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# Amidophosphonate ligands as cerium extractants in supercritical CO<sub>2</sub>

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## ABSTRACT

Industrial-scale rare earth extraction is typically performed by liquid-liquid extraction with large amounts of solvents, acids and organophosphorus ligands. An alternative is to use these extractants in supercritical CO<sub>2</sub> (SC-CO<sub>2</sub>), where the crucial operating parameter is their solubility. Different molecules with amidophosphonate backbones have been synthesized and investigated in view of improving their solubility in SC-CO<sub>2</sub> and thereby their cerium extraction capacity. The CO<sub>2</sub>-philicity of these extractants was adjusted by attaching branched or linear alkyl chains with four, six and eight carbons. Using a dynamic gravimetric setup, the solubility and cerium extraction capacity of these molecules were measured to vary from 1.56 to 2.47 mmol/mol and 0.25 to 0.46 mmol/mol, respectively. The two properties were correlated and in both cases the highest values were obtained

with a diisobutylamine chain. The solubility of the corresponding amidophosphonate extractant was found to be optimal at 320 K and 28 MPa.

*Keywords:* Supercritical carbon dioxide, cerium, amidophosphonate, solubility, extraction capacity.

## 1. Introduction

Rare earth extraction and recycling has become a major branch of industry driven by a rapid increase in demand and prices. At the time of writing, the prices of rare earth oxides range from about 2 \$/kg for Ce, La and Sm to ~400 \$/kg for Tb [1]. Rare earths are found in most high-technology and renewable energy processes, in the nuclear industry and in consumer electronics with a global consumption of about 120,000 to 150,000 t in 2015 [1]. The interest in recovering rare earths is therefore also increasing. This study focusses on Ce as a model rare earth element because of its relatively high abundance in the Earth's crust (about 66 ppm) and wide range of industrial applications, notably in catalysis, metallurgy, batteries, LED lamps, and glasses [2].

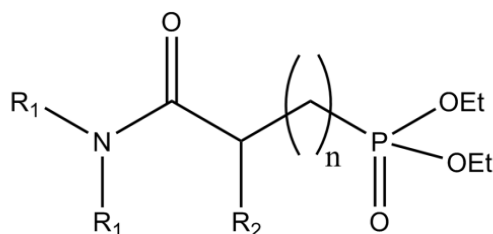
Rare earths are typically extracted by milling and basic (NaOH) or acid (HCl, H<sub>2</sub>SO<sub>4</sub>) leaching, followed by hydrometallurgical extraction using conventional organic solvents. The extractants for liquid-liquid extraction processes described in the literature are generally organophosphorus compounds with extraction capacities of 10–300 mmol Ce per mol (mmol/mol). For example, Cyanex<sup>®</sup>272, Cyanex<sup>®</sup>301 and D2EHPA have been used to extract up to 98 mmol/mol of cerium from monazite and Indian red mud ore [3, 4]. Elsewhere, Lu et al. [5] measured a Ce extraction capacity of 80 mmol/mol with Cextrant 230 in a 3 M sulphate medium.

In recent years, supercritical CO<sub>2</sub> (SC-CO<sub>2</sub>) has emerged as a low-cost (around 1 \$/kg), energy-saving (low critical point: 304.2 K, 7.38 MPa) and green (low environmental impact)

alternative for rare earth extraction. Supercritical CO<sub>2</sub> can be used as both a vector and an extractant to recover metals from solids (ore...), avoiding the use of organic solvents and the leaching/dissolution step. Its high diffusivity minimizes grinding requirements and its high solvent power, achieved by modulating the pressure and temperature of the process, can in some cases allow back-extraction and the recycling of the CO<sub>2</sub> and the extractant.

Carefully choosing a sufficiently soluble extractant that rapidly forms ligand-cerium complexes with a high extraction capacity is crucial. The most commonly used complex for Ce extraction in SC-CO<sub>2</sub> is TBP-HNO<sub>3</sub> [6–10], but the ore has to be pretreated to achieve good extraction capacities (< 5% without vs ~100% with pretreatment) [6–9]. In another study investigating Ce extraction from an acidic solution (6 M HNO<sub>3</sub> and 3 M LiNO<sub>3</sub>) using SC-CO<sub>2</sub> (333 K, 35 MPa), adding a second molecule (thenoyltrifluoroacetone) was found to enhance the extraction yield from 60% to 72% [10]. The focus of present study is on the solubility of the amidophosphonate extractants shown in Fig. 1 for the extraction of cerium nitrate previously deposited on cotton (94% cellulose).

