Journal Pre-proof

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PII: S0263-8762(20)30322-1

DOI: <https://doi.org/10.1016/j.cherd.2020.07.016>

Reference: CHERD 4171

To appear in: *Chemical Engineering Research and Design*

Received Date: 24 March 2020

Revised Date: 27 May 2020

Accepted Date: 15 July 2020

Please cite this article as: Regadío, M., Batchu, N.K., Binnemans, K., Selection criteria of diluents of tri-*n*-butyl phosphate for recovering neodymium(III) from nitrate solutions, *Chemical Engineering Research and Design* (2020), doi: <https://doi.org/10.1016/j.cherd.2020.07.016>

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Journal of Chemical Engineering Research and Design

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

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Graphical Abstract

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

Highlights

- Aliphatic diluents provided higher extraction efficiencies than aromatic diluents
- Free extractant concentration is reduced in aromatic diluents

- Phase disengagement times were relatively fast with aromatic diluents
- No extraction differences between diluents at highly concentrated nitrate feed

Abstract

The selection of a proper diluent should be based on several criteria such as the distribution ratio, phase disengagement time, cost, safety and environmental impact of the process. The effect of different diluents on the solvent extraction of Nd(III) by the neutral extractant tri-*n*-butylphosphate (TBP) from nitrate feed solutions was studied. The nature of the diluent had little effect on the extraction kinetics of Nd(III) by TBP above 2.5 minutes. In general, phase disengagement times were relatively shorter 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 maybe 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. Under the experimental conditions, the differences in extraction between aliphatic and aromatic diluents decreased with increasing the salting-out effect of nitrate ions in the feed. At nitrate concentrations of 4.5 mol L⁻¹ or more, the different diluents had a limited influence on the metal extraction with 1 mol L⁻¹ TBP from feed solutions of 1 g L⁻¹ Nd(III). Thus, under these conditions, the selection of the diluent can be preferably based on its cost, safety and biodegradability rather than on its physico-chemical properties.

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

Introduction

Solvent extraction (SX) is an important unit operation in hydrometallurgical processes used for the separation of mixtures of metal ions [1-5]. 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 [6]. 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 an important role in the solvent extraction of metals because it dissolves the extractant and the extracted metal complex [2-7]. 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, diluents can be used 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) [8]. 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). Third-phase formation is more common for aliphatic 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 traditionally been paid to the selection of the extractant [14-16]. 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 [17-31]. 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 [30, 32]. The same relationship was observed for the extraction of actinides by TBP and of di-, tri- and tetravalent metals by thenoyltrifluoroacetone with trialkylphosphine oxide or dialkylphosphate ($D_{\text{cyclohexane}} > D_{\text{hexane}} > D_{\text{carbon tetrachloride}} > D_{\text{benzene}} > D_{\text{chloroform}}$) [18, 21]. In some studies, the distribution ratio is also related to the dielectric constant of the diluent, decreasing the former when the latter increases ($D_{\text{kerosene}} > D_{\text{cyclohexane}} > D_{\text{benzene}} > D_{\text{chloroform}}$) [2, 33, 34]. 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 [35]. However, the distribution ratios could not be correlated to any particular one of the physical or chemical properties of the diluent [32].

Solvent extraction is the preferred industrial technology for separation of rare earths. In a previous paper, we found that the extraction of Nd(III) from chloride solutions by D2EHPA is largely defined by the aromatic content of the diluent [36]. It is in the present paper on the extraction of Nd(III) from nitrate solutions by TBP, where we elucidate the differences found between diluents and link it to decision making. TBP is used as it is a well-known neutral extractant for the solvent extraction of rare earths from nitrate feed solutions (Figure 1) [37, 38]. 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 concentration 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).

Experimental and Methods

Chemicals and Solutions

Tri-*n*-butyl phosphate (TBP, 98%) and $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (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 extraction 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} $\text{Nd}(\text{NO}_3)_3$ (solution 1 and 2); and one LiNO_3 stock solution of 6.5 mol L^{-1} (solution 3), were prepared by dissolving $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 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 where the TBP concentration in the organic phase and the nitrate concentration in the feed solution were varied. For the extraction isotherms at room temperature, different initial neodymium concentration in the aqueous feed solutions were obtained from solution 2 (100 g L^{-1} $\text{Nd}(\text{NO}_3)_3$) and serial dilutions of it (5, 10, 20 and 50 g L^{-1} $\text{Nd}(\text{NO}_3)_3$) by dissolving the amount of LiNO_3 necessary to keep in all the same total nitrate concentration (3 mol L^{-1}). These composite dilutions of 100 g L^{-1} $\text{Nd}(\text{NO}_3)_3$ in 3 mol L^{-1} nitrate matrix were also used in the experiments of phase disengagement time, loading capacity of the organic phase and aqueous-to-organic phase volume ratio.

