Graphical abstract

Selection of diluents considering extraction, cost, safety and biodegradability criteria

Selection criteria of diluents of tri-*n*-butyl phosphate for recovering neodymium(III) from nitrate solutions

Mercedes Regadío*, Nagaphani Kumar Batchu, and Koen Binnemans

KU Leuven, Department of Chemistry, Celestijnenlaan 200 F, bus 2404, B-3001, Heverlee (Belgium)

* Corresponding author

E-mail: m.regadio@sheffield.ac.uk

Phone: +44 (0) 114 222 5786

Abstract

Diluent plays an important role in the solvent extraction of metals. The selection of a proper diluent is important since it affects the economics of the process. The effect of different diluents (aliphatic, mixed aliphatic-aromatic and aromatic) on the solvent extraction of Nd(III) by the neutral extractant tri-*n*-butylphosphate (TBP) from nitrate aqueous feed solutions was studied with variation of the following process parameters: extraction kinetics, phase disengagement time, TBP concentration, nitrate concentration, loading capacity of TBP and aqueous-to-organic phase volume ratio. The present study shows that the nature of the diluent has no effect on the extraction kinetics of Nd(III) by TBP. Phase disengagement times were relatively faster for aromatic diluents

compared to aliphatic diluents. Conversely, extraction efficiencies were the highest for aliphatic diluents, slightly lower for mixed aliphatic-aromatic diluents and much lower for aromatic diluents. The poorer extraction efficiencies of aromatic diluents may be due to the lower concentration of free extractant as a result of the stronger interactions of the diluent with water and/or of the diluent with the extractant. The differences in extraction performance between aliphatic and aromatic diluents decrease with increasing nitrate concentration in the aqueous feed solution. Thus, the negative effect on the extraction of the aromatics in the diluent can be compensated by the positive effect of a higher concentration of salting-out nitrate ions in the feed. The present results reveal that the selection of the diluent can be preferably based on its cost, safety and biodegradability rather than on its physico-chemical properties, since the physico-chemical properties have a limited influence on the extraction of Nd(III) by TBP at highly concentrated nitrate solutions.

Keywords: diluents; neutral extractant; rare earths; TBP; solvent extraction

1. Introduction

Solvent extraction (SX) is an important unit operation in hydrometallurgical processes used for the separation of mixtures of metal ions [1-6]. The separation and extraction of the metal values takes place by the preferential distribution of the metals between two immiscible phases: the aqueous and the organic phase. The aqueous phase is the metal-containing feed solution. The organic phase (or solvent) contains an extractant and a diluent, and, if necessary, a modifier [7]. The extractant actively reacts chemically with the metal ions to be transferred from the feed

solution. The diluent is an organic fluid used to dissolve the extractant and modifier, to form the solvent. The modifier improves some properties such as solubility, viscosity/hydrodynamic or kinetics.

The diluent plays a significant role in the solvent extraction of metals [2, 8]. Most of the extractants cannot be directly used in their pure form for separation and purification of metal ions because they have a density close to that of the aqueous phase, are very viscous and some of them are even solid at room temperature. By dissolving the extractant in a diluent, the viscosity and density decrease, making the extractant suitable for practical use in solvent extraction. In addition, the diluent allows to prepare solvents with a desired concentration of extractant, which is often necessary to achieve a specific metal separation or metal loading of the organic phase (extracted metal concentration). Furthermore, the diluent greatly influences third-phase formation, which is a major concern, for instance, in the solvent extraction of actinides by tri-n-butyl phosphate (TBP). Aliphatic diluents cause more easily third-phase formation than aromatic diluents [9]. Among the aliphatic diluents, typically diluents with longer alkyl chains are more susceptible to third-phase formation than diluents with shorter alkyl chains [10-13].

Any organic liquid used as a diluent in solvent extraction processes should have certain characteristics: mutual miscibility with the extractant and modifier, high solvency for the extracted metal complex, low volatility, high flash point, low surface tension, low solubility in the aqueous phase, low toxicity, low viscosity, a low price and being readily available. Additionally, the diluent should not strongly interact with the extractant/modifier in order not to influence the extraction efficiency significantly. In many cases the choice of a diluent is simply based on its cost and a few physicochemical properties. On the contrary, much more attention has been paid to the selection of the extractant. However, the selection of a proper diluent is important and cannot be readily

predicted since it strongly influences many extraction variables such as the phase disengagement times, extractant and diluent chemical stability, performance of the extractant, solubility of the metal-extractant complex; third-phase, CRUD and gel formations, selectivities of metal values or extractant loading capacity, which can all seriously affect the economics of the total process.

