EFFECT OF ANION COMPOSITION ON THE EXTRACTION OF CERIUM (III) AND YTTRIUM (III) BY OLEIC ACID

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ABSTRACT

The extraction of cerium (III) and yttrium (III) was studied by oleic acid from nitrate, chloride and sulfate media. The anion series is selected according to the increase in the "chemical hardness" of the inorganic ligand anion by Pearson. It's shown that when passing from a nitrate medium to a chloride and a sulfate one, the hydrogen index of the semiextraction ($pH_{1/2}$) increases from 4.2 to 4.65 for cerium (III) and from 4.7 to 5.12 for yttrium (III). Unassociated complexes are formed in the organic phase with the general formula $LnR \cdot HR_{(org)}$. The extraction at the stoichiometric consumption of the extractant proceeds according to the equation: $Ln_{aq}^{3+} + 2(NaR \cdot HR)_{org} = LnR_3 \cdot HR_{org} + H_{aq}^{+} + 2Na_{aq}^{+}$. An increase in the "chemical hardness" of the anion-ligand leads to a decrease in the equilibrium constant, to the growth of the effective Gibbs energy of the formation of rare-earth metal oleates, and to a decrease in recovery into the extract. The hard ligand has a stronger effect on the extraction of the hard rare-earth metal cation as the Pearson base, i.e., in this case yttrium (III). An increase in the concentration of the anion-ligand leads to a suppression of the extraction of the "hard" yttrium cation, consequently, to an increase in the cerium and yttrium separation factor with oleic acid.

Keywords: extraction, separation, cerium, yttrium, REE, oleic acid, equilibrium constant.

INTRODUCTION

Extractive methods are now widely used for the recovery and separation of rare-earth metal ions (REM) (Brill 1980; Gindine 1984; Zelikman *et al* 1991; Michailichenko *et al* 1987).

In the main, extraction of rare-earth metals is carried out from nitrate media; in this case, most of the extractants used in practice are most effective. The expansion of the mineral and raw-material base of rare-earth metals requires the involvement in processing of poor rare-earth raw materials of both natural and technogenic origin, for the decomposition of which are used hydrochloric and sulfuric acids, as a cheaper reagent. In processing such raw materials are formed acidic solutions of complex anionic composition with a low content of rare earth metals. Therefore, the study of the influence of the presence of sulfates or chlorides on the recovery and separation of rare earth metals from low-concentration solutions is an urgent task.

LITERATURE REVIEW

As the extractants of non-ferrous, rare and rare-earth metals has been studied the application of many carboxylic acid: naphthenic, versatic, aliphatic (Korpusov *et al.,* 1975; Illyuviyeva, 1966; Singh *et al.,* 2006; Voropanova *et al.,* 2015, Voropanova, 2016).

However, the properties of oleic acid - a relatively cheap reagent of natural origin - is poorly understood. The extraction of carboxylic acids proceeds by a cation exchange mechanism. The main regularity in the extraction of rare-earth metals by cation-exchange extractants in general and carboxylic acids in particular is a reduction in the recovery rate from lanthanum to lutetium. When an excess amount of extractant is used with regard to the metal cation, the extraction process is described by the equation

$$Ln_{aq}^{3+} + \frac{3+s}{2}(HR)_{2,org} = (LnR_3 \cdot sHR)_{org} + 3H_{aq}^{+}, (1)$$

The equation (1) takes into account the existence of the carboxylic acid in the extractant phase in the form of a dimer and the solvation of the metal carboxylate by the extractant molecules in the organic phase. If the extractant content is too high, the solvate number s when extracting lanthanides is usually three.

By the magnitude of the linear term of the logarithmic mass balance equation, we can determine the value of the general equilibrium constant.

$$\lg D = \lg K_{\Sigma} + \frac{3+s}{2}\lg[(HR)_2] + 3pH, \qquad (2)$$

The angular coefficients of the logarithmic dependences of the distribution coefficient on the pH and the concentration of the extractant give the value of the solvate number. According to the reaction (1), the main factor influencing the extraction of non-ferrous metals and rare earth metals by carboxylic acids is the hydrogen index.

Taking into account the association of carboxylate metal complexes in the organic phase into dimer forms and associates of higher order, the extraction equation according to (Tanaka *et al.,* 1969; Tanaka *et al.,* 1970; Inoue *et al* 1981; Gindine, 1984) is proposed to be written as follows:

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$$xMe_{aq}^{3+} + x\frac{z+s}{2}(HR)_{2,org} = (MeR_z \cdot sHR)_{x,org} + zxH_{aq}^{+}, \ (3)$$

For a thermodynamic description of extraction processes often use the concept of effective or corrected equilibrium constants. In the equation of effective equilibrium constant taken into account non-ideality of the water phase through product activity coefficients, but for thecharacteristics of the organic phase used the notion of concentration in view of the fact that the definition of activity component in multi-component organic system is difficult, and in most cases impossible (Voldman, 2003).