Instrumental Analyses

Solvent extraction batch experiments were carried out by mixing equal volumes (except for phase ratio tests) of aqueous and organic phases (total volume 10 mL) in 20 mL closed glass vials with a flat magnetic stirrer (MIX 15 eco model, 2mag magnetic motion) 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 clearly separated. The metal ion concentrations were measured in aqueous (when the distribution ratios were low) and organic (when the distribution

ratios were high) solutions with a benchtop total-reflection X-ray fluorescence (TXRF) spectrometer (S2 Picofox model, Bruker). In some cases (specifically of toluene), only the aqueous phase results were selected, as the metals concentration in the diluent was overestimated due to its greater equilibrium vapour pressure than water at room temperature. Then, a sample from the lower aqueous phase was pipetted and the concentrations of neodymium ions after extraction was determined in the aqueous solution, together with the concentrations of neodymium ions before extraction in the feed solution. 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 [39,40]. The *phase disengagement time* (PDT) in aqueous continuous was measured in triplicate by recording the time taken for the complete separation of aqueous and organic phases after mixing them for 5 minutes. The aqueous phase was stirred first and then the organic phase was added to mix together. The pH of aqueous samples was measured by a Slimtrode (Hamilton) pH-electrode connected to a S220 SevenCompact™ pH/Ion meter (Mettler–Toledo).

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:

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

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:

$$\%E = \frac{D}{D + V_{aq}/V_{org}} \cdot 100 = \frac{C_{in,aq} - C_{eq,aq}}{C_{in,aq}} \cdot 100 \quad (2)$$

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

$$\Theta = \frac{V_{aq}}{V_{org}} \quad (3)$$

The surface loading or settling speed (q in m/h) was calculated as the settling distance ($SD = 0.0110$ m in all cases) divided by the phase disengagement time (PDT in hours):

$$q = \frac{SD}{PDT} = Q B L \quad (4)$$

where Q is the flow (m^3/h), B and L are the width and the length of the mixer-settler, respectively (m).

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 isoalkanes derived from a “Gas-to-Liquid” process (e.g., Fischer-Tropsch process). The composition fluctuates with crude feedstock and distillation range.

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

Set	Diluent code ^a	Composition (wt.%)				Density, 15 °C	Viscosity, 25 °C		Dielectric constant	δ ^c	Boiling range	Flash point,	Vapour pressure,
		Iso+n paraffins		Naphth enes	Aroma tics	g/cm ³	mm ² /s or cSt		cal ^{1/2} /cm ^{3/2}	°C	°C	kPa	
		C ^b	wt.%										
I	DD	12	100	0	0	0.749 ^g	1.65		2.01	7.9	216–217	71	0.018 ^h
	FTS-A	10-13	97	3	<0.01	0.754	1.60		2.02	7.7	187-205	63	0.03
	FTS-B	12-15	98	2	<0.01	0.767	2.20		2.03	7.5	218–247	85	<0.01
	FTS-C	14-16	98	2	<0.01	0.775	3.20		2.05	7.5	253–270	110	<0.01
	FTF-A	8-26d	98	2	<0.01	0.778	3.58		2.05	7.5	177-343	73	0.02
	D70	11- 14	50	50	<0.01	0.796	2.00		2.10	7.6	203-337	78	0.05
	D80	^e	31	69	<0.5	0.82	2.60	–		7.5	212–295	83	0.01
II	MS-A	6-16 f	45	36	19	0.814 ^g	2.20	–		7.7	217–241	85	<0.05
	MS-B	–	57	27	16	0.818	2.50	–		7.8	212–271	87	<0.05
III	A150	9-11	<0.5	0	>99.5	0.887	1.20		2.40	8.7	185–198	63	0.09
	Toluene		0	0	100	0.867 ^g	0.65		2.38	8.9	100–111	4	3

^a DD – *n*-dodecane, FTS – Fischer-Tropsch Solvents: FTS-A – Shell GTL solvent GS190, FTS-B – Shell GTL solvent GS215 and FTS-C – Shell GTL solvent GS250. FTF – Fischer-Tropsch Fluids: FTF-A – Shell GTL Fluid G70. D70 – ShellSol D70, D80 – ShellSol D80. MS – Mineral spirits: MS-A – ShellSol 2325, MS-B – ShellSol 2046AR. A150 – ShellSol A150.