The physical properties of diluents such as polarity, dielectric constant, density, viscosity and solubility parameter affect extraction and distribution ratios of metal ions. There are reports in the literature where the difference in extraction behavior was explained by considering the physical properties of the diluents [14-28]. The extraction of rare earths by the basic extractant Aliquat 336 and by the solvating extractant tetraoctyl-diglycolamide (TODGA) decreased with increasing polarity of the diluent [27, 29]. The same relationship was observed for the extraction of actinides by TBP and of di-, tri- and tetravalent metals by thenoyltrifluoracetone with trialkylphosphine oxide or dialkylphosphate ($D_{\text{cyclohexane}} > D_{hexane} > D_{carbon\ tetrachloride} > D_{\text{benzene}} > D_{\text{chloroform}}$) [15, 18]. In some studies, the distribution ratio is also related to the dielectric constant of the diluent, decreasing the former when the latter increases ($D_{\text{kerosene}} > D_{\text{cyclohexan}} > D_{\text{benzene}} > D_{\text{chloroform}}$) [2, 30, 31]. Alguacil et al. reported that extraction of Fe(III) by the primary amine Primene 81R decreased with increasing dielectric constant and dipole moments of the diluents [28]. However, the distribution ratios could not be correlated to any particular one of the physical or chemical properties of the diluent [29].

In a recent paper, we reported the effect of diluents on the extraction of Nd(III) from aqueous chloride solutions by D2EHPA [33]. The extraction efficiency was found to be largely defined by the aromatic content of the diluent. As a continuation of this work, we discuss in present paper the effect of different diluents on the solvent extraction of Nd(III) by the neutral extractant, TBP from aqueous nitrate solutions. Solvent extraction is the sole industrial technology for separation of rare

earths. TBP is a well-known extractant for the solvent extraction of rare earths from nitrate feed solutions [34, 35] (Figure 1). The objective is to study the effect of different diluents on extraction parameters such as extraction kinetics, phase disengagement time, extractant concentration and loading capacity of the organic phase, nitrate and metal concentrations of the feed solution, and aqueous-to-organic phase volume ratio. A total of 11 diluents, including aliphatic diluents with different carbon chain length, mixed aliphatic-aromatic diluents and aromatic diluents, are considered.
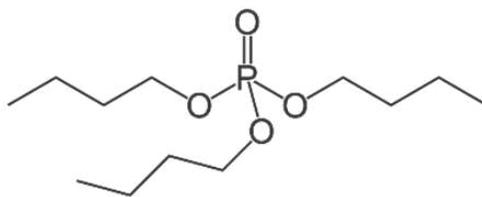
Figure 1. Structure of tri-n-butyl phosphate (TBP)

2. Experimental and methods

2.1 Chemicals and solutions

Tri-n-butyl phosphate (TBP, 98%) and $Nd(NO_3)_3 \cdot 6H_2O$ (99.9%) were purchased from Alfa Aesar (Karlsruhe, Germany). $LiNO_3$ (99%) and toluene were obtained from Sigma−Aldrich (Diegem, Belgium). Hydrochloric acid (HCl, 37% in water) and n-dodecane (>99%) were bought from Acros Organics (Geel, Belgium). A 1000 mg L^{-1} praseodymium standard solution was purchased from Chem-Lab NV (Zedelgem, Belgium). The silicone solution in isopropanol SERVA (used to make the TXRF quartz glass carriers hydrophobic) was purchased from Electrophoresis GmbH (Heidelberg, Germany). Diluents other than the previously mentioned toluene and n-dodecane, were provided by Shell Global Solutions (Amsterdam, The Netherlands). All chemicals were used as received, without any further purification.

The organic solutions for the extractions tests consisted of 1 mol L^{-1} TBP dissolved in all the different diluents, except in the tests where the extractant concentration in the organic phase varied (0.1, 0.3, 0.7, 1 mol L^{-1} TBP). Two aqueous neodymium stock solutions of 10 and 100 g L^{-1} Nd(NO$_3$)$_3$ (solution 1 and 2); and one LiNO$_3$ stock solution of 6.5 mol L^{-1} (solutions 3), were prepared by dissolving Nd(NO$_3$)$_3$·6H$_2$O and LiNO$_3$, respectively, in ultrapure water. Solutions 1 and 2 were acidified with a drop of 37 w% HCl to avoid hydrolysis of neodymium. Solution 3 was used as a source of nitrate ions. Solution 1 and solution 3 were combined to prepare the composite feed solutions (1 g L^{-1} Nd in a 3 mol L^{-1} nitrate matrix) for the extraction kinetics experiments and for the experiments were the TBP concentration in the organic phase and the nitrate concentration in the feed solution were varied. For the experiments where the initial neodymium concentration was varied, the aqueous feed solutions were obtained from solution 2 (100 g L^{-1} Nd(NO$_3$)$_3$) and serial dilutions of it (5, 10, 20 and 50 g L^{-1} Nd(NO$_3$)$_3$), after dissolving the amount of LiNO$_3$ necessary to keep in all the same total nitrate concentration (3 mol L^{-1}). The composite solution of 100 g L^{-1} Nd(NO$_3$)$_3$ in 3 mol L^{-1} nitrate matrix was also used in the experiments of phase disengagement time, extraction isotherms at room temperature, loading capacity of the organic phase and aqueous-to-organic phase volume ratio.

