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Solvent Extraction of Didymium by TBP, Aliquat 336 and HDEHP in The Presence of $Ca(NO_3)_2$

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Abstract: Three commercially available extractants (tri-butyl-phosphate (TBP), di-(2-ethylhexyl)phosphoric acid (HDEHP) and Aliquat 336 (a mixture of quaternary ammonium bases)) were tested for separation of Pr(III) and Nd(III) in both static and dynamic modes. In the case of HDEHP, phase stability and influence of nitric acid were considered. Extraction isotherms were constructed, and influence of water-soluble complexing agents on the separation factor was investigated for Aliquat 336. In the case of TBP, influence of calcium nitrate in aqueous phase on the extraction efficiency was investigated. Model countercurrent experiments were conducted for TBP and Aliquat 336. It was shown that TBP is the best choice due to its high capacity and cation extraction order (Nd > Pr).

Keywords: rare earth elements; solvent extraction; separation; neodymium; praseodymium; TBP; HDEHP; Aliquat 336

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1. Introduction

Rare earth elements (REEs) are a group consisting of lanthanides as well as yttrium and scandium. Most part of these elements demonstrate unique physical properties that are used in a wide range of high-tech industries. However, in many cases (e.g., production of luminescent and magnet materials, additives in nuclear fuels, etc.), implementation of an individual pure REE is required. From a chemical point of view, all of these elements possess very close chemical properties: the same oxidation state (+3), the same character of electronic shells ($[Xe]4f^n5d^16s^2$ for lanthanides) and close values of ionic radii. Separation of rare earth elements is a complex chemical and technological task. One of the preferable ways to separate REEs and to isolate individual elements is with liquid–liquid extraction. This method allows the organization of a continuous separation process and the possibility to deal with high concentration of metals (>100 $g \cdot L^{-1}$) [1].

Separation of a REE is complicated by the fact that isolation of a certain individual rare earth element requires its separation from two neighboring elements. For this reason, the processing of a total REE concentrate is a multi-stage procedure where all REEs are divided into groups (e.g., “light” and “heavy” REEs). Then, components of these groups are separated with isolation of pairs of elements. The last step is a separation of an individual element. The whole separation scheme is determined by the content of certain groups of elements in the initial ore, the media used to dissolve the REE ore [2], the availability of suitable equipment and the technological and economic aspects of the REE production [3].

The highest content in the natural REE mixtures have elements of the “light” group La-Nd [2]. Among La-Nd, neodymium has the greatest value as a component of permanent magnets (Nd-Fe-B) [4–6] and lasers [7,8]. Praseodymium based materials have a prospective use in catalysis [9–11]. A group of La-Nd can be separated from a whole mixture of REEs relatively easily due to the absence of promethium in natural REEs. Thus, a gap between Nd and Sm allows their easier separation than a pair of neighboring elements. Mutual separation of Ce and Nd can be simplified by oxidation of cerium from +3 to +4 oxidation state [12], so the separation of the neodymium–praseodymium pair is the most difficult part in isolation of pure Nd and pure Pr (for a long time, this pair was considered as one element called didymium [13]).

The basis of any extraction system is an extractant, which defines the extraction efficiency (can be estimated as a distribution ratio, *D*, see Section 2.2.1) and the selectivity (can be estimated as a separation factor, *SF*, see Section 2.2.1). In the case of metal cations with close chemical properties (close values of *D* and small values of *SF*), technological realization of their separation requires a multi-stage countercurrent process. The distribution ratios and separation factors affect the main parameters of the separation process—number of stages, volume ratios of organic and aqueous phases, product yields, etc. [14].

One of the acute research topics is the search for new extractants with high selectivity towards a certain REE. The main drawback of this approach is a high cost of new extractants and their unavailability in amounts sufficient for industrial scale applications. On the other hand, there are many classes of commercially available extractants that are already used in industry. Organophosphorus extractants and quaternary ammonium bases (QABs) are some of the most studied extractants in hydrometallurgy [15]. In particular, in the treatment and separation of f-elements tri-n-butyl-phosphate (TBP) [16–18], soluble in organic phases phosphoric acids [19–22], and mixtures of QABs [23–25] are widely used.

Beside the extractant, other important factors are the medium REEs are extracted from and the presence of a salting-out agent. It is a non-extractable salt containing the same anion as the extractable components, the addition of which increases the total content of anions and reduces the activity coefficient of water. This results in a shift of the equilibrium to the formation of the organic soluble complex, i.e., enhances the extraction. Nitrate media is more preferable during ore processing due to high solubility of REE nitrates in aqueous solutions and lower corrosion activity towards materials of the separation equipment (e.g., in comparison with chlorides). The choice of a salting-out agent is largely determined by its availability. Previously, we have shown that calcium nitrate can be used as an effective salting-out agent [18] for the REE separation in the system "100% TBP–nitric acid solutions of $REE(NO_3)_3$".