For the reaction (3) equation of the effective equilibrium constant

$$K = \frac{C_{org} \cdot a_{H_{aq}^{+}}^{z \cdot x}}{C_{HR_{org}}^{\frac{x+s}{2}} \cdot a_{Me_{aq}^{z+}}^{x}}, \tag{4}$$

can be transformed into a logarithmic form:

$$\lg C_{org} = \lg K + x\frac{z+s}{2}\lg C_{HR} + x \cdot zpH + x\lg C_{aq}, \quad (5)$$

in which the value of $\widetilde{K}$ includes the product of the activity coefficients.
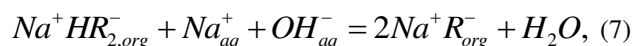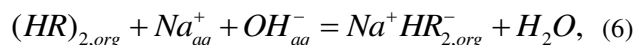
Angular coefficient of dependence $\lg C_{org}$ from $x \cdot zpH + x\lg C_{aq}$ for a constant extractant concentration in the organic phase or dependence $\lg C_{org}$ from $x\frac{z+s}{2}\lg C_{HR} + x\lg C_{aq}$ at a constant value of the ρH of the aqueous solution should correspond to the degree of polymerization.

Researches of the mechanism of the extraction by cation exchange showed that the equation (1) is the sum for the following equilibria (Inoue *et al.,* 1981; Wang *et al.,* 2003; Xiong *et al.,*2006):

▪ dissociation of dimerized form in organic phase;

▪ distribution of extractant between organic and aqueous phases;

▪ its dissociation in aqueous phase (or at the Phase boundary);

▪ formation of the extracted compound;

▪ distribution in organic phase;

▪ solvation by extractant molecules.

With an increase in the ρH of the aqueous phase due to the addition of alkali in the system are realized the following equilibria:

$$(HR)_{2,org} + Na_{aq}^{+} + OH_{aq}^{-} = Na^{+}HR_{2,org}^{-} + H_2O, \ (6)$$

$$Na^{+}HR_{2,org}^{-} + Na_{aq}^{+} + OH_{aq}^{-} = 2Na^{+}R_{org}^{-} + H_2O, \ (7)$$

At pH < 3 the number of compounds the composition $Na^{+}HR_{2,org}^{-}, Na^{+}R_{org}^{-}$ in the organic phase is negligible. In the surface layer there are only HR_{org}, R_{org}^{-}, dimerized molecules of composition $(HR)_{2,org}$ in the surface layer can not be adsorbed.

When cation-exchange extraction, inorganic anions do not pass into the organic phase. However, the nature of the mineral acid anion in aqueous phase affects the course of dependence of $\lg(D) = f(pH)$ This is due to the varying complexing ability of the cations in aqueous phase with different anions. The formation of complexes with inorganic ligands in aqueous phase are invited to take into account the conversion of mass balance equation to the form (Flett, 1963; Ashbrook, 1972).

$$\lg D = \lg K + \frac{3+s}{2}\lg[(HR)_2] + 3pH - \lg(1 + \sum_i \beta_i [L]^i), (8)$$

where β_i - constant of instability of a complex of a metal of composition $LnAn_i^{3-i}$ with an inorganic ligand; [L] - is the concentration of the inorganic anion-ligand in aqueous solution.

According to equation (8) while increasing the concentration of inorganic anion-ligand should be observed decrease of recovery of lanthanide cation into composition of the extract. Equation applicable to describe the extraction of non-ferrous metals under the condition of excessive content of extractant and anion-ligand in compare with stoichiometric.

For processing solutions, depleted by the content REM the use of excess amounts of impractical as from the position of the economy, and from the point of view of reducing the technogenic impact on the environment.

The purpose of the work

Study of the extraction properties of oleic acid in relation to the first members of the light and heavy series REM -cerium (III) and yttrium (III) in various media - nitrate, chlorideand sulfate - at the lowest possible amount of extractant.

Technique experiment

The research of yttrium and cerium extraction from aqueous solutions of various anionic composition is based on the concept of the influence of nature of anion on the extractability of a rare-earth metal cation, founded on

the notion of hard and soft acids and bases. Anion series is selected in accordance with known methods of acid leaching of mineral raw materials, i.e. considered the influence of nitrate, chloride and sulfate anions on the extraction equilibrium. In a series of anions "nitrate-sulphate-chloride" should decrease the extraction of cerium and yttrium by oleic acid.

Extraction of rare-earth metals was carried out by solutions of oleic acid in an inert diluent (xylene). The average molar mass of oleic acid is 282.5 g/mol, gross-formula $C_{18}H_{34}O_2$, average dissociation constant is characterized by a value of pKd = 5.9. To simulate the composition solution of acid decomposition of poor mineral resources, the original concentration of each REM studied in aqueous solution was 0.01 mol/l.

In an experimental study of the extraction of cations of rare-earth metals, the molar ratio of oleic acid to the cation of the rare-earth metal is equal to the stoichiometric according to equation (1).

Contact phases carried out using Parallel Auto-MATE® Reactor System manufactured by HEL with automatic maintenance of specified pH values.

Phase separation is made on the centrifuge production Koehler K61002. Pointed out that the increase in pH leads to an increase in the length of separation of phases.

Dependences of coefficient of distribution of pH of the aqueous solution was obtained at a constant concentration of oleic acid in the extractant composition 0.5 mol/l. Dependences on the concentration of distribution coefficient of oleic acid in the extractant composition were obtained at a pH of an aqueous solution equal to five. Dependence on the concentration of distribution coefficient of inorganic anion-ligand obtained at constant pH aqueous solution equal to 5 and concentrations of oleic acid in the extractant composition of equal 0.5 mol/l.

Analysis of the concentration of lanthanide ions in an aqueous solution before and after extraction was performed by complexometric titration with Trilon B in the presence of an indicator with arsenazo (III) using automatic titrator Mettler Toledo T58, with a photosensitive electrode Mettler Toledo DP 5 Phototrode.

