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Binary extraction of neodymium nitrate using 2-ethylhexylphosphonic acid 2-ethylhexyl mono ester and tri-*n*-octylamine



S.N. Kalyakin, V.I. Kuz'min, M.A. Mulagaleeva *

Institute of Chemistry and Chemical Technology SB RAS, Federal Research Center "Krasnoyarsk Science Center SB RAS", Russian Federation

A R T I C L E I N F O

ABSTRACT

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In this study we investigate the $Nd(NO_3)_3$ extraction from neutral aqueous solutions with a binary extractant based on 2-ethylhexylphosphonic acid 2-ethylhexyl mono ester (*HA*) and tri-*n*-octylamine (*NR*₃) in toluene. It is established that the *NR*₃*HA* extracts $Nd(NO_3)_3$ in agreement with the laws of binary extraction of salts. The extraction isotherms of $Nd(NO_3)_3$ are linear in the initial segment. The *Nd* concentration in the saturated extractant corresponds to the formation of the neutral *NdA*₃*NR*₃*HNO*₃ complex. Only slight variation of pH is observed during the extraction from neutral solutions.

It is established that for the $Nd(NO_3)_3 - NR_3HA$ extraction system the introduction of salting-out agents in the aqueous or the organic phase ($NaNO_3$ or NR_3HNO_3) makes it possible to vary the neodymium partition coefficient. It is shown that the Nd extraction process can be quantitatively described on the basis of the equations of the concentration constant of binary extraction and the association constant of amine nitrate in a wide range of concentrations of $Nd(NO_3)_3$ and extractant compositions.

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1. Introduction

Phosphorus-containing cation-exchange extractants are widely used for the separation of lanthanides [1–3]. At present, EHEHPA (2ethylhexylphosphonic acid 2-ethylhexyl mono ester) is most commonly used in industrial countercurrent cascades for the extraction of REE. Trade names of EHEHPA are PC-88A, P-507, and Ionquest 801 [4]. The main advantage of this extractant in comparison with the previously used di-2-ethylhexylphosphoric acid (DEHPA) is a lower capacity for acid dissociation. The pKa values of DEHPA and EHEHPA are 3.24 and 4.51, respectively [5]. At the same time DEHPA and EHEHPA are maintaining relatively large separation coefficients between adjacent elements. This allows carrying out the stage of re-extraction in countercurrent cascades with less concentrated solutions of mineral acids, which is especially important for heavy-group lanthanides. However, the separation of all 15 REEs (including Y) using the EHEHPA in countercurrent extractor cascade systems with sump-mixers requires approximately 10 kg of HCl and 2–3 kg of NaOH per one kilogram of REE oxide [6].

The organic amines can be added to the cation-exchange extractants to reduce the distribution coefficients of lanthanide cations and reduce the acidity of re-extraction solutions. It is necessarily to maintain stoichiometric ratio of the components in order to successfully obtain the organic salts. Using the terminology of previous research studies [7–9]

* Corresponding author. *E-mail address:* maral7508@mail.ru (M.A. Mulagaleeva). such salts are conventionally named as the bifunctional ionic liquids or binary extractants. A detailed review of extraction systems based on EHEHPA and amines is given in paper by Quinn [9]. In these extraction systems it is possible to carry out extraction – re-extraction processes of some REE salts at pH of solution that is close to neutral. Under these conditions it becomes possible to develop countercurrent extractive cascades for separation of REE in which *HCl* and *NaOH* are not consumed and demineralized water is used at the stage of reextraction. The direction of the distribution of various lanthanides between the aqueous and organic phases in different parts of the countercurrent cascade (extraction or re-extraction) can be determined by varying the phase flow ratio. The chemical driving force of the separation process can be the dilution of solutions rather than the neutralization reaction of *HCl* and *NaOH*.

When creating countercurrent extraction cascades, it is necessary that the coefficients of the interfacial distribution (D) of the separated metals are in the range of values between 0.1 and 10. However, in extractive systems based on EHEHPA the interfacial distribution can vary by several orders of magnitude for lanthanides of different groups. Thus, it is crucial to investigate the factors that affect D and the features of binary extraction of lanthanide salts in the neutral pH. The main purpose of this study is elucidation of the extraction mechanism of lanthanide salts by binary extractants based on stoichiometric mixtures of tri*n*-octylamine and EHEHPA.

Neodymium is in the highest demand among all of the REE. Moreover, the preparation of *Nd* compounds in pure form (separation of Pr) is rather complicated problem, which is most successfully solved by extraction methods. Due to the factors described above we chose to focus on the *Nd* compounds as the extractable salts. The choice of nitrate systems is based on the higher solubility (comparing to chloride) of *Nd* extraction products in nonpolar organic phases. The use of a tertiary amine for the preparation of binary extractants is due to the fact that the extraction of neutral trinitrate complexes of lanthanides with a solvate mechanism (Eq. (1)) for tertiary amine nitrates is less common than for quaternary ammonium nitrates [10]:

$$Ln^{3}+_{(aq)}+3NO_{3(aq)}-nNR_{4}NO_{3}(org) \Leftrightarrow [Ln(NO_{3})_{3}]\cdot (NR_{4}NO_{3})_{n(org)}.$$
 (1)

The extraction of lanthanides according to Eq. (1) is a process that runs parallel to binary extraction, but it is substantial only at high concentrations of the nitrate ion in the aqueous phase. This becomes possible through salting-out effect when background electrolytes are introduced.