Despite the large volume of experimental results existing at the moment, very often there are no data in literature on specific conditions of separation (concentrations of extractants and other components of extraction systems, temperature, stream flows, etc.), especially in the case of macro-quantities (grams per liter) of REEs. The existing data are insufficient to calculate parameters of the process for separating a pair of elements with a certain composition. In particular, such an object can be a mixture of praseodymium and neodymium with a Pr/Nd ratio = 70:30, which can be formed in technological schemes during the isolation of neodymium [26].

The main systems for the separation of a Pr-Nd pair described in literature are Aliquat 336 in the presence of NH_4NO_3 as a salting-out agent [27,28]; organophosphorus acids (di-(2-ethylhexyl)phosphoric acid, HDEHP, and 2-ethyl-hexylphosphonic acid mono-2-ethylhexyl ester, EHEHPA) in chloride media [29] or synergetic systems of EHEHPA + 8-hydroxyquinoline [30]. TBP was also used to separate of the "light" group of REEs in the presence of nitric acid as a salting-out agent [31] and to model the extraction of $Nd(NO_3)_3$ and $Pr(NO_3)_3$ in the presence of NH_4NO_3 as a salting-out agent [32]. There are also some examples of the application of phosphine oxides for extraction of REEs from nitric acid media [33]. Nevertheless, even with using these systems, separation of the Pr-Nd pair is still a difficult task, and the growing consumption of these metals requires the development of new effective and cheap extraction systems.

Therefore, the aim of this work was to apply existing commercially available extractants as a basis for new extraction systems for Pr and Nd separation (in both static and dynamic conditions). We have chosen the following extractants: tri-butyl-phosphate (TBP), di-(2-ethylhexyl) phosphoric acid (HDEHP) and Aliquat 336 (a mixture of quaternary ammonium bases). The choice of these three extractants is based on their availability and their fundamentally different extraction mechanisms: solvation (TBP), cationic exchange (HDEHP) and anionic exchange (Aliquat 336) [15].

As already mentioned, a large amount of experimental data have been obtained for extraction systems based on these extractants, but in this work, it was important to examine the extraction of a specific mixture with a Pr/Nd ratio of 70:30 and assess how the main affecting factors can influence extraction and separation performance. As the main factors, we have chosen concentration of $Ca(NO_3)_2$ as a salting-out agent in the case of TBP and Aliquat 336, concentration of REEs and nitric acid in the case of HDEHP and presence of a water-soluble complexing agents in the case of Aliquat 336.

2. Materials and Methods

2.1. Reagents, Chemicals and Analytical Tools

Tri-butyl-phosphate (TBP) (99% purity, Acros, Geel, Belgium), di-(2-ethylhexyl)phosphoric acid (HDEHP) (99% purity, Acros, Geel, Belgium) and a mixture of quaternary ammonium bases (Aliquat 336) (99% purity, Acros, Geel, Belgium) were used as extractants. TBP was used without a solvent, and HDEHP was dissolved in dodecane (99%, Himmed company, Moscow, Russia). A relatively stable emulsion (stratification time was about 30 minutes without application of centrifugation) formed when dodecane was used as a solvent for Aliquat 336. The addition of 10 vol. % 1-octanol (99% purity, Acros, Geel, Belgium) suppressed the formation of emulsion [34]. The formation of the stable emulsion was not observed in the case of use of toluene as a solvent. However, due to the high volatility of toluene, a mixture of dodecane and 1-octanol was used in all the experiments.

The commercially available Aliquat 336 is a mixture of quaternary ammonium bases with chloride as a counter-ion. Its use in a nitrate medium requires conversion it to a nitrate form. For this, 0.5 $mol \cdot L^{-1}$ solution of Aliquat 336 was contacted with a solution of 1 $mol \cdot L^{-1}$ of calcium nitrate twice. According to argentometry [35], the degree of conversion was 99.7% after two contacts.

Aqueous solutions of REE(III) were prepared by dissolving nitrates of praseodymium and neodymium with the declared purity of 99.9% in deionized MiliQ water. Calcium nitrate (chemical grade purity, Himmed company, Moscow, Russia) was used as the salting-out agent. Acidity of aqueous solutions was adjusted by nitric acid (chemical grade purity, Himmed company, Moscow, Russia). All reagents were used as received without additional purification.