The content of lanthanide in the organic phase was calculated from the difference in concentrations in the aqueous solution before and after extraction, taking into account the ratio of the volumes of phases:

$$C_{org} = \frac{C_0 - C_{aq}}{\alpha}, \tag{9}$$

where C_{org} and C_{aq} - the concentration of lanthanide in the extract and the equilibrium aqueous phase, respectively, mol/l; C_o - initial concentration of REM in aqueous solution, mol/l; under experimental conditions $\alpha = 0,1$.

Distribution coefficient is calculated according to the equation:

$$D = \frac{C_{org}}{C_{aq}}, \tag{10}$$

The lanthanide separation coefficient is calculated by the equation:

$$\beta_{2/1} = \frac{D_2}{D_1}, \tag{11}$$

where the index 2 is assigned a better extractable element. To determine the coefficients of reaction extraction and the overall equilibrium constant angular coefficients analysis method of logarithmic distribution coefficient dependency onconcentration of solvent and pH of the aqueous solution.

To determine the reaction coefficients and the general equilibrium constant, a method is used to analyze the angular coefficients of the logarithmic dependences of the distribution coefficient on the concentration of the extractant and the pH of the aqueous solution.

The results of the experiment

Change in the concentration of nitrate ion in aqueous solution has not led to noticeablechanges in distribution coefficient. The increased chloride ion and sulfate ion leads to a decreasein the extraction of both elements into the organic phase. With yttrium (III) this process is more intense.
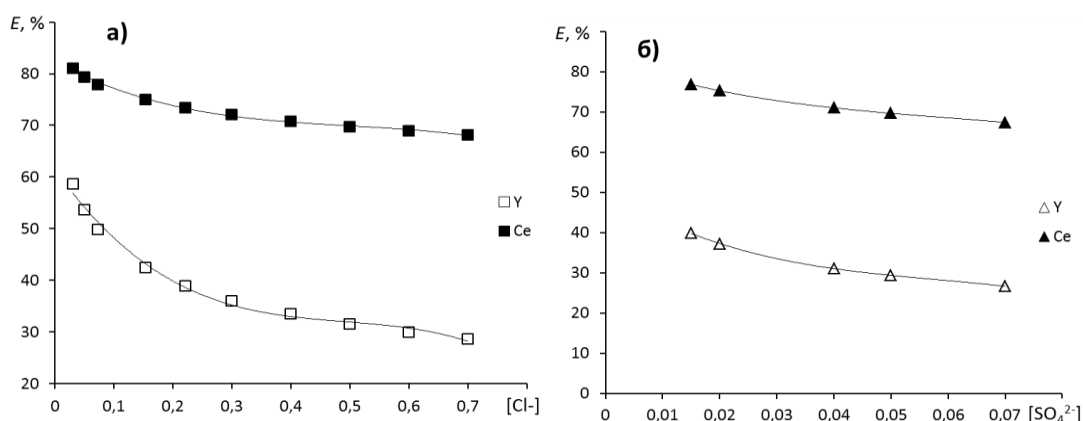
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Figure-1. Dependence of the degree of recovery of cerium (III) and yttrium (III) on the molar concentration of chloride ion (a) and ion sulfate (b) in aqueous solution.

At pH values less than 3.5 differences in extracting cerium (III) and yttrium (III) by oleic acid is not affected due to the lack of metal extraction in organic phase. When you increase the pH going natural increase extraction and, consequently, there are differences in the behavior of cerium (III) and yttrium (III) in different media (Figure-1). With an increase in concentration of extractant recovery in organic phase is also increasing.
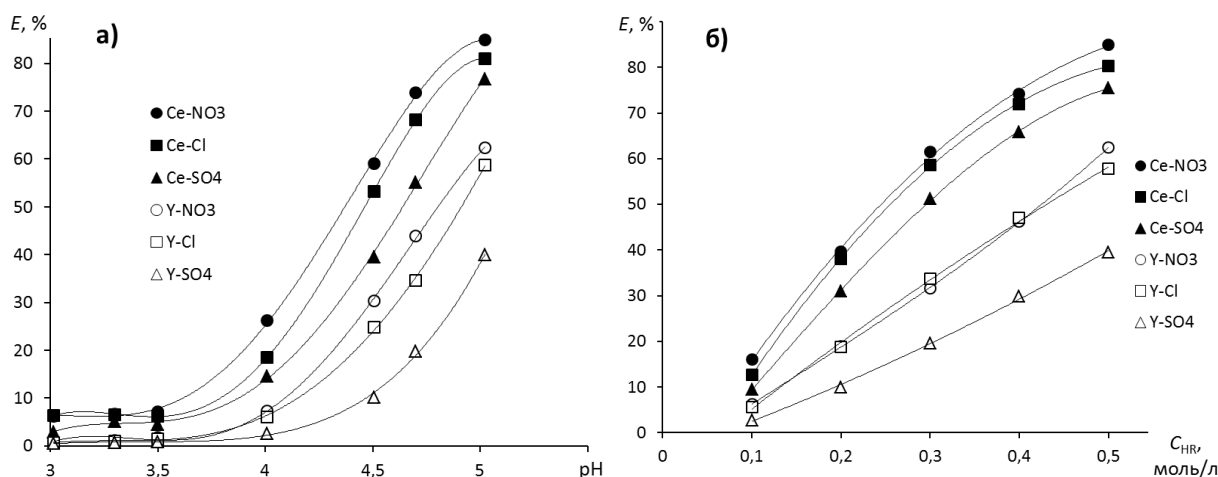

Figure-2. Dependence of the degree of recovery of cerium (III) and yttrium (III) on the ρH aqueous phase (a) and the concentration of naphthenic acid in composition of extractant (b).