This family of molecules has been investigated previously in liquid-liquid extraction processes in sulphuric and phosphoric acid media [11], and for solid phase extraction using functionalized mesoporous silica powders [12]. Its potential as a Ce extractant has remained unexplored to date.



**Fig. 1.** Amidophosphonate-based extractant molecules investigated in this study. R2 = methyl, n = 0

One of the objectives of this study was to understand how the chains (R1) attached to the nitrogen atom influence the solubility of the molecule and its ability to extract cerium in SC-CO<sub>2</sub>. Many studies have shown that a molecule's structure affects its solubility in SC-CO<sub>2</sub> [13–23]. Since SC-CO<sub>2</sub> is an apolar medium, adding R1 carbon chains should improve the solubility of the molecule. The effect can be opposite however if the chains are too long (heavy). Indeed, increasing the chain length has been shown to decrease SC-CO<sub>2</sub> solubility [15], as has adding aromatic [15,16] or hydroxyl moieties [17]. On the contrary, adding siliceous [18] or fluorinated [19, 20] substituents or branching chains [21–23] has been shown to increase solubility. This can also be adjusted by varying the temperature and/or pressure (i.e. the density) of the SC-CO<sub>2</sub>.

We therefore investigated how the solubility in SC-CO<sub>2</sub> and Ce extraction capacity of different amidophosphonate ligands (Fig. 1) are affected by their structure and how the solubility of the optimal extractant molecule varied with the density of the SC-CO<sub>2</sub>.

## 2. Materials and methods

### 2.1. Reagents

#### 2.1.1. Preparation of the amidophosphonate ligands

All organic reagents and solvents were purchased from Aldrich and were used as received (see Table 1). Carbon dioxide (> 99.99% purity) was obtained from Air Liquide. No further purification was performed.

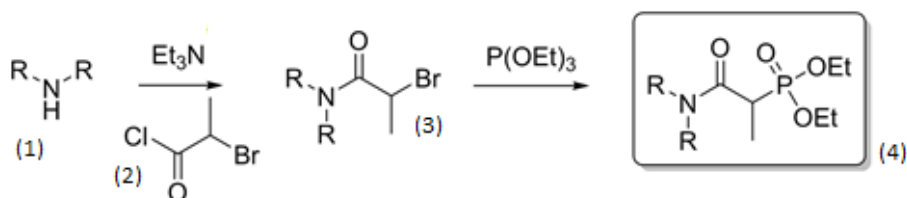
**Table 1**

Chemicals used to synthesize the extractants

Chemical name	CAS	Source	Purity
Diisobutylamine	110-96-3	Aldrich	99%

Bis(2-ethylhexyl)amine	106-20-7	Aldrich	99%
Dibutylamine	111-92-2	Aldrich	≥ 99.5%
Dihexylamine	143-16-8	Aldrich	97%
Triethylamine	121-44-8	Aldrich	≥ 99%
2-bromopropionyl chloride	7148-74-5	Aldrich	99%
Diethyl ether	60-29-7	Aldrich	≥ 99.5%
Triethyl phosphite	122-52-1	Aldrich	98%

The amidophosphonate ligands were synthesized as described by Turgis et al. [11,24]. The two steps are depicted in Fig. 2. Briefly, the first step involved reacting carbamoylmethyl-phosphonate functions (R = dibutylamine (butyl), diisobutylamine (isobutyl), dihexylamine (hexyl) or bis(2-ethylhexyl)amine (ethylhexyl)) with an amine (compound 1) and 2-bromopropionyl chloride (compound 2) in the presence of trimethylamine at room temperature for 3 h in order to obtain compound 3 after filtration. The second step was an Arbuzov reaction at 453 K of compound 3 with triethyl phosphite that yielded a pure amidophosphonate ligand (compound 4) after distillation of the phosphite. The products were obtained with good yields (> 95%), and were isolated and fully characterized by NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ). The NMR spectra were recorded on a Bruker<sup>®</sup> 400 ultrashield VS spectrometer (400.13 MHz for  $^1\text{H}$ , 100.613 MHz for  $^{13}\text{C}$ , 161.976MHz for  $^{31}\text{P}$ ) using deuterated chloroform as solvent and internal standard.