The mixed aqueous solutions of neodymium and praseodymium nitrates with total content of 80–590 $g \cdot L^{-1}$ (as a $REE(NO_3)_3$) were prepared by dissolution of rare earth element nitrates in volumetric flasks with adding of a required amount of a standardized nitric acid solution and a certain mass of calcium nitrate. The final concentration of HNO_3 was 0.3 $mol \cdot L^{-1}$, and the concentration of $Ca(NO_3)_2$ varied from 0 to 300 $g \cdot L^{-1}$.

Solutions were analyzed by ICP-OES technique (Agilent ICP-OES 720, Santa Clara, CA, US), but preliminarily were checked by UV–Vis analysis (Shimadzu UV 1800, Kyoto, Japan) for rough estimation of a metal concentration range.

2.2. Solvent Extraction Experiments

2.2.1. Batch Extraction Experiments

The organic phase was preliminarily equilibrated with an aqueous phase. The pre-equilibration was performed by contact (three times) with the aqueous phase of the same composition (concentration of nitric acid and calcium nitrate) as the aqueous phase in a subsequent batch or countercurrent experiment, except that the aqueous phase for pre-equilibration did not contain praseodymium and neodymium nitrates. The organic-to-aqueous phase (O/A) volume ratio was 1:1. This was necessary to prevent the extraction of water further in the experiment, which could lead to a change in the volume of the organic phase and the extraction of nitric acid, which could lead to the precipitation of REE hydroxides in the aqueous phase during the experiment due to a decrease of nitric acid concentration. In the batch extraction experiments, the pre-equilibrated organic phase was contacted three times with a praseodymium and neodymium aqueous solution every time a fresh portion of the aqueous phase was used. Composition of the aqueous phase after the third contact was identical to the initial solution. The O/A volume ratio was 15:15 mL. Then, rare earth elements were back-extracted three times by a pure 0.3 mol·L^{-1} HNO_3 aqueous solution in the case of TBP and Aliquat 336 or by a 3 mol·L^{-1} HNO_3 aqueous solution in the case of HDEHP. Tests with radioactive tracers have shown that such a procedure results in complete back-extraction of REEs. All back-extracts from certain experiment were mixed together. All experiments were carried out in separatory funnels.

The distribution ratio, *D*, for each element was calculated as a ratio of its content in a back-extract (accounting the dilution factor "3") to its content in the aqueous phase after phase separation (Equation (1)):

$$D = \frac{3 \cdot C(Me)_{be}}{C(Me)_{aq}} \tag{1}$$

where $C(Me)_{be}$ is concentration of a metal cation in the final back-extract; $C(Me)_{aq}$ is concentration of a metal cation in the aqueous phase after extraction and "3" is dilution factor.

Separation factor was calculated according to Equation (2):

$$SF = \frac{D(Me_1)}{D(Me_2)} \tag{2}$$

where $D(Me_1)$ and $D(Me_2)$ are distribution ratios for metal (1) and metal (2).

All the experiments were performed three times. Corresponding *D* values were averaged, and the resulting *D* value was plotted in graphs along with relative errors.

2.2.2. Countercurrent Extraction Mode

Modeling of constant flow countercurrent extraction was performed according to Craig's method [36] with a ratio of 1:2, i.e., one funnel was equal to two theoretical stages of a cascade process. The experimental scheme is presented in Figure 1. Funnels were filled with organic and aqueous solutions and then were shaken. These starting funnels are indicated with superscript "1" on the scheme. After phase separation, an aqueous phase from the 5th funnel (51) was removed (a raffinate, R1) and an aqueous phase from the 4th funnel (41) was transferred to the 5th funnel (52), as well as from the 3rd (31) to the 4th (42), from the 2nd (21) to the 3rd (32) and from the 1st (11) to the 2nd (22). Then, a fresh aqueous solution (F, a feeding solution) was added to the first funnel. All funnels were shaken again. After phase separation, in this second step an organic phase from the 1st funnel (12) was removed (an extract, E1), and an organic phase from the 2nd funnel (22) was transferred to the 1st funnel (13), as well as from the 3rd (32) to the 2nd (23), from the 4th (42) to the 3rd (33) and from the 5th (52) to the 4th (43). Then, a fresh organic phase (S, a solvent) was added to the fifth funnel (53). These operations were repeated until a steady state had been reached, so each aqueous (or organic) phase in one funnel contacted two times with another organic (or aqueous) phase every time contact was with a new phase. Thus, five funnels realized a ten-stage countercurrent cascade. The O/A volume ratio was 15:15 mL. Achievement of the steady state was controlled by analysis of the raffinates (R_i, aqueous outputs) coming from the 5th funnel. It was found for all of the investigated extraction systems that the steady state was reached after passing three cascade volumes; five funnels contained 5 organic and 5 aqueous phases, and at the steady state, we obtained 15 raffinates and 15 extracts. After achievement of the steady state, every odd step of repetition of the "shaking procedure" corresponded to stage numbers 1, 3, 5, 7, 9 and every even step to stage numbers 2, 4, 6, 8, 10. For all countercurrent extraction experiments, we analyzed stage numbers 1, 3, 5, 7, 9. Calculated mass balance was not less than 96%.