As the "hardness" of the inorganic anion-ligand increases, the pH of the semi-extraction increases. For cerium (III) $\rho H_{1/2}$ in nitrate medium is 4.20; in the presence of chloride salts - 4.45, sulfated medium - 4.65 . Extraction of yttrium in the composition of the extract is going worse than cerium. The pH of the semi-extraction of yttrium (III) from the nitrate medium - 4.70, from chloride - 4.90 and from sulphate - 5.12. In the presence of chloride ion and sulfate ion extraction is declining both inthe organic phase. The influence of sulphate is more significant than the effect of chloride, especially in the case of yttrium, for which extraction from the nitrate medium differs little from extraction from the chloride medium.

Discussion of the results of the experiment

The logarithmic dependencies of the distribution coefficient on the anion-ligand concentration shown in Figure-3 are linear and described by empirical equations

$$\lg D_{Ce} = 0.2 pC_{Cl^-} + 1.30; \tag{12}$$

$$\lg D_{Y} = 0.4 pC_{Cl^-} + 0.54; \tag{13}$$

$$\lg D_{Ce} = 0.3 pC_{SO_4^{2-}} + 0.96; \tag{14}$$
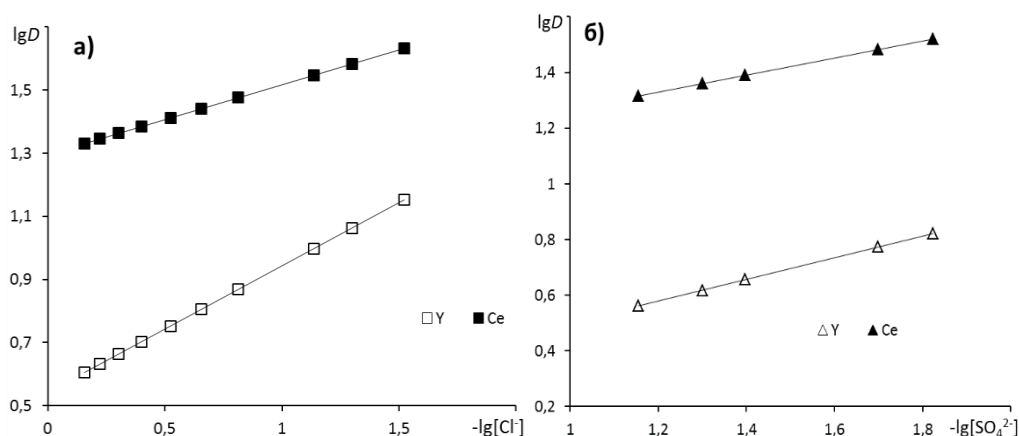
$$\lg D_{Y} = 0.4 pC_{SO_4^{2-}} + 0.11; \tag{15}$$

Figure-3. Logarithmic dependence coefficients distribution of cerium (III) and yttrium (III) on the content chloride ion (s) and sulfate ion (b).

The value of the angular coefficient of logarithmic dependencies distribution coefficient on the ligand-anion concentrations close to zero shows a lack of extraction of chloride or sulphate complexes of cerium and yttrium. Analysis of anions chloride, nitrate and sulfate also showed complete absence of their transition into the organic phase, therefore, extraction can take place only with the involvement Ln^{3+} or its hydrolyzed form $LnOH^{2+}$.

Analysis of logarithmic dependencies distribution coefficients of cerium (III) and yttrium (III) on the pH and concentration of oleic acid in the extractant composition (Figure-4) showed that the dependency can be described by linear equations

$$\lg D = 1.2pH + A, \tag{16}$$

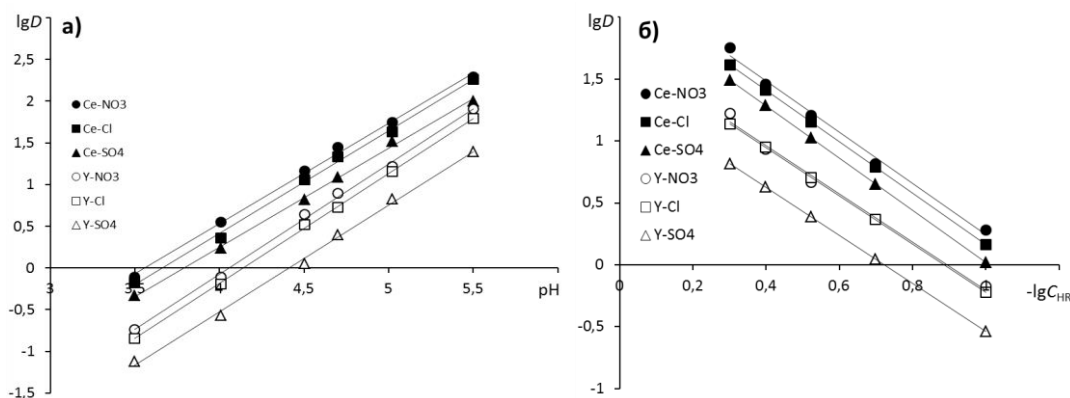$$\lg D = 2\lg[HR] + B, \tag{17}$$

Figure-4. Logarithmic dependence coefficients distribution of cerium (III) and yttrium (III) on the pH of the aqueous phase (a) and the concentration of oleic acid in the extractantcomposition (b).