**Fig. 2.** Schematic representation of the two-step synthesis of amidophosphonate extractants with alkyl chains of different lengths and branching architecture (dibutylamine, 321.4 g/mol; diisobutylamine, 321.4 g/mol;

dihexylamine, 377.5 g/mol; bis(2-ethylhexyl)amine, 433.6 g/mol). Molar masses as measured by Turgis et al. [11].

### 2.1.2. *Solid matrix sample*

Cerium was deposited as cerium nitrate hexahydrate (Aldrich, CAS n° 10294-41-4) on cotton pads (94% cellulose; diameter, 4 cm; thickness, 1 mm; mass, 0.33 g). The salt was dissolved in water to a concentration of  $10^{-3}$  mol/L (pH = 4). The samples were prepared by drying pads impregnated with 10 mL of the cerium nitrate solution in a stove at 313 K until all the water had evaporated (12 h). To ensure each experimental run was reproducible, the mass of cerium deposited was measured by ICP-AES ( $\pm 1\mu\text{g/L}$ ) after diluting the sample in sulfuric acid (VWR, 95 wt%, CAS n° 7664-93-9).

## 2.2. *Solubility measurements*

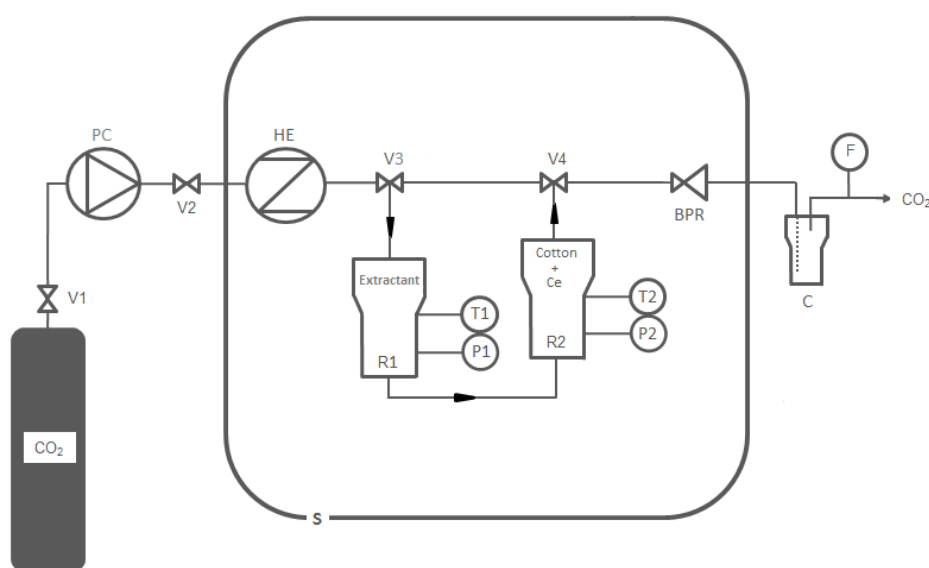
### 2.2.1. *Rationale*

The effect of the structure of the alkyl chains on the solubility in SC-CO<sub>2</sub> of the amidophosphonate compounds was first studied at 25 MPa and 318 K ( $\rho_{\text{CO}_2} = 0.879$  g/mL). These operating parameters (P, T) were chosen to achieve a CO<sub>2</sub> density close to that of hexane (0.655 g/mL) and dodecane (0.750 g/mL), which were used for liquid-liquid extraction at room temperature (see section 2.3.1). Further experiments were then performed at 313, 320 and 331 K and 13, 15, 20 and 28 MPa to identify the conditions under which the optimal ligand was most soluble.

### 2.2.2. *Experiments*

The solubility in SC-CO<sub>2</sub> of the extractants was measured using the dynamic gravimetric device described and validated by Dartiguelongue et al. [25, 26] (Fig. 3). The cotton pads containing the amidophosphonate compounds were placed in a reactor (38 cm<sup>3</sup>, Top