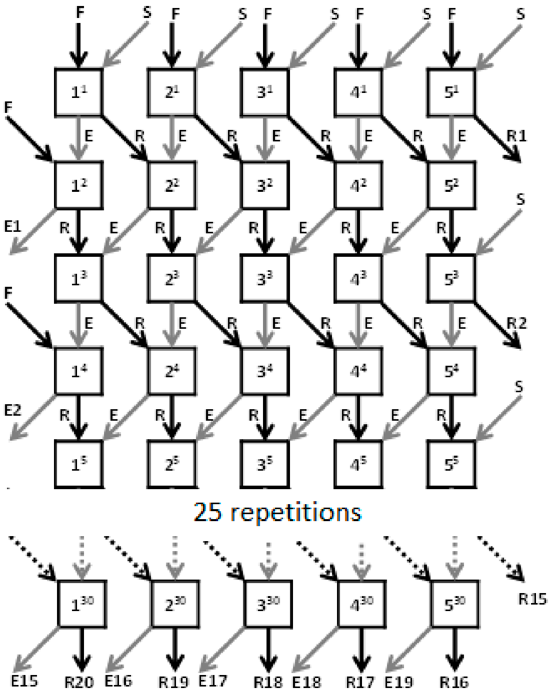

Figure 1. A schematic diagram of simulating a 10-stage countercurrent cascade with 5 separatory funnels: F: feed aqueous solution of the REEs, S: fresh organic phase, E: extract and R: raffinate.

3. Results

3.1. Batch Extraction

3.1.1. Di-(2-ethylhexyl)phosphoric Acid (HDEHP)

(a) Phase Stability

During solvent extraction, it is necessary that only two liquid phases remain in the system. It is known that in the case of a cationic exchanger class of extractants, there is a possibility of the third phase formation [37,38]. Table 1 presents data on the stability of heterogeneous systems containing 1 mol·L^{-1} solutions of HDEHP in dodecane and aqueous phases containing different amounts of nitric acid and neodymium and praseodymium nitrates. In general, due to the nature of HDEHP as a cationic exchanger and a weak acid, the phase stability of such systems increases with a decrease in the REE content in the solution and with an increase in acidity that results in lower concentration of REE–HDEHP complexes. The instability of such systems is associated either with the formation of the third phase (see Figure S1), or with the formation of a homogeneous gel. Gel formation usually occurred at high REE levels in the solution. The third phase is a precipitate of REE organic salts insoluble in the organic phase.

Table 1. Third phase formation in systems containing nitric acid and didymium. Organic phase—1 mol·L^{-1} of di-(2-ethylhexyl)phosphoric acid (HDEHP) in dodecane.

C(Pr + Nd), g·L^{-1} **C(HNO$_3$), mol·L^{-1}**	**10**	**25**	**50**	**75**
0.005	stable	Third phase	Gel	Gel
0.03	stable	stable	Third phase	Gel
0.07	stable	stable	stable	Gel
0.1	stable	stable	stable	Gel

Based on the data on phase stability, we selected the extraction system with the maximum content of REE—50 g·L^{-1} and 0.1 mol·L^{-1} nitric acid—for further research.

(b) Influence of Nitric Acid Concentration

In the following experiments, initial total content of Nd and Pr was 50 g·L^{-1}, and nitric acid concentration was varied from 0.1 to 1 mol·L^{-1}. As expected (due to cationic nature of extractant), with an increase in the content of nitric acid in the aqueous phase, both the extraction efficiency and the selectivity of this extractant towards Nd(III) in the presence of Pr(III) decreases (Figure 2). The maximal *SF*-value in a concentration range of 0.1–1 mol·L^{-1} of nitric acid is 1.3. The organic phase capacity was 20 g·L^{-1} (0.1 mol·L^{-1} of nitric acid) and 5 g·L^{-1} for 1 mol·L^{-1} of nitric acid.