Equal angular values of the coefficients of the equations (10) and (11), received for various media indicate a single mechanism for the extraction equilibrium. The difference in the magnitude of the angular coefficient from the literature data, where it is equal to 3 when the amount of carboxylic acids is excess, indicates a difference in extraction at an extractant consumption close to the stoichiometric ratio and indicates possible participation in the extraction equilibrium of neutralized to the sodium form molecules of oleic acid or hydroxycomplexes of cerium and yttrium.

The magnitude of the free term of the linear equation of the coefficient

distribution from the pH or concentration of the extractant is related to the value of the effective equilibrium constant for the formation of the metal cation carboxylate:

$$\lg D = \lg K_\Sigma + 2\lg[(HR)] + 1.2pH \tag{18}$$

$$\lg K_\Sigma = B - 1.2pH = A - 2\lg[HR] \tag{19}$$

and is composed of the equilibrium constant of extraction of the lanthanide cation K, and the sum of the reaction equilibrium constants associated with dimerization and the acid-base properties of the extractant K':

$$K_{\Sigma} = K \cdot K'$$ (20)

The values of the empirical equilibrium constants calculated from equation (19) are shown in Table-1.

Table-1. The values of the coefficients A and B of logarithmic dependencies the distribution coefficient of the pH and the concentration of naphthenic acid in the extractant.

Anion	Coefficient A		Coefficient B		$-\lg K_{\Sigma}$	
	Ce	Y	Ce	Y	Ce	Y
NO_3^-	-4,4	-5,4	2,3	1,8	3,75	4,50
Cl^-	-4,5	-5,5	2,2	1,7	3,85	4,60
SO_4^{2-}	-4,6	-5,6	2,1	1,4	3,95	4,80

When moving from nitrate medium to the chloride medium and to the sulphate medium a decrease in the overall equilibrium constant is observed.
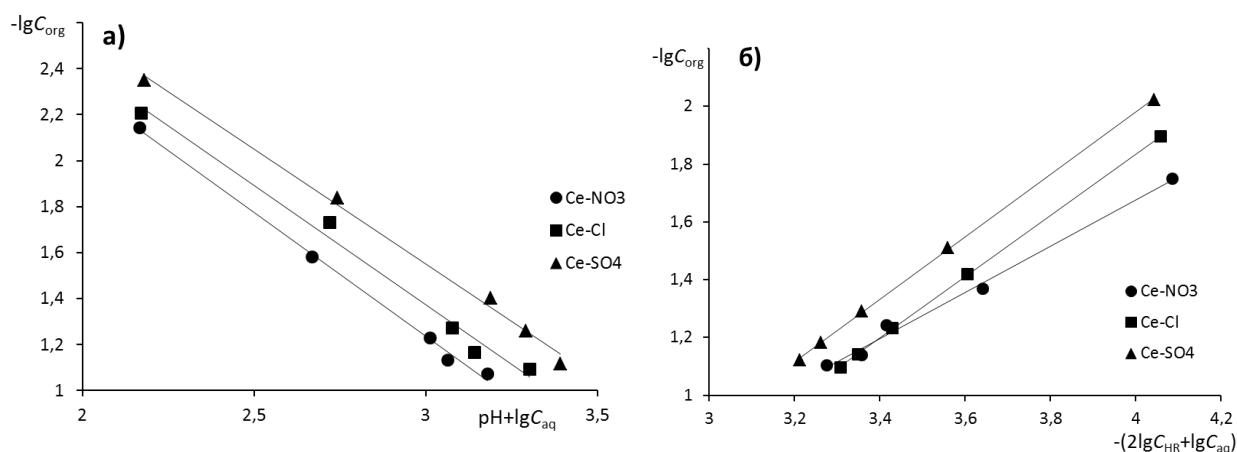

Figure-5. Graphical determination of the degree of association of the oleate complex cerium (III) from the dependence of the distribution coefficient on the pH (a) and the concentration of oleic acid in xylene (b).

To establish the degree of association of the REM oleate in the organic phase, taking into account the angular coefficients of equations (16) and (17), logarithmic dependences on the pH function of the aqueous solution and the function of the concentration of oleic acid in the extractant composition were obtained, shown in Figures 5 and 6.
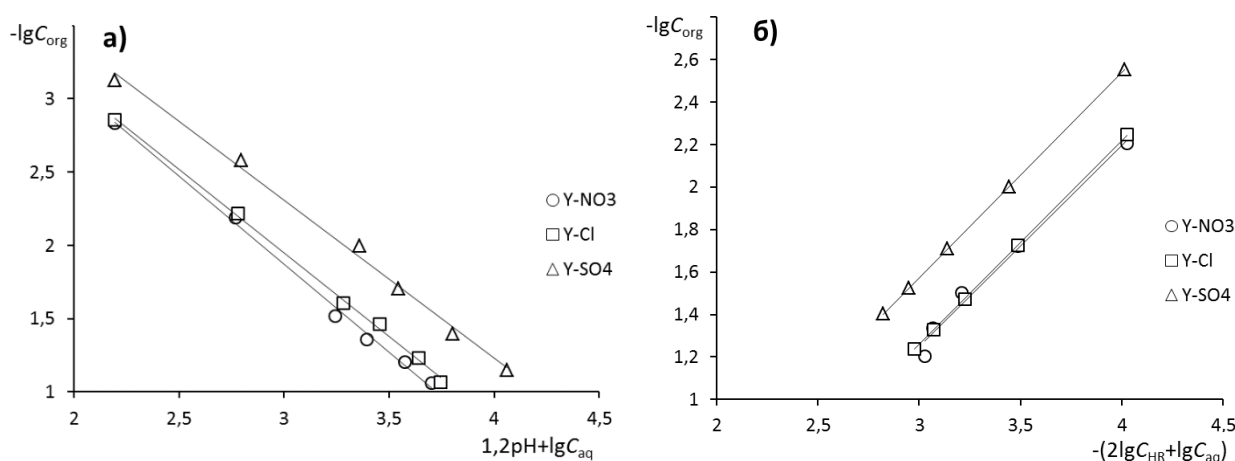