Industries) capped with two 20  $\mu\text{m}$  sintered stainless steel disks to prevent mechanical entrainment. The liquid  $\text{CO}_2$  was pumped at 1 mL/min and 25 MPa using a high pressure pump (PU-2080- $\text{CO}_2$  plus, Jasco, standard uncertainty on the  $\text{CO}_2$  flow rate,  $\pm 3.3 \cdot 10^{-5} \text{ cm}^3/\text{s}$ ) and circulated in a heat exchanger attached to a stove (FED 115, Binder) enclosing the whole device. The solubilized portion of the amidophosphonate compound was transported in the  $\text{SC-CO}_2$  to a back-pressure regulator (Tescom, 26-1700 series), before being gathered downstream in a collector placed outside the oven as the  $\text{CO}_2$  became depressurized, thereby reducing its solvent power. The total mass of  $\text{CO}_2$  flowing through the device was measured using an SLA5860 flow meter (Brooks, standard uncertainty on the  $\text{CO}_2$  mass flow,  $\pm 1.7 \cdot 10^{-7} \text{ kg/s}$ ). All solubility measurements were triplicated. The flow rate was chosen in the middle of the range (0.5–1.5 mL/min) reported by Hung et al. [27] to ensure thermodynamic equilibrium and minimal solubility variations ( $\sim 4\%$ ).



**Fig. 3.** Experimental setup used to measure the solubility of amidophosphonate ligands in supercritical  $\text{CO}_2$ . V1, V2, V3 and V4, valves; PC,  $\text{CO}_2$  pump; HE, heat exchanger; R1, solubilization reactor; R2, extraction reactor; BPR, back-pressure regulator; S, stove; C, collector; F, mass flow meter.



The solubility was determined (mol/mol) by weighing the amount of extractant collected in the collector ( $\pm 0.1$  mg), using Eq. (1):

$$y = \frac{m_L^c}{m_L^c + \frac{M_L}{M_{CO_2}} m_{CO_2}} \quad (1)$$

where  $m_L^c$  (g) is the mass of amidophosphonate ligand collected after solubilization in SC-CO<sub>2</sub>,  $m_{CO_2}$  (g) is the total mass of CO<sub>2</sub> flowing through the device, and  $M_L$  and  $M_{CO_2}$  (g/mol) are the respective molar masses of the amidophosphonate ligand and CO<sub>2</sub>. The overall uncertainty in the measurements,  $u(y)$  (mol/mol), is given by Eq. (2):

$$u(y) = y \sqrt{\frac{u(m_{CO_2})^2}{m_{CO_2}^2} + 2 \frac{u(m_L)^2}{m_L^2}} \quad (2)$$

where  $u(m_{CO_2})$  (g) is the uncertainty on the mass flow measurements and  $u(m_L)$  (g) the uncertainty of the balance.

The percentage change in the masses of amidophosphonate and CO<sub>2</sub> were calculated using Eqs (3–5),

$$\overline{\Delta m_L} = 100 \cdot \frac{|m_L^0 - (m_L^c + m_L^d)|}{m_E^0} \quad (3)$$

$$\overline{\Delta m_{CO_2}} = 100 \cdot \frac{|m_{CO_2}^P - m_{CO_2}^F|}{m_{CO_2}^P} \quad (4)$$

with  $m_L^0$  (g) the mass of extractant initially loaded into the reactor,  $m_L^d$  (g) the mass collected after depressurization,  $m_{CO_2}^F$  (g) the mass measured by the mass flowmeter at the

end of the process and  $m_{CO_2}^P$  (g) the mass of CO<sub>2</sub> delivered during the experiment and calculated using Eq. (5):

$$m_{CO_2}^P = F_{CO_2} \rho_{CO_2} t \quad (5)$$

In this equation,  $F_{CO_2}$  (cm<sup>3</sup>/min) is the incoming CO<sub>2</sub> flow rate,  $\rho_{CO_2}$  (g/cm<sup>3</sup>) is the density of CO<sub>2</sub> at 263 K and  $t$  (min) is the length of the experiment.

### 2.3. Extraction experiments

Cerium extraction experiments were performed using SC-CO<sub>2</sub> and conventional solvents to compare the corresponding extraction capacities.