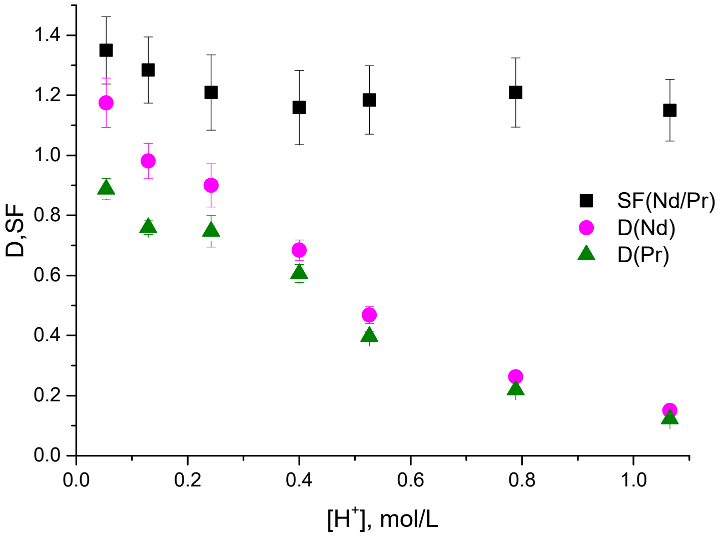

Figure 2. Distribution ratios and separation factors for Nd(III) and Pr(III) in the system "1 mol·L^{-1}HDEHP in dodecane—50 g·L^{-1} REE$(NO_3)_3$ + HNO_3".

Thus, this extraction system is not appropriate for the separation of Nd(III) and Pr(III) due to the low selectivity and high sensitivity to the acidity of the aqueous phase.

3.1.2. Aliquat 336

Earlier, it was shown that Aliquat 336 has the highest separation factor (the highest selectivity) for Pr/Nd pair among other extractants (*SF*(Pr/Nd) ≈ 2) [27]. However, it should be mentioned that QABs preferentially extract lighter elements, which makes them different compared to organophosphorus extractants (TBP and HDEHP). On the other hand, many aqueous soluble polyaminocarboxylates such as diethylenetriaminepentaacetic acid (DTPA) and ethylenediaminetetraacetic acid (EDTA) bind "heavy" REEs (Tb-Lu) more efficiently than "light" REEs (La-Gd) [39], so addition of such acids as a complexing agents can increase the *SF*(Pr/Nd) values.

(a) Extraction Isotherms for REEs by Aliquat 336 in The Presence of $Ca(NO_3)_2$

An extraction isotherm was constructed for the system "0.5 mol·L^{-1} Aliquat 336 in dodecane/10% vol. 1-octanol—$Pr(NO_3)_3$ and $Nd(NO_3)_3$ + $Ca(NO_3)_2$ + 0.3 mol·L^{-1} HNO_3 " (Figure 3). It is seen that the capacity of the organic phase is relatively low and is 7–10 g·L^{-1}, which is consistent with the data obtained in the system containing ammonium nitrate as a salting-out agent [27]. With an increase in the content of the salting-out agent in the aqueous phase, the shape of the isotherms becomes steeper; the saturation of the organic phase is achieved with smaller amounts of REEs in the aqueous phase. Along with this trend, the separation factor of neodymium and praseodymium falls down. The highest value of the separation factor was found at a calcium nitrate concentration of 1 mol·L^{-1} and has a value of 2.0 (in the case of 2,5 mol·L^{-1} $Ca(NO_3)_2$ *SF*(Pr/Nd) ≈ 1.2), which is the same as the maximum value of *SF*(Pr/Nd) published in literature [27]. Further decrease of the salting-out agent content leads to a dramatic decrease in the efficiency of REE extraction (*D* values are less than 0.1).