Figure-6. Graphical determination of the degree of polymerization of oleate complex of yttrium (III) from the dependence of the distribution coefficient on the pH (a) and the concentration of oleic acid in xylene (b).

Linear dependence Figures 5 and 6 describe the equations shown in Table-2, with the angular coefficient

close to 1, which means that there is no association of cerium and yttrium oleates in the extractant phase.

Table-2. Equations of the logarithm of the element concentration in the extract from the pH function and the extractant concentration function.

Anion	Approximation equation	
Cerium		
NO_3^-	$\lg C_{org} = 1.08 i_{pH} - 4.48$	$\lg C_{org} = 0.8 i_{C_{HR}} + 1.52$
Cl^-	$\lg C_{org} = 1.04 i_{pH} - 4.49$	$\lg C_{org} = 1.06 i_{C_{HR}} + 2.41$
SO_4^{2-}	$\lg C_{org} = 0.98 i_{pH} - 4.55$	$\lg C_{org} = 1.08 i_{C_{HR}} + 2.34$
Yttrium		
NO_3^-	$\lg C_{org} = 1.20 i_{pH} - 5.48$	$\lg C_{org} = 0.94 i_{C_{HR}} + 1.58$
Cl^-	$\lg C_{org} = 1.14 i_{pH} - 5.37$	$\lg C_{org} = 0.96 i_{C_{HR}} + 1.62$
SO_4^{2-}	$\lg C_{org} = 1.08 i_{pH} - 5.55$	$\lg C_{org} = 0.97 i_{C_{HR}} + 1.32$

Taking into account possible processes of hydrolysis of the cation and surface dissociation of the carboxylic acid, the formation of naphthenate REM occurs at the phase interface according to equation:

$$Ln_{aq}^{3+} + zH_2O + (3-z)R_{org}^- = Ln(OH)_z R_{(3-z),org} + zH_{aq}^+ \quad (21)$$
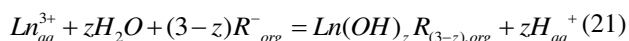
for which the material balance is presented in the form of a logarithmic equation

$$\lg D = \lg K + zpH - (3-z)\lg(1 + \frac{a_{H^+}}{K_d}) + (3-z)\lg(C_s - (3-z)C_{org}) + \lg C_{Ln_{aq}^{3+}} \quad (22)$$

The magnitude of the linear term depending on the pH of the function

$$i_{pH} = zpH + (3-z)\lg(C_s - (3-z)C_{org}) - (3-z)\lg(1 + \frac{a_{H^+}}{K_d}), \quad (23)$$

proportional to the effective equilibrium constant.

By the linear term of the dependence of the logarithm of the coefficient distribution from the function of the equilibrium concentration of the extractant

$$i_{C_{HR}} = \lg(C_s - (3-z)C_{org}), \quad (24)$$

the value of the effective equilibrium constant в can be calculated from equation

$$\lg K^o = b - zpH - (3-z)\lg(1 + \frac{a_{H^+}}{K_d}), \quad (25)$$

The criterion for the validity of the model is the match Gibbs energies and extraction constants defined for this value of z from equations (23) and (24) that was obtained for z = 0.

The average values of the Gibbs differential energy for the formation of yttrium oleate are -31.3 kJ / mol in nitrate, -30.0 kJ / mol in chloride and -28.0 kJ / mol in the sulfate medium.

The average values of the Gibbs differential energy for the formation of cerium oleat are -35.1 kJ / mol in nitrate, -34.0 kJ / mol in chloride and -32.8 kJ / mol in sulfate medium.

Taking into account the angular coefficients of the logarithmic empirical dependences of the lanthanide distribution coefficients on pH and oleic acid concentration, and also taking into account the electroneutrality rule, the extraction equation can be written as:

$$Ln_{aq}^{3+} + 2(NaR \cdot HR)_{org} = LnR_3 \cdot HR_{org} + H_{aq}^+ + 2Na_{aq}^+, \quad (26)$$

Differences in the course of the dependences are consistent with the result of calculating the mole fraction of equilibrium forms of existence in the aqueous solution of cerium (III) and yttrium (III).

In the nitrate medium, cerium (III) and yttrium (III) exist in the form of a simple cation Ln^{3+} (Figure-7).
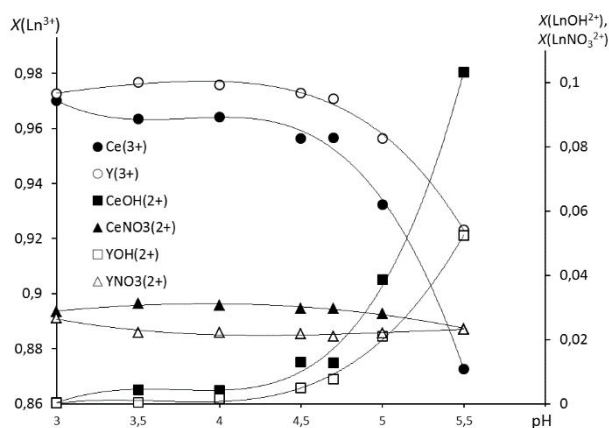
Figure-7. Dependence of the mole fraction of the basic forms of the existence of cerium and yttrium in the nitrate medium on the pH of the aqueous solution.

