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Binary extraction of lanthanide(III) chlorides using carboxylates and dialkylphosphates of secondary and tertiary amines

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ABSTRACT

The use of binary extractants based on carboxylates and dialkylphosphates of secondary and tertiary amines and their mixtures for the separation of lanthanide (III) ions has been investigated. It is established that the solutions of these extractants in non-polar organic solvent extract lanthanide chlorides from aqueous phase according to the laws of binary extraction. The synergetic effect for the system of di-(2-ethylhexyl)carboxylate, caprinate of di-n-octylammonium and tri-n-octylammonium has been found.

1. Introduction

The purification and separation of lanthanides are a difficult chemical and technological problem. Their preparative separation and purification use is made of the sorption, deposition methods, ion-exchange chromatography, recrystallization and extraction (Gupta and Krishnamurthy, 2004). The separation coefficients range from 1.05 to 2.5 for the lanthanide pairs of neighboring atomic numbers during one stage of the separation process in different methods (Shaohua et al., 2010). The extraction is the most efficient and selective process. The given process is usually carried out using countercurrent extraction cascades, including several tens of successively located devices — extractors. In producing rare-earth metals, organic phosphate extractants are mainly applied, namely TBP (Gupta and Krishnamurthy, 2004), di-(2-ethylhexyl)phosphorous acid (D2EHPA) (Banda et al., 2012a,b), dialkylphosphinic, dialkyl dithiophosphinic and carboxylic acids (Fontana and Pietrelli, 2009; Banda et al., 2012a,b; Belova et al., 2009; Abreu and Morais, 2014; Singh et al., 2006; Eskandari et al., 2011; Kim et al., 2012; Wang et al., 2011).

Cation-exchange extractants based on dialkyl ethers of phosphorous acid (D2EHPA) are among the most selective ones in the lanthanide separation. However, these extractants have high coefficients of lanthanide distribution. Therefore, concentrated mineral acids are required for re-extraction of the metals. Applying binary extractants based on D2EHPA could solve this problem. Binary extractants are salts formed from organic acids and bases. The D2EHPA binary extractants consist of the salts formed from D2EHPA and organic amines (secondary/tertiary amines or quaternary amine bases) in organic solvent. For these extractants, re-extraction of lanthanides can be done by water (Khol'kin et al., 1987).

Binary extractants can be prepared based on stoichiometric mixtures of the common cation-exchange and anion-exchange extractants. For the binary extraction systems the interphase transition of the cation and anion of an inorganic salt is conjugated, allowing for re-extraction by water. The selectivity of the binary extractants is determined by the nature of the organic acids and bases that were originally used in the synthesis. In the case of metal cation separation, the selectivity is comparable with the selectivity of cation-exchange extractants that are used for obtaining the binary extractants. The distribution coefficients of inorganic salts depend both on the nature of the cations and of the anions. Therefore, it is possible to vary the distribution coefficient of the cation by choosing an appropriate inorganic anion (Khol'kin and Kuz'min, 1982). The binary extraction of salts has a linear dependence for the initial section of the interphase distribution isotherms. The isotherms have a decrease of slope in the high concentration area due to the extractant saturation.

Few previous studies were focused on separation of lanthanides by extractants based on ionic liquids (Sun et al., 2011; Zhang et al., 2012, 2013). In some cases the extraction by ionic liquids has mechanism which is similar to binary extraction. However, the term of binary extraction has been proposed a long time ago (for the extractant, based on stoichiometric mixtures of organic acid and organic base (Khol'kin

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and Kuz'min, 1984; Khol'kin et al., 1994)). Therefore, the binary extractants represent the ionic liquids with diluent.

Another problem connected with the extractants based on D2EHPA is the formation of low-soluble compounds in the organic phase with the lanthanide concentration higher than 0.005 mol/L. Preliminary experiments have revealed that carboxylic acids and their salts with organic amines – carboxylates – are effective solvating additives increasing the solubility of di-(2-ethylhexyl)phosphates of lanthanides. However, amine carboxylates are also capable of extracting rare-earth salts by binary extraction. Yet, the selectivity of the lanthanide extraction with carboxylic acids is significantly lower as compared to phosphorous extractants.

In this paper we investigate rare-earth chloride extraction with dialkylphosphates and carboxylates of secondary/tertiary amines, as well as with their mixtures. The change of the extraction selectivity depending on the organic phase content is investigated.

2. Experimental

2.1. Reagents and apparatus

Reagents of chemically pure grade were used. Initial solutions of lanthanide chlorides were prepared by dissolving the corresponding salts in water. Exact concentrations were determined by titrimetric analysis (Prshibil, 1975). The practical quality D2EHPA (HA) was purified through recrystallization of its copper salt [Cu(D2EHPA)$_2$] using a common purification technique (Stoyanov et al., 1984).

The X-axis of the extraction isotherms represents the equilibrium concentrations of metals in water phase, while the Y-axis represents the concentration of metals in organic phase. The equilibrium concentrations of metals in both phases were determined by chemical analyses (after reaching the extraction equilibrium and separation of phases). Initial concentration of metal in water phase was equal to the sum of its concentration in both phases at equilibrium (when ratio between volume of organic and water phase is equal to 1:1).