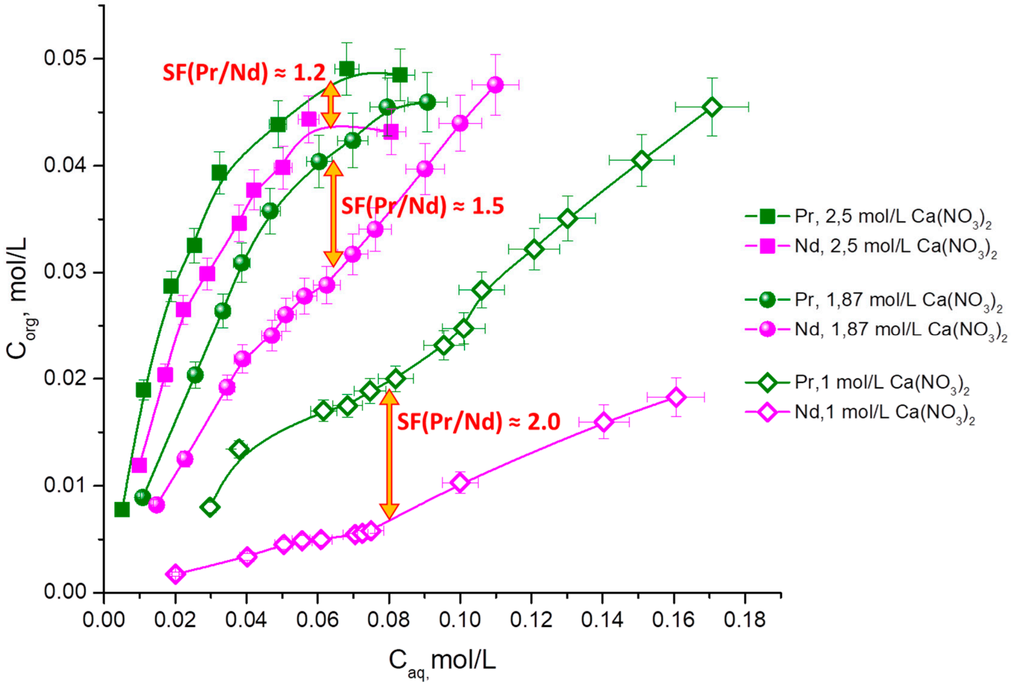

Figure 3. Extraction isotherms for the system "0.5 mol·L^{-1} Aliquat 336 in dodecane/10% vol. 1-octanol—$Pr(NO_3)_3$ and $Nd(NO_3)_3$ + $Ca(NO_3)_2$ +0.3 mol·L^{-1} HNO_3".

(b) Effect of Complexing Agents on The Extraction of REEs by Aliquat 336 in The Presence of $Ca(NO_3)_2$ and $NaNO_3$

As indicated above, in order to achieve higher SF(Pr/Nd)s, additional experiments were performed to determine the effect of the water-soluble complexing agents (EDTA and DTPA). Initial concentration of the REE mixture was 0.01 mol·L^{-1}, and initial pH of the solution was 2.0–2.5. Addition of calcium nitrate as a salting-out agent resulted in precipitation of calcium polyaminocarboxylates. Thus, calcium nitrate was replaced with sodium nitrate. The obtained data are presented in Table 2.

Table 2. Distribution ratios and separation factors for the system "0.5 mol·L^{-1} Aliquat 336 in dodecane/10% vol. 1-octanol—$Pr(NO_3)_3$, $Nd(NO_3)_3$ + 1 mol·L^{-1} $NaNO_3$ + polyaminocarboxylate". C(REE) = 0.01 mol·L^{-1}, initial pH = 2.0–2.5. "Na_2EDTA or Na_2DTPA", %: percentage relative to REE concentration.

Na_2EDTA, %	**20**	**40**	**60**	**80**	**100**
D(Nd)	0.07 ± 0.01	0.06 ± 0.005	0.03 ± 0.002	0.02 ± 0.002	0.01 ± 0.001
D(Pr)	0.15 ± 0.02	0.14 ± 0.005	0.08 ± 0.005	0.04 ± 0.002	0.016 ± 0.002
SF(Pr/Nd)	1.8 ± 0.3	2.3 ± 0.2	2.6 ± 0.2	2.1 ± 0.2	1.6 ± 0.2
SF_{max}	2.6 ± 0.2				
Na_2DTPA, %	**20**	**40**	**60**	**80**	**100**
D(Nd)	0.08 ± 0.01	0.05 ± 0.005	0.02 ± 0.002	0.014 ± 0.003	0.011 ± 0.002
D(Pr)	0.16 ± 0.01	0.14 ± 0.01	0.07 ± 0.005	0.040 ± 0.006	0.019 ± 0.005
SF(Pr/Nd)	2.1 ± 0.2	2.7 ± 0.2	3.6 ± 0.3	2.9 ± 0.3	1.8 ± 0.2
SF_{max}	3.6 ± 0.3				

From the data in Table 2, it can be stated that the presence of water-soluble complexing agents can actually increase the separation factor for the Pr-Nd pair from 2 to 2.6 (EDTA) and up to 3.6

(DTPA). However, under experimental conditions, the maximum values of the separation factors were reached at low values of distribution ratios (<0.1), which will require the use of high (>10) O/A volume ratios, which will reduce the overall efficiency of the separation industrial process.