An increase in the pH of the aqueous solution naturally leads to an increase in the fraction of the hydrolyzed form of both cerium and yttrium, but in the studied pH range their fraction is much smaller than the fraction of the simple cation Ln^{3+}.
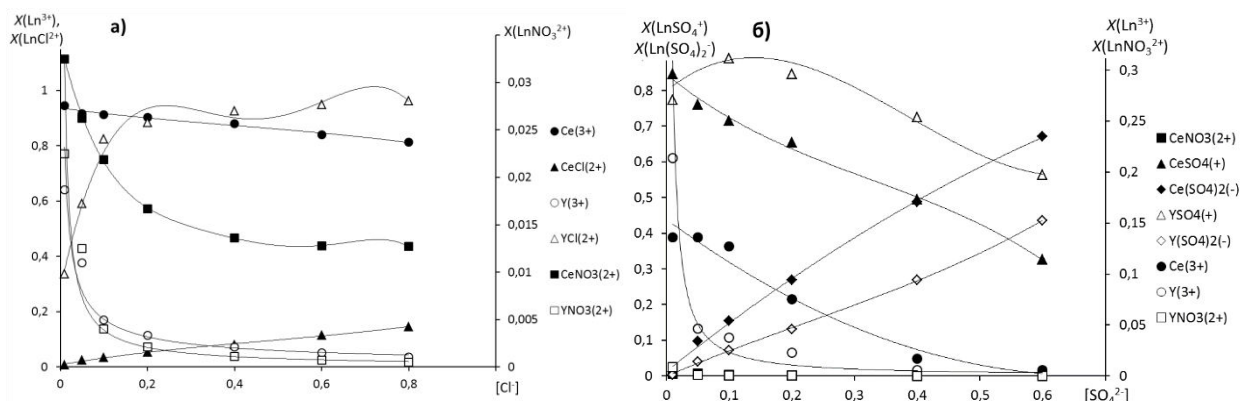
With an increase in the chloride ion concentration, the share of mono-chloride complexes $LnCl^{2+}$ also increases. When chloride ion concentration of no more than 0.2 mol / l, both forms of existence (Ln^{3+} and $LnCl^{2+}$ are in comparable amounts (Figure-8-a). Nitrate complexes are practically absent. The main form of the existence of yttrium (III) is its monochloride complex, the content of which increases sharply with increasing concentration of chloride ion in the solution. When the concentration of chloride ion is close to stoichiometric, there are both Y^{3+} and YCl^{2+} in comparable amounts. When a small concentration of chloride ion in solution of cerium (III) exists mainly in the form of simple cations Ce^{3+} (Figure-8- a). With an increase in the concentration of chloride is a redistribution of cerium between the form of a simple cation and its chloride complexes. To the concentration of chlorine in a solution of 1 mol/l of chloride forms the prevailing is $CeCl^{2+}$

Figure-8. Distribution of cerium (III) and yttrium (III) on equilibrium forms of existence depending on the molar concentration of chloride ion and sulfate ion (b) at pH = 3.

With increasing concentrations of sulfate ion (Figure-8-b) naturally increases theproportion of sulphate complexes composition $LnSO_4^+$ and $Ln(SO_4)_2^-$.With a sulfate ion content less than 0.4 mol / l, the monosulfate form predominates, at a higher concentration sulfate ion - a disulfate form. With increasing concentration of sulfate ion sharply increases the proportion of yttrium мoтosulfate complexes, which is the main form of existence of yttrium in the presence of sulfate ion. For cerium with increasing concentration of sulfate-ion there is a gradual replacement of monosulfate complex on the disulfate. Although the main amount of both cerium (III) and yttrium (III) in the sulfate solution in this range of sulfate ion concentrations is in the form of a monosulfate

complex $LnSO_4^+$ (Figure-8-b) the number of simple cations capable to participate in the extraction reaction with carboxylic acids in the case of cerium (III) is somewhat larger than that of yttrium (III).

An increase in pH to 5 - 5.5 (Figure-9) does not lead to a noticeable increase in the content of the hydrolyzed form in the form of a monohydroxo complex.