^bC: range of carbon number. Black, grey and light grey correspond to high, middle and low proportion of iso+n paraffins.

^c δ : Hildebrand solubility parameter of water in the diluent.

^d branched and linear.

^e distillates (petroleum), hydrotreated light.

^f kerosene (petroleum).

–: data not available.

^g: at 20 °C.

^h: at 25 °C.

The TBP (molecular mass of 266.32 g/mol and density of 973 kg/m³) was very soluble in the diluents, being possible to prepare 3.3 mol L⁻¹ of TBP in all the studied diluents (as high as 90 v% TBP). Concentrations of 0.6 mol L⁻¹ [41] and 1.8-2 mol L⁻¹ [42, 43] of TBP were used in previous studies on solvent extraction of rare earths. An extractant concentration of 1 mol L⁻¹ TBP (27 v%) was chosen as a starting point for the experiments. The extraction kinetics resulted in fast extraction reactions, which achieved the solvation equilibrium in less than 5 minutes (Figure 2). For process optimization studies, the time range below 2.5 minutes should be considered.

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 NO₃⁻ (supplemented by 3 mol L⁻¹ LiNO₃) in feed solution, 1 mol L⁻¹ TBP in FTS-A, D80, MS-B and A150; $\Theta = 1$, 800 rpm, 0–40 min, RT.

The effect of the nature of the diluent on the *phase disengagement time* (PDT) was measured in aqueous continuous at two initial metal concentrations: 5 and 50 g L⁻¹ Nd(III) with 3 mol L⁻¹ NO₃⁻. The separation of both phases in all diluents and with the different feed aqueous solutions was fast: 0.3 to 1.7 minutes. In general, the PDT was faster in aromatic than in aliphatic diluents and in the lowest metal concentration of feed, being the fastest PDT with toluene. This may be due to the low metal loading of the organic phase and low density (Table 2). Aromatic diluents have higher densities than aliphatic diluents (Table 1), but this can be switched after extraction as the latter have higher metal loading than the former (≈ 1.5 times less loaded in Nd(III)). This would increase the density of the aliphatic organic phase to closer values to the density of the aqueous phase and, therefore, decrease the coalescence and the ease of disengagement. The higher uptake of Nd(III) with aliphatic diluents is related to their higher maximum load capacity (*vide infra*). Feed solutions with lower concentration of metals provide lower absolute loading of metals in the organic phase. In relative terms of percentage of actual metal load to maximum load, then there was little difference between aliphatic and aromatic (30% and 97% of the maximum load capacity for feed solutions of 5 and 50 g L⁻¹ Nd(III), respectively). Finally, the higher surface loadings (q) of aromatic diluents (Table 2) means lower costs than with aliphatic diluents, as the flow of the feed can be increased for the same design/size of multistage mixer-settler extractors (Eq. (4)).

Table 2. Phase disengagement time in seconds (PDT), concentration of the extracted Nd(III) to the organic phase in g L⁻¹ ([Nd]_{eq,org}) and surface loadings in m/h (q) as a function of the diluent, at two different initial feed solution concentrations ([Nd]_{in,aq}).

Diluent code ^a	[Nd] _{in,aq} = 5 g L ⁻¹ ^b			[Nd] _{in,aq} = 50 g L ⁻¹ ^b		
	PDT	[Nd] _{eq,org}	q	PDT	[Nd] _{eq,org}	q

Toluene	21	2.2	1.89	26	6.6	1.52
A150	32	2.5	1.24	45	7.3	0.88
FTS-A	53	3.3	0.75	90	10.8	0.44
DD	54	3.4	0.73	29	12.2	1.37
MS-B	60	3.2	0.66	44	11.7	0.90
D80	24	3.6	1.65	75	11.1	0.53
FTS-C	72	3.9	0.55	106	13.2	0.37
FTF-A	27	3.4	1.47	95	12.2	0.42

^a 1 mol L⁻¹ TBP dissolved in the diluents, ^b 3 mol L⁻¹ NO₃⁻ 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 4). The extraction efficiency of Nd(III) increased with increasing extractant concentration, as expected according to Le Chatelier's principle. The increase in the concentration of TBP would shift the extraction equilibrium of Equation 4 to the right, towards the formation of more neutral nitrate complexes Nd(NO₃)₃·3TBP.