3.1.3. Tri-N-Butyl-Phosphate (TBP)

It is well known that tri-n-butyl phosphate has a high capacity (over 100 g·L^{-1}) towards REEs. Use of TBP without the diluent can achieve the maximum possible capacity. The distribution ratios were determined for the system "Pure TBP—neodymium + praseodymium + calcium nitrates + 0.3 mol·L^{-1} HNO_3". The total REE content was 300 g·L^{-1}. An increase in the concentration of the salting-out agent in the aqueous phase leads to an increase in both the distribution ratios and separation factors. The most intensive increase of these parameters is observed in a range of 0–300 g·L^{-1} in the concentration of the salting-out agent (*SF*(Nd/Pr) = 1.4–1.5) with a slow growth at its higher concentration (Figure 4). There was also an increase in the viscosity of aqueous solutions, which decreased the efficiency of the whole process. Therefore, further extraction experiments were carried out with the content of calcium nitrate of 300 g·L^{-1}.

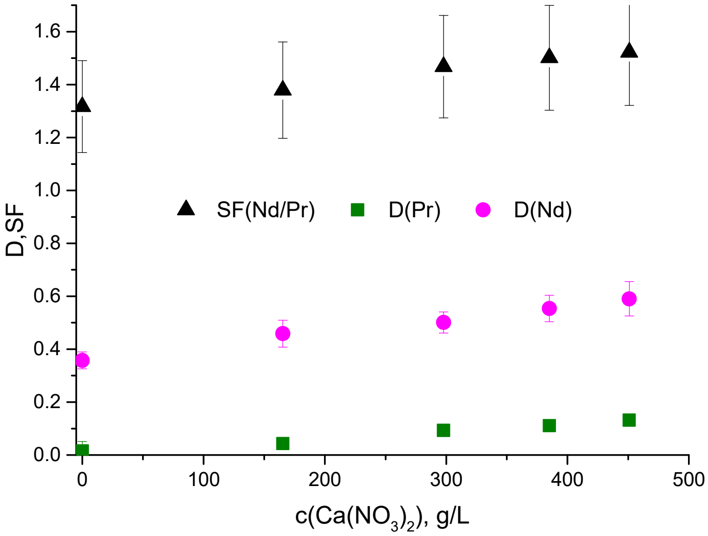

Figure 4. Dependence of distributions ratios and separation factors for Nd and Pr in the system: "Pure TBP—neodymium + praseodymium + calcium nitrate + 0.3 mol·L^{-1} HNO_3".

3.2. Countercurrent Experiments

Since the process of the separation of REEs is performed in a multistage countercurrent process, the distribution ratios should be established in two modes—batch extraction and countercurrent. For the modeling of a countercurrent mode, we choose two extraction systems: "Pure TBP - neodymium + praseodymium + calcium nitrates + 0.3 mol·L^{-1} HNO_3" and "0.5 mol·L^{-1} Aliquat 336 in dodecane/10% vol. 1-octanol—neodymium + praseodymium + calcium nitrates + 0.3 mol·L^{-1} HNO_3".

3.2.1. Countercurrent Experiment with Aliquat 336

The simulated process consisted of 10 stages. Due to the low capacity of this extractant, the experiment was performed at an O/A volume ratio of 2:1. The total content of REEs in the initial solution was 35 g·L^{-1} with a ratio of 70:30 (Pr/Nd), and the content of calcium nitrate was 1 mol·L^{-1}. The distribution ratios were the same for all stages in the system: *D*(Pr) = 0.24 and *D*(Nd) = 0.12. In a steady state of the dynamic mode (a stationary regime), the raffinate contained 60:40 (Pr/Nd) with a total content of 24 g·L^{-1} $REE(NO_3)_3$, and the extract contained 5 g·L^{-1} (82% Pr and 18% Nd).

3.2.2. Countercurrent Experiment with TBP

The experiment was performed in a countercurrent mode on a ten-stage cascade. As a result, the total content of didymium in the raffinate was 90 g·L^{-1} (initial solution: 300 g·L^{-1} 70% Pr and 30% Nd) with praseodymium content of 90%. Figure 5 represents compositions of the aqueous phases in the cascade in a steady state.