The process of binary extraction of lanthanide salts is similar to ionexchange and obeys the following equation of the basic heterogeneous reaction:

$$Ln^{3} + _{(aq)} + 3NO_{3(aq)} - 3NR_{3}HA_{(org)} \Rightarrow LnA_{3}(org) + 3NR_{3}HNO_{3}(org), \quad (2)$$

where NR₃HA_(org) is a binary extractant such as salt that formed by a tertiary amine and EHEHPA. The interphase transition of the cation and anion of the extracted inorganic salt occur with preservation of their stoichiometric ratio. The pH during the extraction is unchanged. The salt extraction is reversible. The extraction of lanthanide salts with extractants based on DEHPA and quaternary ammonium bases takes place in good agreement with Eq. (2). Due to the complete reversibility of the extraction-reextraction processes, we previously proposed a liquid-liquid chromatography method using a binary extractant as a stationary phase and deionized water as the eluent [11]. Separation of the lanthanides of the light group (chlorides, bromides or nitrates) in a chromatographic column containing this extractant takes several thousand theoretical separation steps. Unfortunately, DEHPA-based binary extractants do not allow the solubility of extraction products in the organic phase with concentration above 0.006 M. This makes them not very suitable for industrial separation. The introduction of effective solvating additives into the organic phase usually reduces the selectivity of REE extraction [12].

There are various opinions on the mechanism of extraction of lanthanide salts by ionic liquids in the literature. Notable example is the study by Chen et al. [13] in which authors proposed the extraction of lanthanide salts by mixtures of DEHPA or EHEHPA and quaternary ammonium bases in accordance with the solvation extraction mechanism:

$$Ln^{3} +_{(aq)} + 3NO_{3(aq)} + 3NR_{4}A_{(org)} \leftrightarrows Ln(NO_{3})_{3} \cdot 3NR_{4}^{+}A^{-}_{(org)},$$
(3)

Taking into account that in aqueous solutions the formation constants of dihydrogen phosphate complexes of lanthanides are several orders of magnitude higher than the formation constants of nitrate complexes one should expect the predominant coordination of lanthanide ions with phosphorus-containing anions [14,15].

In the paper by Belova [16] the mathematical modeling of the isotherms for the extraction of lanthanide nitrates by trioctylmethylammonium salt of bis(2,4,4 trimethylpentyl)phosphinic acid was carried out. The authors proposed several extraction equations for different isotherm sections corresponding to mixed- ion-exchange and solvate mechanism (Eqs. (4) and (5)):

$$Ln^{3} + _{(aq)} + 3NO_{3(aq)}^{-} + 2NR_{4}A_{(org)} \Leftrightarrow Ln(NO_{3})A_{2}(org) + 2NR_{4}NO_{3}(org), (4)$$

$$2Ln^{3} + {}_{(aq)} + 6NO_{3(aq)}^{-} + 2NR_{4}A_{(org)} \Longrightarrow Ln(NO_{3})_{2}A_{(org)} + NR_{4}NO_{3}(org) + NR_{4}[Ln(NO_{3})_{3}A]_{(org)}.$$
(5)

On the right-hand side of the Eq. (5) the first and second reaction products can participate in an additional interaction which leads to formation of additional amount of $NR_4[Ln(NO_3)_3A]$ (third product). Accordingly the stoichiometric coefficients for the products on the right side of the equation could not be integers in wide range of concentrations. The correct evaluation of these types of extraction processes requires a detailed analysis of possible concentration dependencies such as extraction isotherms with variation of all chemical components.

2. Experimental

2.1. Reagents and apparatus

 NR_3HCl was obtained as a white solid from a heptane solution of NR_3 and an aqueous solution of HCl [17].

EHEHPA (lonquest 801, P507, PC-88A) (CAS No. 14802-03-0, 95 wt %) was sourced from Luoyang Mine Friend Trading Co., Ltd. China and used without further purification. Solutions of Nd (III) were prepared by dissolving the corresponding REE oxide (99.9%) in concentrated nitric acid, evaporated and diluted with distilled water.

The pH of the solutions was determined as other potentiometric measurements were made using a pH-meter "Expert-001". Spectrophotometric measurements were carried out using a Fiber Optic Spectrometer AvaSpec-ULS2048L.The element concentrations in aqueous phases were analyzed by mass-spectrometry with inductive-coupled plasma using ICP-MS Agilent 7500A.

2.2. Solvent extraction procedure

For the preparation of binary extractants the exact weights of EHEHPA and NR_3HCl (taken in the stoichiometric ratio) were dissolved in an organic solvent (80% of the total volume). The organic phase was washed once with a solution of ammonia (the ratio of the volumes of phases is 1:0.9) that had concentration equal to the concentration of the EHEHPA. Upon the completion of washing step, the organic phase was brought to the required volume. The extractant 7 time was treated with equal volumes of 0.001 MNH₃ solution until Cl^- was removed from the system and the pH of the aqueous phase changed from the neutral to basic. After that the extractant was washed 3 times with water.

The exact contents of EHEHPA and *NR*₃*HCl* in the initial reagents were determined by alkalimetric and argentometric titration methods.



Fig. 1. The isotherms of $Nd(NO_3)_3$ extraction. (\blacklozenge), 0.22 mol/L C(NR_3HA); (\blacksquare), 0.151 mol/L C (NR_3HA); (\blacktriangle), 0.1 mol/L C(NR_3HA). Diluent is toluene. Points represent experimental data, while curves correspond to model data.

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