

Solvent Extraction of Cerium (III) and Yttrium (III) by Carbonic Acids from Nitrate Medium

T. Litvinova

St. Petersburg State Mining Institute, St. Petersburg, 21 line, Russia

Die Daten in Extraktion von Zerium (III) und Ytter (III) durch Ölsäure- und Naphtensäurelösungen in Oxytol aus Nitratmedium sind erhalten. Mit Abhängigkeiten des Verteilungskoeffizienten von pH und des Bestandes der organischen und wässrigen Phase sind Festdaten und Gibbsenergien der Extraktionsgleichgewichten ausgerechnet, der Bestand der Solvatationskomplexe ist bestimmt.

Experimental data were obtained on solvent extraction of cerium (III) and yttrium (III) from nitrate media with solutions of oleinic and naphthenic acids in *o*-dimethylbenzene. Composition of solvate complexes as well as constants and Gibbs energies of the extraction equilibrium were calculated basing on dependences of the distribution coefficient on pH and composition of the organic and aqueous phases.

1 Introduction

It is possible to use such sources of technogenic pollution as tailings storages, refuse ores, waste water from mining-and-metallurgical plants as sources of high-value raw materials i.e. non-ferrous and rare-earth metals. It can be feasible to recover valuable components from leaching solutions or waste water by solvent extraction method. Use of tributyl phosphate (TBP) in this case is uneconomical because of its high cost and toxicity level.

The aim of this research was to study cerium (III) and yttrium (III) behavior in solvent extraction with carbonic acids from nitrate medium.

2 Experimental Study

In the experimental part of the investigation we studied solvent extraction of Ce (III) and Y (III) from binary water solutions, which contained 0.01 mol/kg of these elements, with 0.5 M solution of oleinic or naphthenic acids in *o*-dimethylbenzene as the extractant. As the result of these experiments we obtained the dependence of Ce and Y distribution coefficients on pH level and extractant concentration in the organic phase.

Fig. 1 shows dependence of the distribution coefficient D on pH levels at constant value of the extractant concentration.

Ce (III) and Y (III) distribution coefficients are increasing with increasing pH levels. In case of naphthenic acid yttrium (III) is extracted better than cerium. On application of oleinic acid at pH

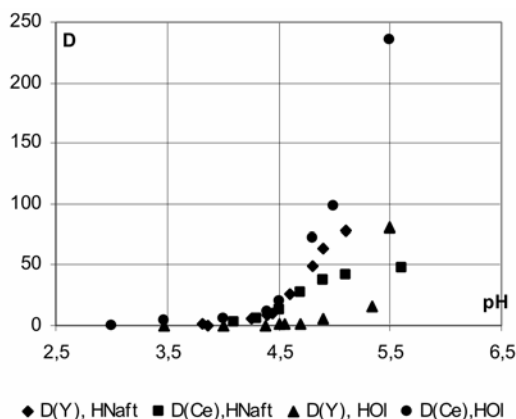


Fig. 1: Dependence of Ce and Y distribution coefficients on pH levels.

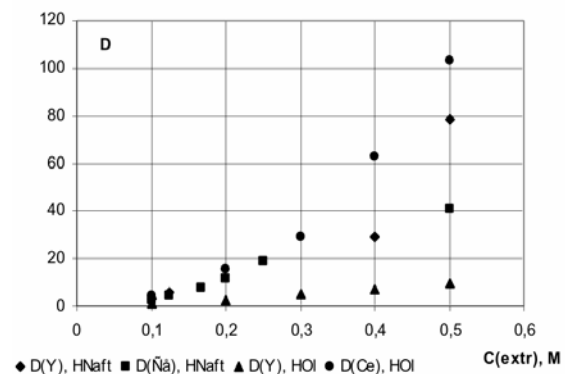


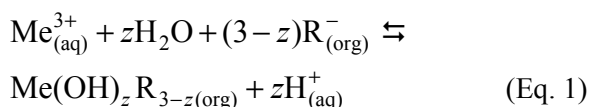
Fig. 2: Dependence of Ce and Y distribution coefficients on extractant concentration levels.

4–5, yttrium (III) is not extracted into organic phase, which creates conditions for extraction separation of rare earth metals of cerium and yttrium groups.

Dependence of the distribution coefficient on extractant concentration was investigated at constant pH values of 5.0 ± 0.1 and molecular ratio of carboxylic acids to metal, which was equal to 4. Results of this experiment are presented in Fig. 2.