In a sulfate medium in the studied pH range and concentrations of the anion-ligand the main amount of cerium and yttrium is in the form of monosulfate complexes $LnSO_4^+$ and a relatively small amount of metal exists as a simple ion or in the form of a disulfate complex. In chloride and nitrate media prevails Ln^{3+}, which explains the high distribution coefficient.
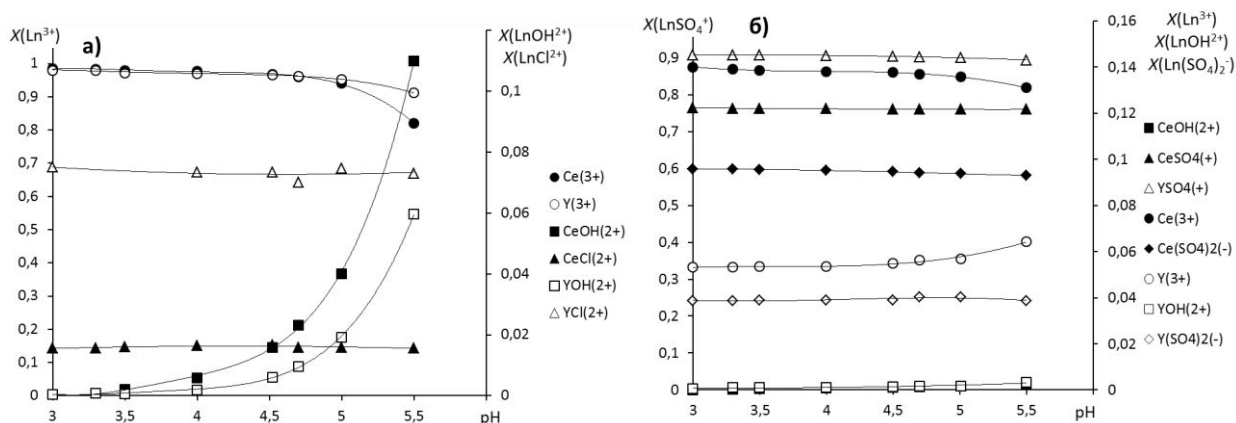
Figure-9. Distribution of cerium (III) and yttrium (III) in equilibrium forms existence in the chloride
(a) and sulfate (b) media, depending on the pH.

The difference in the stability of chloride and sulfate complexes of cerium and yttrium, consenquently, difference in proportion of metal cations related to acidocomplexes in depending on the concentration of the inorganic anion ligand in the system leads to increased separation factor cerium and yttrium by oleic acid Figure-10.
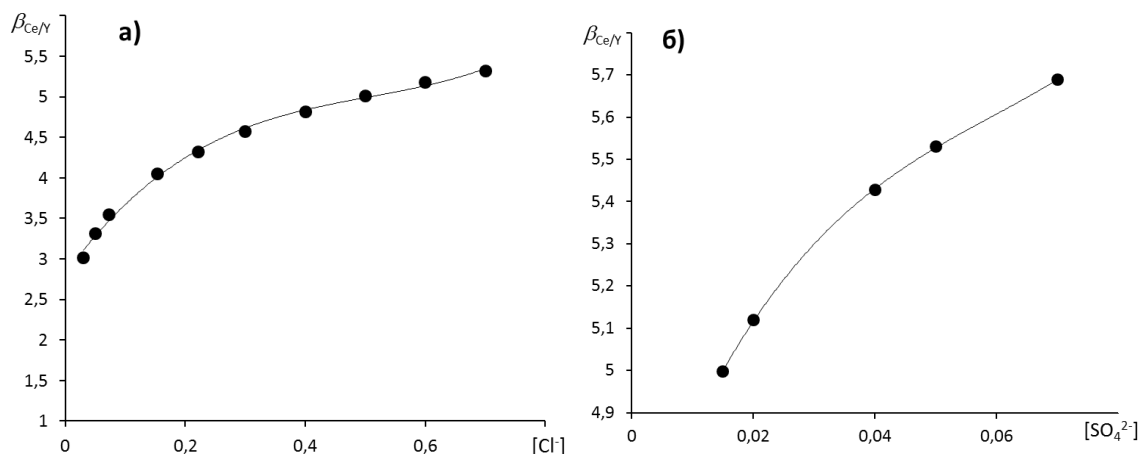

Figure-10. Influence of concentration of chloride ions (a) and sulfate ions (b) on separation of cerium
(III) and yttrium (III) by extraction with 0.5 M solution of oleic acid in o-xylene at pH = 5.

Cerium (III) has a larger distribution coefficient and an increase in the concentration of the anion-ligand in the solution for cerium extraction is less pronounced. The yttrium cation (η = 20.6) is a more "hard" acid according to Pearson than cation of cerium (η = 8.28), accordingly, it shows a greater propensity to the formation of strong complexes with more "hard" ligands - sulfate or chloride ions, which leads to a greater reduction in the extraction of yttrium (III) by oleic acid in sulfate and chloride media and, as a result, growth of the separation factor.

CONCLUSION

An increase in chloride or ion sulfate concentration leads to a decrease extraction of cerium (III) and yttrium (III) into the organic phase during extraction with oleic acid. Defined the pH of the semi-extraction of cerium and yttrium by oleic acid in nitrate, chloride and sulfate media. It is shown that in the transition from nitrate medium to chloride and sulfate $\rho H_{1/2}$ increases, which is associated with an increase in the proportion of non-extractable chloride and sulfate complexes of REM. Obtained the values of the general equilibrium constants for the extraction of cerium and yttrium and values of effective Gibbs energies for the formation of cerium and yttrium oleates for various media. It is shown that an increase in the hardness of the anion-ligand leads to a decrease in the overall equilibrium constant and to the growth of the effective Gibbs energy of the formation of REM oleates.

Established distribution of cerium and yttrium by forms of existence in various media, depending on the acidity of the water solution. In nitrate and chloride media the main form of cerium (III)-cation Ce^{3+}; in the sulfate medium - monosulfate complex $CeSO_4^{2+}$. The chloride

and sulphate media yttrium exists mainly in the form of chloride YCl^{2+} and sulphate YSO_4^+ complexes.

Introduction of sulphate or chloride supplementation leads to increased separation factor of cerium and yttrium by oleic acid.

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