2.2 Instrumental analyses

A flat magnetic stirrer (MIX 15 eco model, 2mag magnetic ^{e}motion) was used to mix the two phases in solvent extraction batch experiments. The metal ion concentrations in aqueous solutions were measured with a benchtop total-reflection X-ray fluorescence (TXRF) spectrometer (S2 Picofox model, Bruker). The pH of aqueous samples was controlled by a Slimtrode (Hamilton) pH-electrode connected to a S220 SevenCompact™ pH/Ion meter (Mettler–Toledo).

2.3 Solvent extraction method

Solvent extraction experiments were carried out by mixing equal volumes (except for phase ratio experiments) of aqueous and organic solutions (total volume 10 mL) in 20 mL glass vials using the flat magnetic stirrer at 800 rpm, room temperature (RT, 20 ± 2 °C). After attaining the equilibrium, the mixing was stopped and allowed to settle until both phases were clearlyseparated. Then, a sample from the lower aqueous phase is pipetted and the concentrations of neodymium ions after extraction was determined there in the aqueous solution, together with the concentrations of neodymium ions before extraction in the feed solution, by a TXRF spectrometer. The metal concentration in the organic phase was then obtained by mass balance. All samples were measured in duplicate for 200 seconds by the TXRF spectrometer after proper dilutions and optimum internal standardization with praseodymium [36, 37].

The *distribution ratio* (*D*) is defined as the ratio of the concentration of metal ion in the organic phase to that in the aqueous phase at equilibrium:

$$D = \frac{C_{eq,org}}{C_{eq,aq}} = \frac{C_{in,aq} - C_{eq,aq}}{C_{eq,aq}} \cdot \frac{V_{aq}}{V_{org}} \tag{1}$$

where $C_{eq,org}$ is the metal ion concentration in the organic phase after the extraction, $C_{in,aq}$ is the initial metal ion concentration in the aqueous phase, $C_{eq,aq}$ is the metal ion concentration in the aqueous phase after the extraction and, V_{aq} and V_{org} are the volumes of aqueous and organic phases, respectively.

The *percentage extraction (%E)* is the amount of the metal extracted in the organic phase with respect to the initial amount in the feed solution and can be represented as:

$$\%E = \frac{D}{D + V_{aq}/V_{org}} \cdot 100 = \frac{c_{in,aq} - c_{eq,aq}}{c_{in,aq}} \cdot 100 \tag{2}$$

The aqueous-to-organic volume phase ratio (Θ) is the volume of aqueous phase divided by that of the organic phase:

$$\Theta = \frac{V_{aq}}{V_{org}} \tag{3}$$

3. Results and Discussion

The eleven diluents studied in the present work can be classified into three sets (Table 1). Set I consists of seven aliphatic diluents: *n*-dodecane (DD), Shell GTL solvent GS190 (FTS-A), Shell GTL solvent GS215 (FTS-B), Shell GTL solvent GS250 (FTS-C), Shell GTL Fluid G70 (FTF-A), ShellSol D70 (D70) and ShellSol D80 (D80). Set II consists of two mixed aliphatic-aromatic diluents: ShellSol 2325 (MS-A) and ShellSol 2046AR (MS-B). And set III consists two aromatic diluents, namely: ShellSol A150 (A150) and toluene. Except *n*-dodecane (*n*-C12) and toluene (methylbenzene), all the diluents have variable and unspecified compositions, normally derived from the processing of crude oil (e.g., mineral spirits), but also synthetic iso-alkanes derived from a "Gas-to-Liquid" process (e.g., Fischer-Tropsch process).

Table 1. Chemical composition and physical properties of the diluents.