Distribution coefficient is increasing with the increase in extractant concentration. The dependence is almost equal, some difference being apparent when the extractant concentration is no less than 0,3 mol/l. As opposed to cerium (III), the value of yttrium (III) distribution coefficient practically does not depend on oleinic acid concentration. This also enables solvent extraction separation of cerium (III) and yttrium (III) in oleinic acid in a wide range of extractant concentrations.

Results of individual experiments show that salt anions do not enter extraction solvate. So the extraction process can be described with the following reaction:



where the correlation between extraction equilib-

rium constant and distribution coefficient is described with the following equation:

$$\lg D = \lg K\gamma_{\pm} + z\text{pH} - (3-z) \lg \left(1 + \frac{a_{\text{H}^+}}{K_d} \right) + \quad (\text{Eq. 2})$$

$$(3-z) \lg [C_{\text{extr}} - (3-z)C_{\text{org}}]$$

Dependences of distribution coefficient $\lg D$ on pH-function:

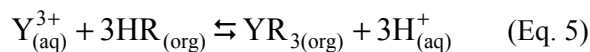
$$\varphi(\text{pH}) = z\text{pH} + (3-z) \lg [C_{\text{extr}} - (3-z)C_{\text{org}}] - (3-z) \lg \left(1 + \frac{a_{\text{H}^+}}{K_d} \right) \quad (\text{Eq. 3})$$

which shown on Fig. 3, and the extractant concentration function

$$\varphi(C_{\text{extr}}) = \lg [C_{\text{extr}} - (3-z)C_{\text{org}}], \quad (\text{Eq. 4})$$

which shown on Fig. 4, were built based on experimental data to calculate the solvate number $(3-z)$ and Gibbs energies of the extraction process calculated for different z values.

Analysis of dependences 3a and 4a show that yttrium (III) solvate number in extraction with naphthenic acid equals 3 and the extraction process can be described with the following equilibrium:



Analyzing dependences 3b and 4b we calculated the value of cerium (III) solvate number as 2.33.

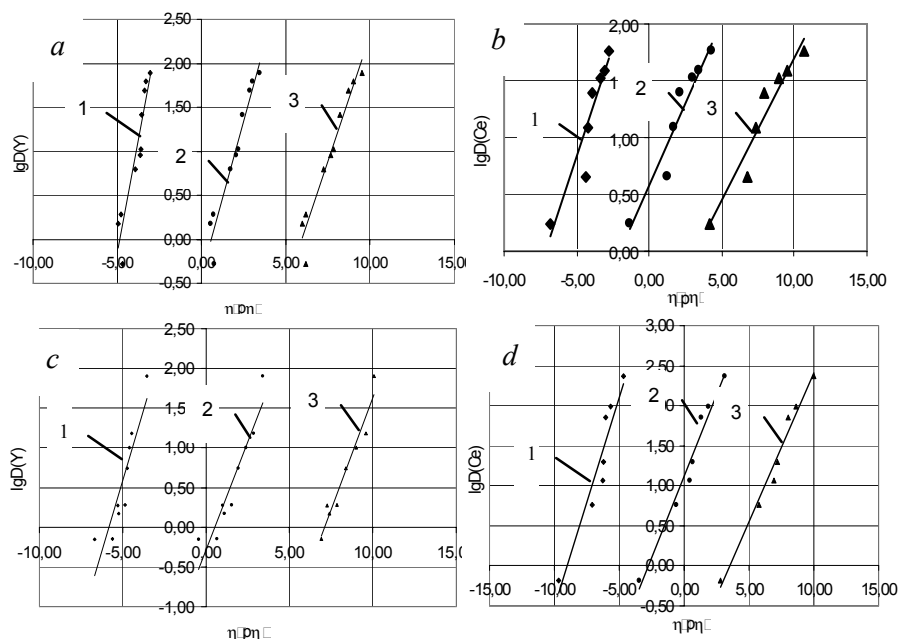
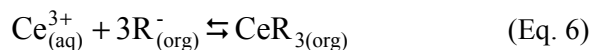


Fig. 3: Dependence of Y(III) (a, c) and Ce(III) (b, d) distribution coefficient log on pH function in extraction with 0.05 M naphthenic acid (a, b) oleinic acid (c, d) at $z=0$ (1), $z=1$ (2), $z=2$ (3).