#### 2.3.1. Liquid-liquid extraction

Liquid-liquid extraction experiments were performed at room temperature and atmospheric pressure using dodecane and hexane, two conventional non-polar organic solvents. The amidophosphonate ligands (0.25 M) were diluted in 5 cm<sup>3</sup> of dodecane or hexane and stirred for 12 h at 60 rpm with 5 cm<sup>-3</sup> of 1 a g/L aqueous solution of cerium nitrate. After extraction, the aqueous and organic phases were separated by centrifugation at 4000 rpm for 30 min to determine the mass of cerium remaining in the aqueous phase. The extraction capacity of the ligand in this type of process is defined as:

$$ECL = \frac{n_{Ce i} - n_{Ce f}}{n_L} \times 10^3 \quad (6)$$

where  $n_{Ce i}$  and  $n_{Ce f}$  (mol) are the amounts of cerium in the aqueous phase before and after extraction and  $n_L$  (mol) is the amount of ligand introduced into the organic phase before extraction.

#### 2.3.2. SC-CO<sub>2</sub> extraction

For each of the amidophosphonate ligands, a cotton pad containing 4.2 mg of cerium was placed in the extraction reactor (25 cm<sup>3</sup>, stainless steel, Parr Instruments, see Fig. 3) and

another pad impregnated with 5 g of the ligand was placed in the solubilization reactor. The ligand was thus solubilized in SC-CO<sub>2</sub> and transported to the cerium-impregnated cotton sample. The resulting cerium-ligand complex was separated from the CO<sub>2</sub> downstream of the back pressure regulator. The cerium was recovered in the collector at low pressure and room temperature and then weighed to calculate the extraction capacity (mmol of cerium per mol of extractant) using Eq. (7):

$$EC = \frac{m_{Ce}M_L}{m_L M_{Ce}} \quad (7)$$

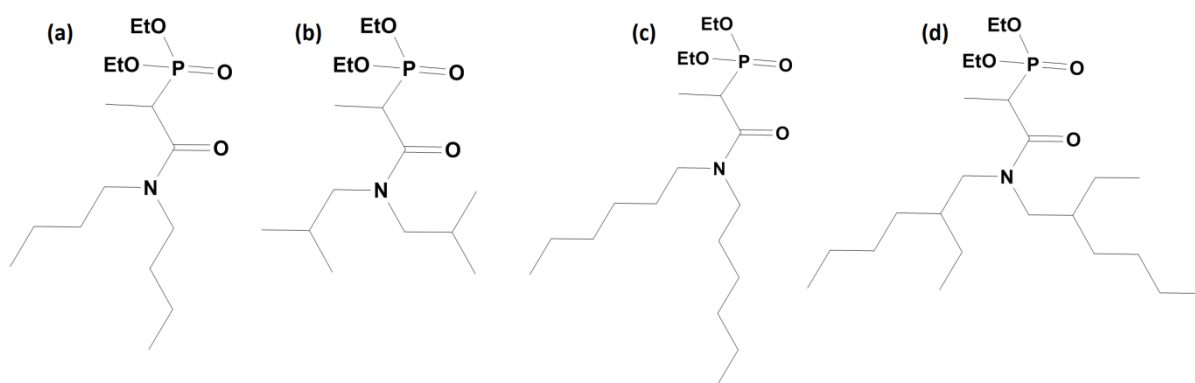
where  $m_{Ce}$  is the mass of cerium extracted,  $m_L$ , the initial mass of ligand placed in the reactor, and  $M_{Ce}$  and  $M_L$  are the corresponding molar masses. All SC-CO<sub>2</sub> extraction experiments were performed for 1 h at  $25 \pm 0.5$  MPa,  $313 \pm 0.5$  K and a CO<sub>2</sub> flow rate of 5 mL/min.

### 3. Results and discussion

#### 3.1. Influence of the structure of amidophosphonate compounds on their solubility in SC-CO<sub>2</sub>

The branching structures of the four amidophosphonate compounds investigated in this study are presented in Fig. 3. Varying the architecture of the alkyl chain alters the polarity and molecular mass of the ligand. Table 2 shows that between the two molecules with linear alkyl chains, butyl (Fig. 3a) and hexyl (Fig. 3c), the one with the shorter chain (butyl) is more soluble. Between the two molecules with the same molecular weight, isobutyl (Fig. 3b), with a more branched alkyl chain, is slightly more soluble than butyl. The least soluble molecule was found to be ethylhexyl (Fig. 3d), with the heaviest and most branched alkyl chain.

PGHERE



**Fig. 3.** Structural formulas of the amidophosphonate extractants with (a) dibutylamine, (b) diisobutylamine (c) dihexylamine, and (d) bis(2-ethylhexyl)amine alkyl chains.