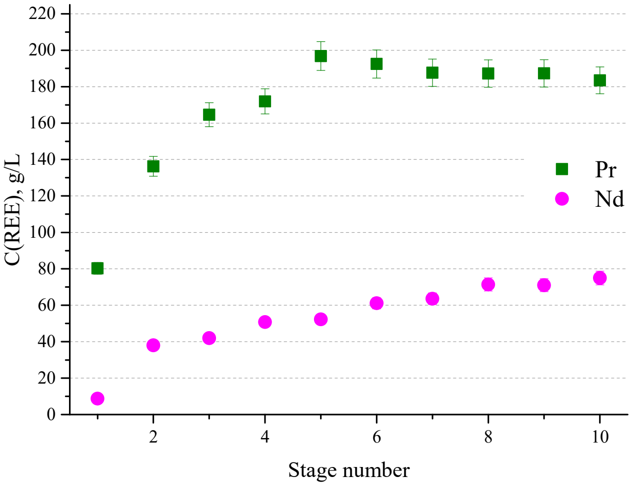

Figure 5. Concentration profiles for the aqueous phases in a steady state. O/A volume ratio = 1:1. Organic phase—100% TBP.

In order to determine the possibility to improve the separation of Pr/Nd by increasing the O/A volume ratio, countercurrent experiments were also performed at ratios of 1.5 and 1.8. The concentration profiles of the stages obtained in this case are shown in Figure 6. One can see that at the ratio of 1.5, the total content of didymium in the raffinate significantly decreases (from 90 to 75 g·L^{-1}). In this case, there is no significant change in the ratio of neodymium and praseodymium. When the volume ratio is even higher (1.8), the metals are completely extracted into the organic phase—the aqueous phases of stages 1–3 contain REEs at concentrations close to zero. The total REEs content in the aqueous phase of stage 4 is 2.5 g·L^{-1} with praseodymium content of 95%, which is slightly higher than for the volume ratio of 1.5, but this separation still cannot be assumed as sufficient.

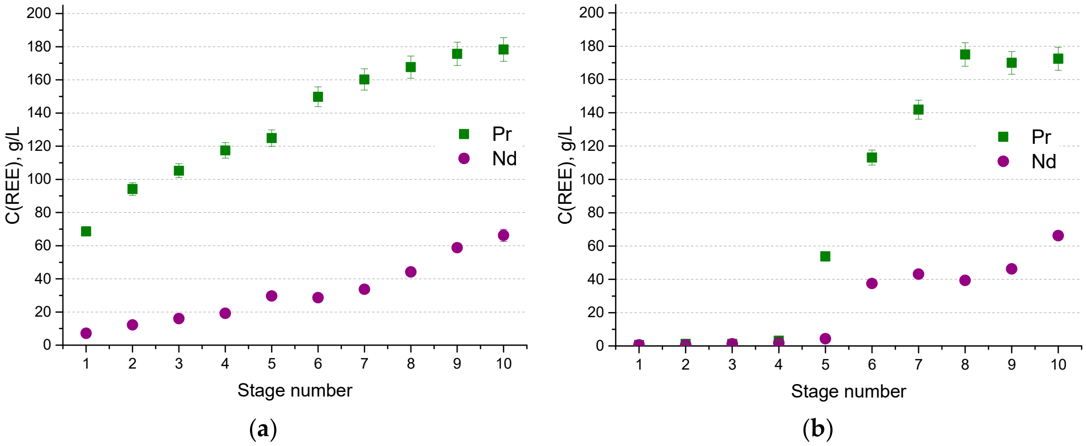

Figure 6. Concentration profiles for the aqueous phases in a steady state. O/A volume ratios = 1.5:1; (**a**) 1.8:1, (**b**) organic phase—100% TBP.

4. Discussion

Considering the extraction properties of the three studied extractants, we can conclude that HDEHP has the lowest selectivity, while Aliquat 336 has the highest value of the separation factor for a single (static) mode of extraction, but in a countercurrent mode, an efficient use of Aliquat 336 is possible only at high (5:1) volume ratios of organic and aqueous phases. Tri-n-butyl phosphate appears to be the most promising among these extractants as a basis of the new extraction system containing calcium nitrate. This new system combines moderate selectivity with a high capacity of the organic phase towards rare earth elements. An extraction order, i.e., an order of metals with the highest to the lowest values of distribution ratios, is also important in the case of TBP. Neodymium, the content of which is much smaller, is extracted better than praseodymium making it possible to obtain praseodymium as a product in raffinate. This process has a smaller number of extraction stages and has no need for the scrubbing stage, which is not the case for Aliquat 336.

Supplementary Materials: The following are available online at www.mdpi.com/2076-3417/10/6/2032/s1. Figure S1, XRF spectra for third phase obtained after extraction of 50 g/L (Pr + Nd) from 0.005 mol/L nitric acid.

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