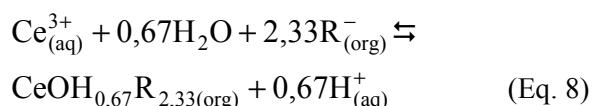
This indicates simultaneous progressing of the following reactions:



and



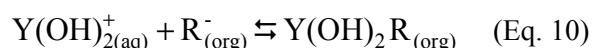
which sum with factors of proportionality, corresponding to one or another form of cerium (III) content, gives up the following chemical equation of cerium extraction with naphthenic acid:



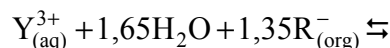
The analysis of the dependences 3c and 4c show, what extraction of yttrium (III) by oleinic acid is carried out with value of yttrium (III) solvate number 1,35 and it point on salvation process of hydroxyl complexes of yttrium (III):



and



Summary, extraction process is described by follow equation:



It is seen from analysis of dependences 3a and 4a what an extraction of cerium (III) by oleinic acid is carried out with the solvate number of yttrium is equal 2 and extraction process can be describes by follow equilibrium:



Table 1 shows comparison characteristics of solvent extraction of cerium (III) nitrates and yttrium (III) nitrates with solutions of the following compounds in *o*-dimethylbenzene: tributyl phosphate (20%), trialkylbenzylammonium nitrate (0.5 M), naphthenic acid (0.5 M) and oleinic acid (0.5 M).

As it is apparent from Table 1, reduction of solvate number and conversion from ion-exchange extraction to solvate extraction leads to a decrease in the distribution coefficient.

In extraction with naphthenic acid, the values of solvate number and distribution coefficient of yttrium (III) are more than those of cerium (III). This is explained by a great ionic potential (z/r ratio) of yttrium i.e. lesser crystallographic radius of this element as compared to cerium. Thus, yttrium (III) forms stronger bonds with acid anions that displace water from the first coordination sphere. Oleinic acid is weaker than naphthenic acid. At pH 5 the naphthenic acid is

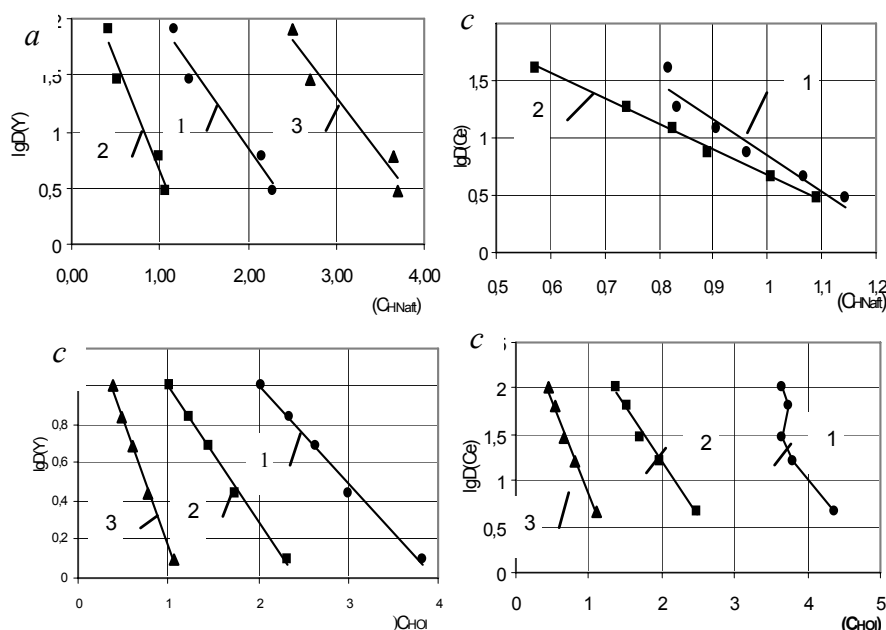
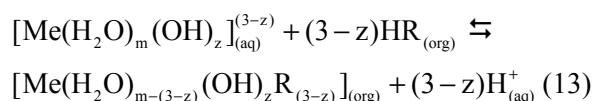


Fig. 4: Dependence of Y(III) (a, c) and Ce (III) (b, d) distribution coefficient log on extractant concentration function in extraction with 0.05 M naphthenic acid (a, b) oleinic acid (c, d) at $z=0$ (1), $z=1$ (2), $z=2$ (3).