The binary extractants, di-(2-ethylhexyl)phosphate of tri-n-octylammonium (R_3NHA) and di-(2-ethylhexyl)phosphate of di-n-octylammonium (R_2NH_2A), were prepared by dissolving equimolar quantities of D2EHPA (HA) and the corresponding amine (R_3N or R_2NH) in toluene. These solutions were washed with distilled water and the organic phase was filtered. Prepared in the same way were also the binary extractants based on the caprinates (HB) of the appropriate amines (R_3N or R_2NH), these extractants being further referred to as tri-n-octylammonium caprinate (R_3NHB) and di-n-octylammonium caprinate (R_2NH_2B).

The pH of the solutions was determined as other potentiometric measurements were made using a pH-meter–ionometer "Expert-001". Spectrophotometric measurements were carried out using a photometer KFK-3. In the case of the lanthanide mixture extraction the element concentrations in aqueous phases were analyzed by mass-spectrometry with inductively-coupled plasma using ICP-MS Agilent 7500A.

2.2. Solvent extraction procedures

The extraction equilibria were studied at 298 ± 1 K. The extraction and stripping were performed in separation funnels with the equal volume ratio between the organic and aqueous phases. The phases were mixed for 10 min, with the time of equilibration in the system being 3–5 min.

Solutions containing combinations of 14 lanthanide chlorides with equal molar concentration of each metal were used in order to study the selectivity of the lanthanide extraction.

The lanthanide concentration in the organic phase was found by the concentration difference in the initial and aqueous phases. In the case of low distribution coefficients, the lanthanide concentration in the organic phase was determined after re-extraction with 0.2 mol/L HCl solutions. Spectrophotometry and potentiometric titration with EDTA were performed to determine the metal concentrations lower than 0.001 mol/L (Sataeva, 2011). A platinum electrode was used as an indicator electrode. The silver-chloride electrode (auxiliary laboratory electrode 1M1) was taken to be a comparison electrode. The titration was carried out in acetate buffer (pH 5.5) solution in the presence of the indicator quantities of ferrous ions. The concentration of chloride ions in the aqueous phase was found by argentometric titration with a silver-chloride electrode (Frumina et al., 1983).

3. Results and discussion

3.1. Extraction behavior

In our earlier investigations it is shown that the process of extraction of lanthanide inorganic salts (chlorides, bromides, nitrates) using di-(2-ethylhexyl)phosphates of secondary, tertiary organic amines and quaternary organic bases proceeds in accordance with the binary extraction regularities (Kalyakin et al., 2001, 2011). The binary extraction of lanthanide chlorides using di-(2-ethylhexyl)phosphates of organic amines can be described by the following equation of the main heterogeneous reaction (without taking into account specific interactions in the organic phase, in particular, solvatation processes):

$$\mathrm{ln}^{+3}_{(\mathrm{aq})} + 3\,\mathrm{Cl}^{-}_{(\mathrm{aq})} + 3R_{\mathrm{x}}\,\mathrm{NH}_{(4-x)}A_{(o)} \leftrightarrows \mathrm{LnA}_{3(o)} + 3R_{\mathrm{x}}\,\mathrm{NH}_{(4-x)}\,\mathrm{Cl}_{(o)} \quad (1)$$

where $R_xNH_{(4-x)}A$ — is di-(2-ethylhexyl)phosphate of di-n-octylammonium or tri-n-octylammonium, the notations (o) and (aq) indicating the organic and aqueous phases, respectively.

The binary extraction reaction with amine carboxylates can consequently be written in the form of Eq. (2).

$$\mathrm{ln}^{+3}_{(\mathrm{aq})} + 3\,\mathrm{Cl}^{-}_{(\mathrm{aq})} + 3R_x\mathrm{NH}_{(4-x)}B_{(o)} \leftrightarrows \mathrm{LnB}_{3(o)} + 3R_{\mathrm{x}}\,\mathrm{NH}_{(4-x)}\,\mathrm{Cl}_{(o)} \quad (2)$$

where $R_xNH_{(4-x)}B$ — is di-n-octylammonium ($x = 2$) or tri-n-octylammonium ($x = 1$) carboxylate.

According to Eqs. (1) and (2) the processes of binary extraction are distinguished by a number of peculiarities:

1. A cation and an anion are extracted into the organic phase in stoichiometric proportion, as in the salt extraction with neutral extractants. This allows, on the one hand, enhancing the extraction of metal salts with salting-out agents being present, and, on the other hand, stripping salts from the organic phase using water.
2. The formation of two compounds, LnA_3 and $R_xNH_{(4-x)}Cl$, in the process of extraction allows one to salt out metals from the organic phase by adding amine chloride. This distinguishes the binary extraction from the metal extraction by neutral extractants. Moreover, the same factor results in the linearity of the initial section of the extraction isotherm (in the case of salting-out additives being absent in the aqueous or organic phases).
3. As contrasted to the cation exchange extraction the metal distribution coefficients in these systems are slightly dependent on pH of the aqueous solutions, at least, in a quite wide range of pH. For D2EHPA systems this range is equal to 3.5–6. At lower pH values the competitive binary extraction of HCl is possible (Khol'kin et al., 1990), while at higher values — the formation of metal hydroxo complexes.
4. The selectivity of the binary extraction of metals is determined by the nature of the organic acid of the binary extractant being used and that of anions — by the nature of the amines being used.