Set	Diluent code	Composition (wt%)			Density, 15 °C	Dielectric constant	δ, cal$^{1/2}$/cm$^{3/2}$	Boiling range, °C
		Iso+n paraffins	Naph-thenes	Aromat-ics				
I	DD	100	0	0	0.749*	2.01	7.9	216–217
	FTS-A	97	3	<0.01	0.754	2.02	7.7	187–218
	FTS-B	98	2	<0.01	0.767	2.03	7.5	218–247
	FTS-C	98	2	<0.01	0.775	2.05	7.5	253–270
	FTF-A	98	2	<0.01	0.778	2.05	7.5	179–323
	D70	50	50	<0.01	0.796	2.1	7.6	203–237
	D80	31	69	<0.5	0.820	–	7.5	212–295
II	MS-A	44	35	15	0.814*	–	7.7	217–241
	MS-B	43	42	19	0.818	–	7.8	212–271
III	A150	0	0	>99	0.887	2.4	8.7	185–198
	Toluene	0	0	100	0.867*	2.38	8.9	100–111

δ: Hildebrand solubility parameter of water in the diluent, FTS: Fischer-Tropsch Solvents, FTF: Fischer-Tropsch Fluids, MS: Mineral spirits, DD: n-dodecane, FTS-A: Shell GTL solvent GS190, FTS-B: Shell GTL solvent GS215, FTS-C: Shell GTL solvent GS250, FTF-A: Shell GTL Fluid G70, D70: ShellSol D70, D80: ShellSol D80. MS-A: ShellSol 2325, MS-B: ShellSol 2046AR, A150: ShellSol A150, –: data not available, *: at 20 °C.

The solubility of TBP in the diluents was very high, being possible to prepare 3.3 mol L^{-1} of TBP in all the studied diluents (as high as 90 v% TBP). However, an extractant concentration of 1 mol L^{-1} TBP was chosen for the experiments. First, the extraction kinetics was studied as this is a crucial parameter in the optimization of the extraction process. The extraction reaction was fast, achieving the equilibrium in less than 5 minutes in all diluents (Figure 2). Thus, the extraction rate of Nd(III) by TBP does not depend on the nature of the diluent.
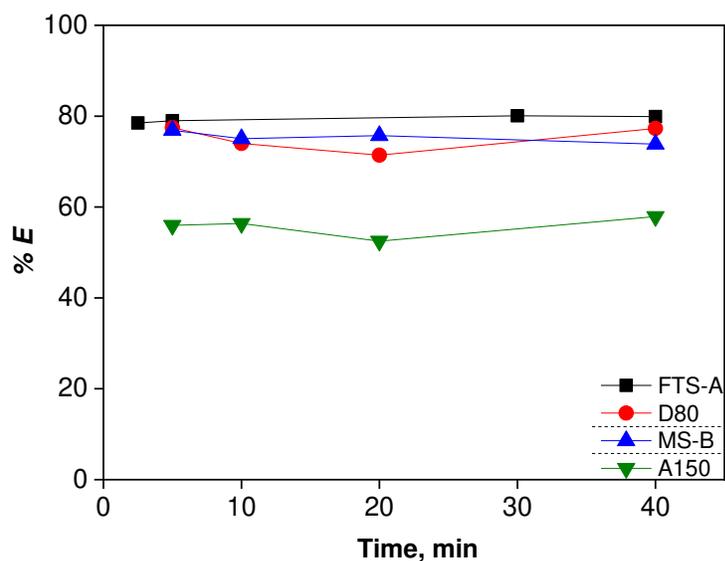
Figure 2. Percentage extraction of Nd(III) as a function of the equilibration time in selected diluents. Conditions: 991 mg L^{-1} Nd(III) + 3 mol L^{-1} NO$_3^-$ (supplemented by 3 mol L^{-1} LiNO$_3$) in feed solution, 1 mol L^{-1} TBP in FTS-A, D80, MS-B and A150; $\Theta = 1$, 800 rpm, 0–40 min, RT.

Secondly, the effect of the nature of the diluent on the *phase disengagement time* (PDT) was measured at two different initial metal concentrations: 5 and 50 g L^{-1} Nd(III) with 3 mol L^{-1} NO$_3^-$. The PDT is an important solvent extraction parameter influenced by the density, viscosity, temperature and interfacial tension. The PDTs were measured in triplicate by recording the time taken for the complete separation of aqueous and organic phases after mixing them for 5 min. The separation of both phases in all diluents and with both feed aqueous solution was fast: 0.3 to 1.7 min in all cases. In general, the PDT was faster in aromatic than in aliphatic diluents. Aromatic diluents have higher densities than aliphatic diluents (Table 2), which could inhibit the dispersion and coalescence properties. In most cases, the PDTs was slower with the highest metal concentration. The higher

the concentration of metals in the feed, the higher is the expected loading of metals in the organic phase. This results in an increased density of the organic phase, which in turn decreases the difference between the two phases and, therefore, decreases the ease of disengagement.

Table 2. Phase disengagement time in seconds as a function of the diluent, at two different initial feed solution concentrations.