Tab. 1: Characteristics of solvent extraction of cerium (III) nitrates and yttrium (III) nitrates with solutions of various extractants.

Extractant	Element	pH	<i>D</i>	$-\Delta_r G_{298}^0$, kJ/mol	Solvate number
Tributyl phosphate	yttrium	5	7.5±0.3	4.1±0.2	2
	cerium	5	9.0±0.4	6.3±0.3	1.6
Trialkylbensylammonium nitrate	yttrium	3	10.2±0.4	7.9±0.5	1
	cerium	3	35±4	8.9±0.3	1
Naphthenic acid $pK_d = 5,1$	yttrium	5	78.5	27.6±0.4	3
	cerium	5	39±1	36.2±0.3	2.33
Oleic acid $pK_d = 5,9$	yttrium	5	10.1±0.2	33.1±0.4	1.35
	cerium	5	100±3	58.6±0.7	2

halfway dissociated whereas oleic acid practically does not dissociate under such pH conditions. Thus, hydrogen cations should be displaced from non-dissociated molecule of oleic acid during the extraction process:



Thereat, water molecules that are less tightly bound with metal cations are displaced during the extraction process. On the one hand, Y^{3+} cations are more hydrated than Ce^{3+} cations and less readily displaces H^+ in the extractant molecules. On the other hand, yttrium (III) is more hydrolysable than cerium (III) ($\Delta_f G([\text{YOH}]^{2+}) = -28.86$ kJ/mol, $\Delta_f G([\text{CeOH}]^{2+}) = -25.87$ kJ/mol), so yttrium (III) has lesser charge of extractive hydrocomplex, less readily interacts with oleation and is characterized with a lower solvate number.

In case of naphthenic acid, naphthenic ions readily displace water from the first coordination sphere. Besides, yttrium Me—Naft bond strength is stronger because of small ion radius, which results in higher value of yttrium distribution coefficient as compared to that of cerium.

If we study the $\text{OH}^- \xrightarrow{+I_1} \text{Me}^{3+} \xleftarrow{+I_2} \text{R}^-$ system, then the I_2 inductive effect is higher than that of I_1 due to π -bond of the carboxyl group with the bond order of 1/2, which easily polarizes increasing the inductive effect. This facilitates displacement of OH^- and results in higher index of yttrium solvate number than in the case with oleic acid, yttrium being characterized by higher level of polarizing action than cerium.

3 Zusammenfassung

In dem Artikel wird die Möglichkeit der Extraktionsscheidung der Elemente der seltenen Erden der Zerium- und Yttergruppen durch die Extraktion

durch Karbonsäuren mit dem Scheidungsfaktor 10 für Ölsäure und 2 für Naphtensäuren gezeigt. Extraktion der EsE durch Naphtensäure ist durch überwiegenden Übergang der Kationen Me^{3+} und teilweise der Hydroxokomplexe $[\text{MeOH}]^{2+}$ in die organische Phase bedingt. Die Extraktion der EsE durch Ölsäure verläuft durch Solvation der Kationen Me^{3+} und teilweise der Hydroxokomplexe $[\text{MeOH}]^{2+}$.

Die Bedeutung der Gibbsenergie des Extraktionsprozesses von Zerium und Ytter durch Naphten- und Ölsäure ist erhalten. Die Senkung der Solvationszahl und Übergang von der Extraktion durch Ionenaustauschmechanismus zur Solvation führt zur Steigerung der Gibbsenergie des Extraktionsprozesses und folglich zur Senkung des Verteilungskoeffizienten.

4 Conclusion

It is possible to separate the rare earth metals of cerium and yttrium groups by method of solvent extraction with carbonic acids with separation factor 10 for oleic acid and 2 for naphthenic acid.

Extraction of rare earth metals by naphthenic acid is due to conversion of Me^{3+} and, partially hydroxyl complexes $[\text{MeOH}]^{2+}$, into organic phase.

Extraction of rare earth metals with oleic acid takes place due to salvation of cations $[\text{MeOH}]^{2+}$ and, partially, hydroxyl complexes $[\text{Me}(\text{OH})_2]^+$ into the organic phase.

Data of Gibbs energies of the extraction equilibrium were obtained for extraction of cerium (III) and yttrium (III) by naphthenic and oleic acids.

Reduction of solvate number and conversion from ion-exchange extraction to solvate extraction leads to an increase of Gibbs energies of the extraction process and, as a consequence, to decrease in the distribution coefficient.