**Table 2**

Solubility and Ce extraction capacity of amidophosphonates in supercritical CO<sub>2</sub> at 25 MPa and 318 K

Amine group	Molecular mass (g.mol <sup>-1</sup> )	Solubility <sup>a</sup> (mmol/mol)	$\overline{\Delta m}_{\text{extractant}}$ (%)	$\overline{\Delta m}_{\text{CO}_2}$ (%)
Butyl	321.4	2.41	1.8	10.3
Isobutyl	321.4	2.47	3.3	10.1
Hexyl	377.5	2.14	2.9	10.5
Ethylhexyl	433.6	1.56	0.8	9.6

Butyl, dibutylamine; Isobutyl, diisobutylamine; Hexyl, dihexylamine; Ethylhexyl, bis(2-ethylhexyl)amine.

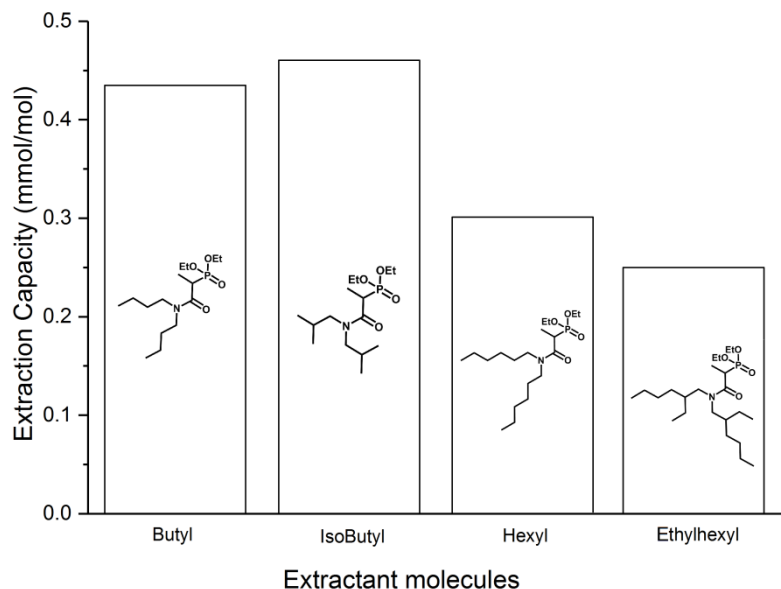
<sup>a</sup>Calculated uncertainties < 10<sup>-2</sup> mmol/mol

### 3.2. Cerium extraction capacities

In the liquid-liquid extraction experiments, the cerium concentration remained constant in the aqueous phase after coming into contact with the extractant (data not shown), showing that these amidophosphonate ligands do not extract cerium in a liquid-liquid process.

The cerium extraction capacities measured in SC-CO<sub>2</sub> varied from 0.25 to 0.46 mmol/mol (Fig. 4) and the length of the experiment and flow rate were sufficient to reach equilibrium. Fig. 4 reveals the extraction capacities of the different ligands follow the same trend as their solubility in SC-CO<sub>2</sub> (Table 2) with in decreasing order isobutyl, butyl, hexyl and

ethylhexyl. The molecule with the highest cerium extraction capacity, isobutyl, is the one with the lowest molecular weight and a branching alkyl chain.