Diluent [a]	Phase disengagement time (s)	
	$[Nd]_{in,aq} = 5$ g L^{-1} [b]	$[Nd]_{in,aq} = 50$ g L^{-1} [b]
FTS-A	53	90
FTS-C	72	106
FTF-A	27	95
D80	24	75
DD	54	29
MS-B	60	44
A150	32	45
Toluene	21	26

[a] 1 mol L^{-1} TBP dissolved in the diluents, [b] 3 mol L^{-1} NO_3^- in the feed solutions, $\Theta = 1$, 800 rpm, 5 min, RT.

Next, the effect of the TBP concentration on the extraction of Nd(III) from the nitrate feed solution using different diluents was studied (Figure 3). The extraction efficiency of Nd(III) increased with increasing extractant concentration, as expected according to Le Chatelier's principle. That is, the increase in the concentration of TBP would shift the extraction equilibrium of Eq. (4) to the right, towards the formation of more neutral nitrate complexes $Nd(NO_3)_3 \cdot 3TBP$.

$$Nd(NO_3)_3(aq) + 3TBP(org) \rightleftharpoons Nd(NO_3)_3 \cdot 3TBP \ (org) \qquad (4)$$

The extraction efficiency of Nd(III) is higher in aliphatic diluents, followed closely by mixed aliphatic-aromatic diluents. The lowest extraction efficiency was observed for the aromatic diluent A 150. Similar trends have been reported for the extraction of rare earths by solvating extractants from nitrate media and by acidic extractants from chloride solutions [27, 33]. The extraction efficiency decreased with increasing density, polarity, dielectric constant and Hildebrand solubility parameter value of the diluent in our tested conditions (Table 1). This lower extraction could have been the result of a lower free extractant concentration (i.e., extractant available for coordinating to metal ions). The availability of free extractant depends on the interaction between diluent and extractant (undesirable)-being the solubility parameter value an indicator to which extent diluent and extractant form a stable homogeneous mixture [38]. Aliphatic diluents have lower densities, dielectric constants and solubility parameter values than aromatic diluents, while aromatic diluents have the lowest average boiling points. These properties of the aromatic diluents may promote the interactions between extractant molecules and diluent molecules at the expense of the interactions between the extractant molecules and the rare-earth ions. The formation of such extractant–diluent species lowers the free extractant concentration, consequently decreasing the extraction efficiency of Nd(III) [39]. Likewise, Ritcey and Lukas proposed that the extraction is negatively affected by increasing the aromatic content of the diluent as more diluent is incorporated into the extracted species [29]. A second explanation is that aromatic diluents with higher dielectric constants interact more strongly with water via π-electrons of the aromatic ring, which leads to co-extraction of water, which in turn reduces the capacity of solvent since it makes less free extractant available.

Similar to the extraction decrease with increasing aromatic content, in aliphatic diluents the extraction efficiency decreased with increasing alkyl chain length, but to a lesser extent than the effect of aromaticity. The extraction decreased with increasing polarity and dielectric constant of

the diluent in our tested conditions. Aromatic diluents have higher mass densities than aliphatic diluents, which could inhibit the dispersion and coalescence properties. As discussed in the introduction, the extraction of metals are influenced by the physical properties of diluents such as mass density, viscosity, dielectric constant, polarity and solubility parameters. However, the extraction efficiencies and distributions ratios cannot be correlated with any one particular physical property of the diluent, because the different factors that influence the distribution ratios are not independent of each other [29].
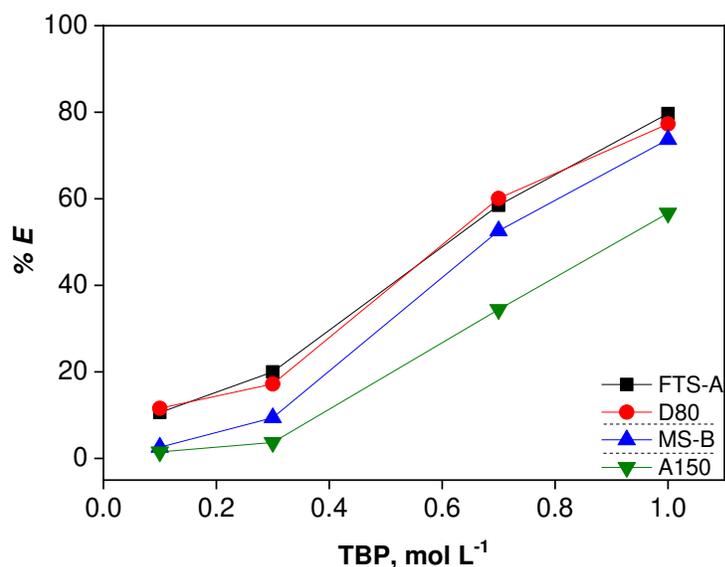

Figure 3. Effect of TBP concentration on the extraction of Nd(III) in selected diluents. Conditions: 1060 mg L^{-1} Nd(III) + 3 mol L^{-1} NO$_3^-$ (supplemented by 3 mol L^{-1} LiNO$_3$) in feed solution, 0.1 – 1 mol L^{-1} TBP in FTS-A, D80, MS-B and A150, $\Theta = 1$, 800 rpm, 30 min, RT.