Figure 4: Effect of TBP concentration on the extraction of Nd(III) in selected diluents. Conditions: 1060 mg L⁻¹ Nd(III) + 3 mol L⁻¹ NO₃⁻ (supplemented by 3 mol L⁻¹ LiNO₃) 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.

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 [30, 36]. 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 [44]. 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) [45]. 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 [32]. 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 percent 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 is 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 [32].

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 5). 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 NO₃⁻) there were no differences between diluents at the conditions of the test used (Figure 5). Therefore, at that studied concentrations of extractant and feed solution, the positive salting-out effect of nitrate salt is compensating the negative effect of the aromatics content. At lower concentrations of TBP, the diluent may show a greater effect at high nitrate ion concentrations, similar to its effect at low nitrate with 1 mol L⁻¹ TBP. When varying the concentration of the salting-out agent, the neutral extractant (TBP) was less influenced by the diluent nature than acidic extractants (D2EHPA), although the lowest extraction in both cases was for the same aromatic diluent (i.e., A 150) [36].

Figure 5: 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 NO₃⁻ (supplemented by LiNO₃) 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.

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 7). The maximal 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, as the nitrate ion is one of the driving forces for the solvating extraction. The difference in the maximal Nd(III) loading capacity can be used for optimising separation processes as the maximum separation occurs at a loading capacity similar to the amount of the easiest extractable rare earth elements in the feed [8]. 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.

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 + LiNO₃ necessary to keep a constant nitrate concentration of 3 mol L⁻¹, 1 mol L⁻¹ TBP, $\Theta = 1$, 800 rpm, 30 min, RT.

Unlike in the case of high metal loadings of the acidic extractant D2EHPA [36], no gel formation in TBP with all diluents for all the parameter values studied was observed. Even when increasing the aqueous-to-organic volume phase ratio (Θ) up to 7 and using a feed solution of 50 g L⁻¹ Nd(III) with 4 mol L⁻¹ nitrate ion (where approx. 13 and 14 g L⁻¹ Nd(III) is loaded in aromatic and aliphatic organic phases, respectively), there was no gel formation. 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. Extraction processes also require solvents with low viscosities like these, which is not the case when using deep eutectic solvents at the same temperature [46].

Overall, 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 [21]. 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 [18, 21, 30, 32–35]. Still, the diluents studied here showed similar extraction performance results, with the exception of the aromatic content in the diluent, that could be counteracted by the nitrate concentration in the aqueous phase. Thus, other properties such as the cost of the diluent, its hazardless and biodegradability become important criteria for selecting the diluent [47,48]. Diluents with hazardous constituents (large polycyclic or aromatic compounds) or high flammability (e.g., toluene) could be replaced by others containing mainly paraffins and naphthenes, and without compromising the extraction efficiency. Within this “safer” diluent group, FT diluents (i.e., FTS-A, FTS-B, FTS-C, FTF-A) are preferred because of its higher biodegradability [49, 50]. They consist predominantly of *n*-alkanes and simple

branched iso-alkanes, which are particularly susceptible to biodegradation relative to other hydrocarbon solvents on the market which consist of aromatics or cyclic alkanes, much more difficult to break by microorganism [51]. In addition, the low aromatic and naphthenic content of FT diluents provide them with weak odour, lower ecotoxicity and photochemical reactivity and less nitrate requirement. Their advantages over other green solvents such as ionic liquids and deep eutectic solvents are their lower cost and lower viscosity [46].

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 above 2.5 minutes. 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 at the highest loading capacities. As a result, under the experimental conditions, 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.

Conflicts of Interest

There are no conflicts to declare.

Funding Statement

The authors acknowledge KU Leuven (projects GOA/13/008 and C32/17/011, postdoctoral fellowship to MR and F+postdoctoral fellowship to NKB) for financial support.

Declaration of interest statement

The submitting author and all the other coauthors have no conflicts of interest to declare.

Acknowledgments

The authors wish to thank Rene Wiersma (Shell Global Solutions Int. B.V., Amsterdam, The Netherlands) for providing samples of the diluents and for scientific discussions.

Data Availability

The authors can make data available on request by contacting the corresponding author by email (<http://mregadio.com/contact-me/>) or ResearchGate (https://www.researchgate.net/profile/Mercedes_Regadio).

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