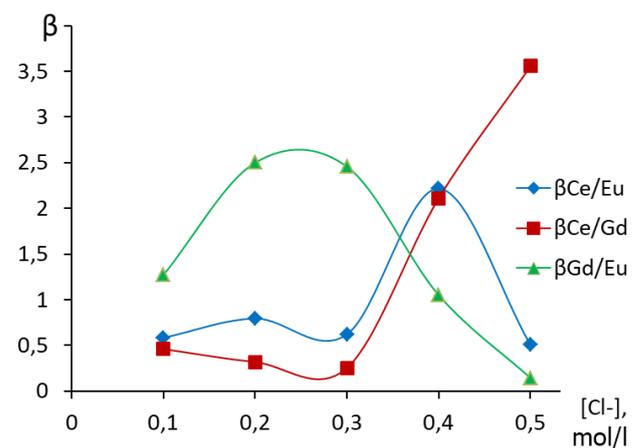
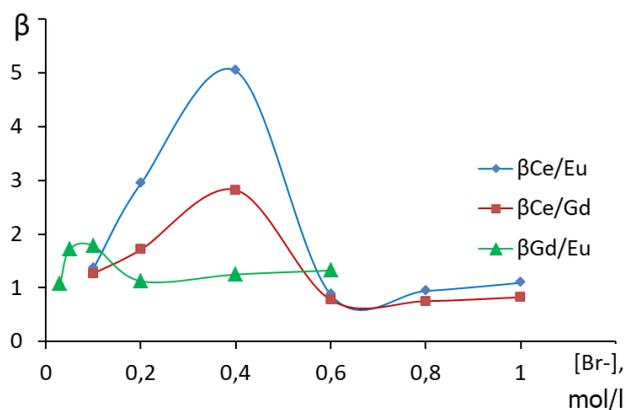
№	Element	The proportion of ionic forms ( $\text{Ln}^{3+}/\text{LnOH}^{2+}$ )		S
		Nitrate	Nitrate - chloride	
1	Ce	0,96/0,037	0,80/0,11	+
2	Eu	0,825/0,16	0,69/0,08	-
3	Gd	0,997/7·10 <sup>-4</sup>	0,9/4·10 <sup>-4</sup>	-

The change in the proportion of hydroxoforms is associated with the redistribution of lanthanide between the forms of existence, including halide complexes and the influence of the ionic strength of the solution on the degree of hydrolysis of the lanthanide, as is the case with cerium. Apparently, a positive synergistic effect appears due to the participation in the equilibrium of REM hydroxocomplexes:



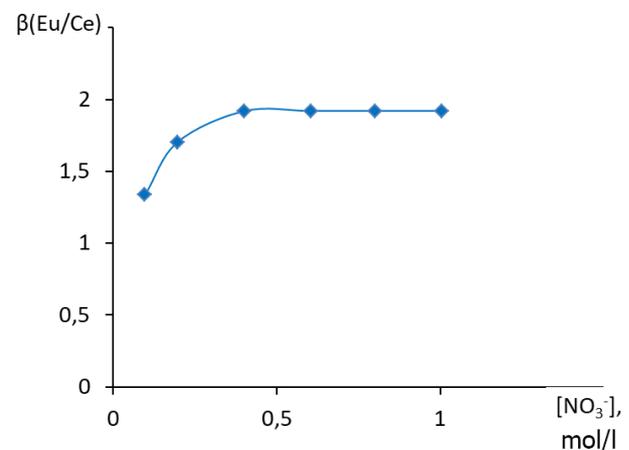
The absence of a positive synergistic effect in europium is explained by the high degree of extraction of its cations due to the low degree of hydration.

The data obtained suggest that halides can be used as additives to increase the separation coefficients of various rare-earth metals. Figure-6 shows the dependences of the separation coefficients of lanthanides on the concentration of halide in an aqueous solution.



**Figure-6.** The dependence of the separation coefficient on the concentration of halide in an aqueous solution.

It should be noted that the separation coefficient for the studied elements in nitrate media does not exceed 2 (Figure-7).



**Figure-7.** Effect of nitrate ion on the separation coefficient.

The maximum values of the separation coefficient are presented in Table-3.

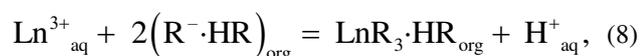
**Table-3.** Maximum values of the separation coefficient.

Nitrate		Bromide		Chloride	
		$\beta_{\text{Ce/Eu}}$	5,0	$\beta_{\text{Ce/Eu}}$	2,2
$\beta_{\text{Gd/Ce}}$	2,66	$\beta_{\text{Ce/Gd}}$	2,9	$\beta_{\text{Ce/Gd}}$	2,1
$\beta_{\text{Eu/Gd}}$	2,34	$\beta_{\text{Gd/Eu}}$	1,8	$\beta_{\text{Gd/Eu}}$	2,5

It is noteworthy that in the presence of a halide ion, the order of extraction of lanthanides is changed. In the absence of impurities, europium has the highest distribution coefficient and minimum value of the Gibbs energy of extraction. Also, the presence of halide salts can improve the separation of elements.

### CONCLUSIONS

An increase in the concentration of the halide ion leads to a regular increase in the ionic strength of the solution. There is an increase in the degree of dissociation of oleic acid, which in turn leads to an increase in the distribution coefficient due to the reaction:



Further addition of chloride does not lead to a noticeable increase in the proportion of the dissociated form of the extractant, but the halide complex becomes the predominant form of the existence of rare-earth metals. The result is a decrease in extractability.

The presence of hydroxocomplexes in an amount comparable to the fraction of chloride complexes leads to an increase in the distribution coefficient of lanthanides due to the reaction  $\text{LnOH}^{2+}_{\text{aq}} + 2(\text{HR})_{2\text{org}} = \text{LnR}_3\cdot\text{HR}_{\text{org}} + \text{H}_2\text{O} + 2\text{H}^{+}_{\text{aq}}$ , and the appearance of an anionic synergistic effect.

If the distribution coefficient is exceeded at any chloride concentration, the distribution coefficient is positive for a chloride concentration of zero and the synergistic effect is positive and occurs when there are comparable amounts of hydroxo and monochloride complexes. A negative synergistic effect is observed in the absence of a hydro complex.

### ACKNOWLEDGEMENT

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