Then, the dependence of extraction efficiency on the nitrate ion concentration by TBP diluted in several diluents was studied by varying the nitrate ion concentration from 1.5 to 6.5 mol L^{-1} (Figure 4). The percentage extraction of Nd(III) increased along with the nitrate concentration, due to the

salting-out effect that occurs with these kind of metal ions that easily form nitrate complexes. At lower nitrate concentrations, the percentage extraction was higher in aliphatic diluents and lower in mixed aliphatic-aromatic and aromatic diluents. The differences in the extraction with TBP were less significant at high nitrate concentrations (<4 mol L^{-1}), and thus also at high extraction efficiencies. When the extraction of Nd(III) by TBP was higher than 90% (4.5 mol L^{-1} NO_3^-) there were no differences between diluents (Figure 4). Therefore, the positive salting-out effect of nitrate salt is compensating the negative effect of the aromatics content. When varying the concentration of the salting-out agent, neutral extractants were less influenced by the diluent nature than acidic extractants, although the lowest extraction by both TBP and D2EHPA was for the same aromatic diluent A 150 [33].
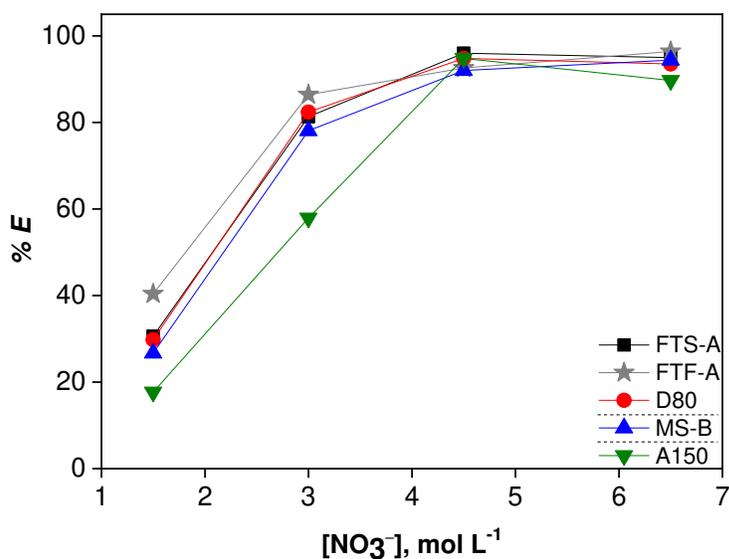

Figure 4. Effect of the nitrate concentration on the extraction of Nd(III) by TBP in selected diluents. Conditions: 981 mg L^{-1} Nd(III) + 1.5–6.5 mol L^{-1} NO_3^- (supplemented by $LiNO_3$) in feed solution, 1 mol L^{-1} TBP in FTS-A, FTF-A, D80, MS-B and A150, $\Theta = 1$, 800 rpm, 30 min. RT.