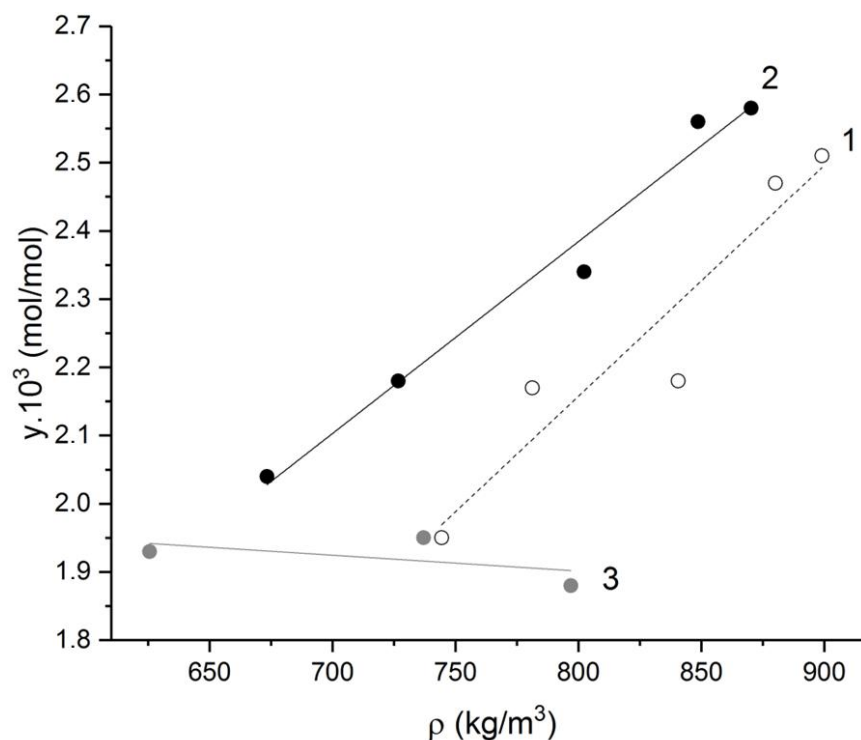
**Fig. 4.** Cerium extraction capacity in SC-CO<sub>2</sub> (25 ± 0.5 MPa, 313 ± 0.5 K, 5 mL/min) and structural formula of the four amidophosphonate ligands with dibutylamine (butyl), diisobutylamine (isobutyl), dihexylamine (hexyl); bis(2-ethylhexyl)amine (ethylhexyl) alkyl chains.

According to its Pourbaix diagram [28], the cerium deposited on the cotton pads is trivalent (pH = 4). As the pads dried, the Ce<sup>3+</sup> may have bonded with NO<sub>3</sub><sup>-</sup> ions to reform cerium nitrate salt. Since the amidophosphonate molecules cannot exchange ions, this would imply that the extraction mechanism involves the complexation of the nitrate salt with the amidophosphonate. These hypotheses will be investigated in further studies.

### 3.3. Solubility of the isobutyl extractant as a function of SC-CO<sub>2</sub> density

Fig. 5 shows that the solubility of the isobutyl extractant increases linearly with the SC-CO<sub>2</sub> density (obtained from the pressure and temperature using NIST data [29]) at 313 and 320 K (respectively from 1.95 to 2.51 mmol/mol and 2.04 to 2.58 mmol/mol), but remains

roughly constant at 331 K. In comparison, the solubility of TBP under the same conditions (313–333 K and 12–25 MPa) varies from 66.1 to 68.1 mmol/mol [30, 31].



**Fig. 5.** Solubility of the diisobutylamine (isobutyl) amidophosphonate ligand as a function of CO<sub>2</sub> density at 313 K (1), 320 K (2) and 331 K (3). The lines are regression fits of the experimental data.

At a given CO<sub>2</sub> density, above 750 kg/m<sup>3</sup>, the ligand is more soluble at 320 K than at 313 K, but less soluble at 331 K. The fact that the solubility of the ligand does not increase with density at 331 K is consistent with the observations of Foster et al. [32], who show that there is a threshold pressure above which the evolution of the solubility with temperature is inverted. The solubility increases with the temperature when the pressure of the system is above the crossover pressure and the effect of the vapor pressure predominates over that of the solvent density. Above this crossover pressure however, the latter effect dominates and the solubility decreases with increasing temperature.

## 4. Conclusions

The solubilities in SC-CO<sub>2</sub> of various organophosphorus extractants have been measured using a gravimetric method and correlated with the structures of their CO<sub>2</sub>-philic chains. At 25 MPa and 313 K, the extractant with the diisobutylamine chain was the most soluble ( $2.47 \pm 0.003$  mmol/mol), compared with the ligands with a heavier chain (dihexylamine and bis(2-ethylhexyl)amine,  $2.14 \pm 0.003$  and  $1.56 \pm 0.002$  mmol/mol, respectively) or a less branched alkyl chain (dibutylamine, same molecular weight.  $2.41 \pm 0.003$  mmol/mol). The cerium extraction capacity in SC-CO<sub>2</sub> of these extractants varied from 0.25 to 0.46 mmol/mol and correlated with their solubility. The solubility of the isobutyl extractant was found to increase with the SC-CO<sub>2</sub> density at 313 and 320 K, but remained constant at 331 K. At a given density, the solubility was higher at 320 K than at 313 K, but was lowest of all at 331 K, suggesting that the threshold temperature for this system is somewhere between 320 and 331 K.

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