Next, the effect of diluents on the extraction of Nd(III) by TBP was studied as a function of the initial Nd(III) concentration in the range of 1–100 g L^{-1} while keeping the nitrate ion concentration at 3 mol L^{-1} (Figure 5). The extraction efficiency decreased with increasing initial metal concentration for all diluents, as expected. The higher the initial metal concentration, the lower was the percentage extraction. The extraction behaviour with different diluents was still following the same trend, being higher in aliphatic diluents, followed by mixed aliphatic-aromatic diluents and the lowest in pure aromatic diluents. The extraction efficiency in all aliphatic diluents was almost the same and there were no significant differences between aliphatic diluents with different hydrocarbon chain length. The extraction performance of these aliphatic diluents did well match with that of *n*-dodecane as diluent. There was only a marginal difference in extraction efficiency between aromatic diluent A150 and toluene.
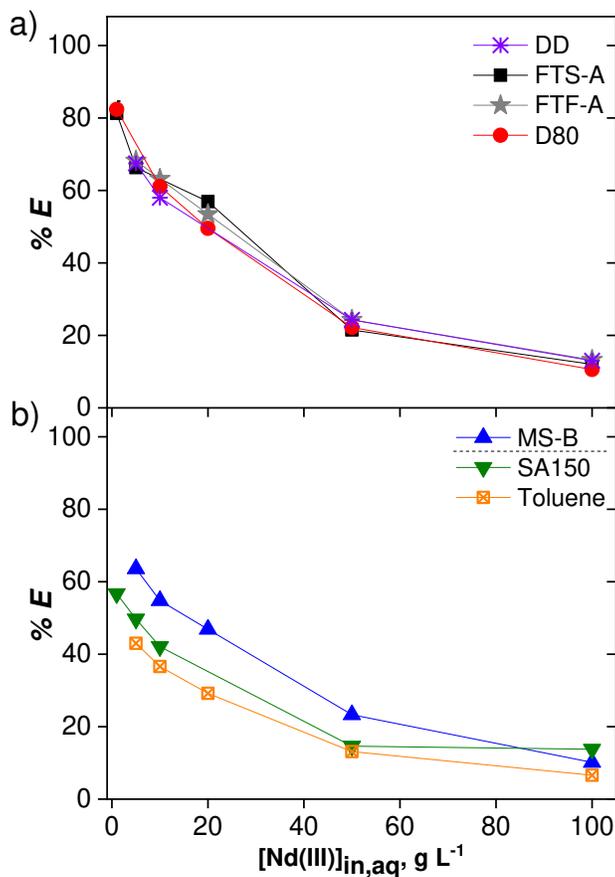
Figure 5. Percentages extraction as a function of the initial metal concentration in selected a) aliphatic and b) aromatic diluents. Conditions: 1–100 g L^{-1} Nd(III) + LiNO$_3$ necessary to keep a constant nitrate concentration of 3 mol L^{-1}, 1 mol L^{-1} TBP, $\Theta = 1$, 800 rpm, 30 min, RT.

The extraction isotherms at room temperature were constructed to calculate the maximum amount of Nd(III) which can be extracted from 3 mol L^{-1} nitrate feed solutions (Figure 6). The maximal Nd(III) loading capacities with 1 mol L^{-1} TBP (organic phase) and 3 mol L^{-1} nitrate (aqueous phase) were: 10–12 g L^{-1} Nd(III), for aliphatic and mixed aliphatic-aromatic diluents and 6–7 g L^{-1}, for pure aromatic diluents. The aromatic organic phases would need higher nitrate concentrations than aliphatic diluents for attaining similar loading capacities.
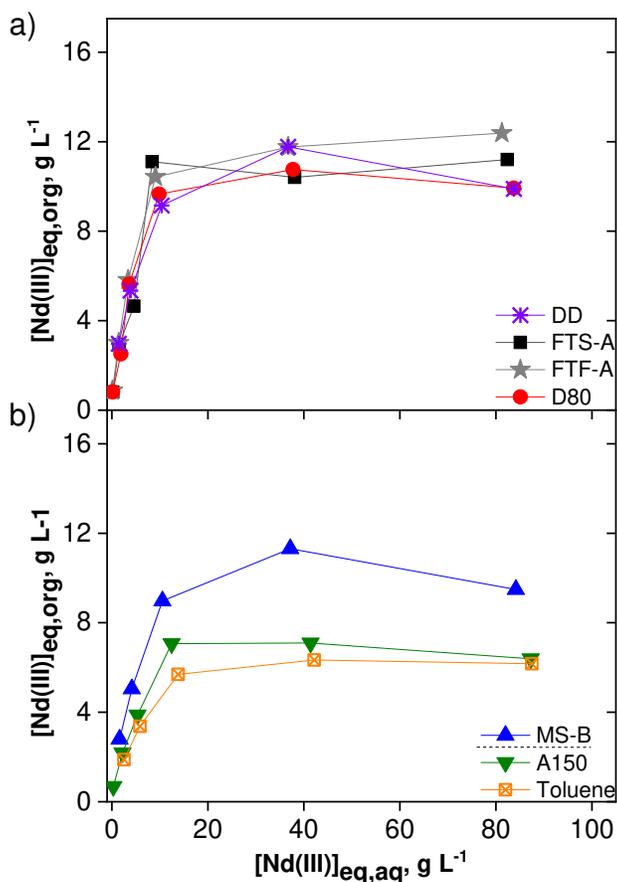
Figure 6. Extraction isotherms representing the equilibrium concentrations of Nd(III) in the organic phase versus of Nd(III) in the aqueous phase in selected a) aliphatic and b) aromatic diluents. Conditions: [Nd(III)]: $1-100$ g L^{-1} + LiNO$_3$ necessary to keep a constant nitrate concentration of 3 mol L^{-1}, 1 mol L^{-1} TBP, $\Theta = 1$, 800 rpm, 30 min, RT.

Finally, the influence of the aqueous-to-organic volume phase ratio (Θ) was examined in all diluents, using a feed solution of 48.9 ± 0.3 g L^{-1} Nd(III) with 4 mol L^{-1} nitrate ion concentration (Figure 7). The maximum loading capacity by 1 mol L^{-1} TBP at 4 mol L^{-1} nitrate ion was 13.8 ± 0.1 g L^{-1} in all aliphatic and mixed aliphatic-aromatic diluents, and 12.7 g L^{-1} for aromatic diluents. These are higher values than the ones noted above (Figure 6) due to the increase from 3 to 4 mol

L^{-1} of the nitrate concentration, as the nitrate ion is the driving force for the solvating extraction. Unlike in the case of high metal loadings of the acidic extractant D2EHPA [33], no gel formation in TBP with all diluents for all the parameter values studied was observed. Gel formation is generated by polymerization of extracted species in concentrated organic viscous solutions, and is a major issue that gives limitations for its use in solvent extraction processes.
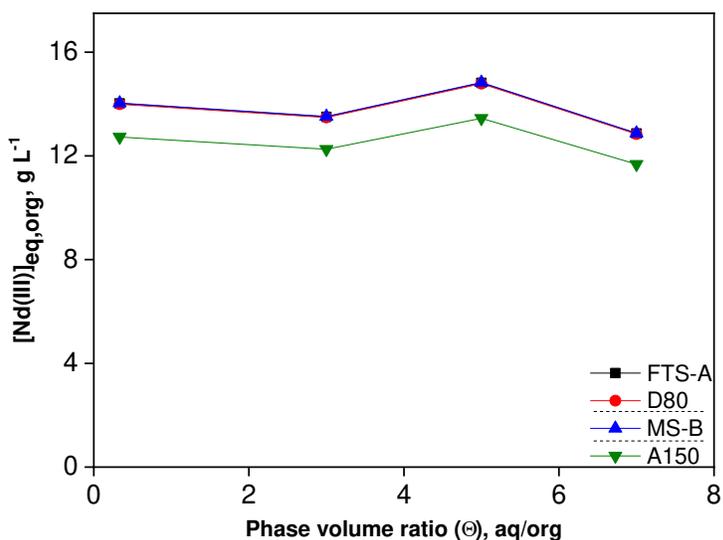

Figure 7. Effect of the phase ratio on the loading of 1 mol L^{-1} TBP in selected diluents from aqueous nitrate solutions. Conditions: 48.9 g L^{-1} Nd(III) + 4 mol L^{-1} NO_3^- (supplemented by 3 mol L^{-1} LiNO$_3$) in feed solution, 1 mol L^{-1} TBP in FTS-A, D80, MS-B, and A150, 800 rpm, 30 min, RT.

The small differences in extraction efficiency between the studied diluents may be due to the symmetry and almost zero dipole moment of the metal complexes with TBP and therefore, there is almost no dipole interaction with the diluent that interferes with the extraction mechanism [18].

As mentioned in the introduction, several studies stressed the importance of the dipole and dielectric constant of the diluent over the extraction of metal complexes [15,18, 27, 29-32]. Still, the diluents studied here showed similar extraction performance results, with the exception of the aromatic content in the diluent, that could be counteract by the nitrate concentration in the aqueous phase. Thus, other properties such as the cost of the diluent, its hazardness and biodegrability become important criteria for selecting the diluent [40, 41]. Diluents lacking of hazardous constituents such as *n*-hexane and/or naphthalene (i.e, FTS-A, FTS-B, FTS-C, FTF-A) would be preferred from the others (D70, D80, MS-A, MS-B), and without compromising the extraction efficiency. Within this "safer" diluent group, FT diluents are preferred because of its higher biodegradability [42, 43]. They consist predominantly of *n*-alkanes and simply branched iso-alkanes, which are particularly susceptible to biodegradation relative to other hydrocarbon solvents on the market which consist of low-molecular-weight aromatics or cyclic alkanes [44].

Conclusions

The performance of different aliphatic, mixed aliphatic-aromatic and aromatic diluents was studied for the extraction of Nd(III) by a neutral extractant TBP. The nature of the diluent was found to have no effect on the extraction kinetics. The separation of the two phases was relatively faster in aromatic diluents than aliphatic diluents. Aliphatic diluents provided the highest extraction efficiencies, followed closely by mixed aliphatic-aromatic and farther behind by aromatic diluents. There was no significant difference in extraction behavior between diluents at higher initial nitrate concentrations. This may be due to almost null dipole interaction between the diluents and the metal nitrate:TBP complexes, and thus, no interference with the extraction mechanism. No gel formation was observed with all studied diluents. As a result, the selection of

a diluent can be made on the basis of factors other than the physico-chemical properties, such as

cost, hazard and biodegradability, without compromising the extraction efficiency.

Acknowledgments

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