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# Supercritical CO<sub>2</sub> process to extract Cerium using CO<sub>2</sub>-phile extractant

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## 1. Introduction

Processes based on supercritical CO<sub>2</sub> (SC-CO<sub>2</sub>) media are attractive alternative to conventional liquid-liquid processes using organic solvents for metals extraction from solid matrixes, such as ores, or WEEE. Indeed, SC-CO<sub>2</sub> is a cheap, non-flammable and environmentally friendly solvent. SC-CO<sub>2</sub> promotes the transport of extractive molecules inside porous matrixes due to its high diffusivity and low viscosity. Such extractants must exhibit high stability, fast kinetics of complex formation with the metal to be extracted, high solubility in SC-CO<sub>2</sub> and high selectivity towards the targeted metal cation. In order to improve their solubility in SC-CO<sub>2</sub>, of selective molecules, was functionalized. In this way, organophosphorus compounds have been synthesized with linear or branched alkyl chains of different size (between 4 and 8 carbons). The solubilities of each extractant were measured using a dynamic gravimetric method<sup>1</sup> at different pressure and temperature. SC-CO<sub>2</sub> extraction runs have been also carried out in order to assess extractant capacity towards cerium.

## 2. Results and discussion

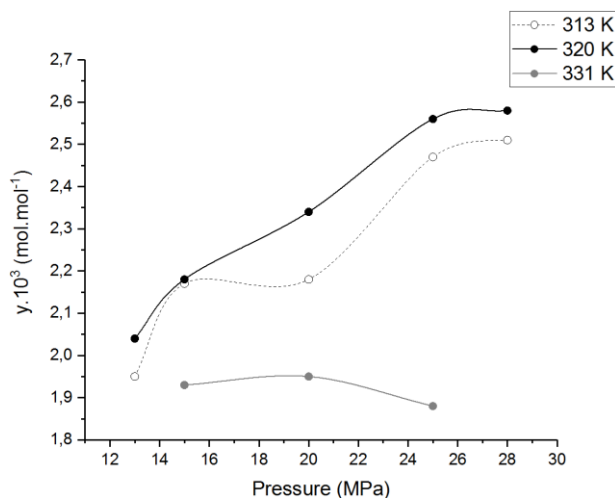
First, the influence of linear and branched alkyl chains on the solubility of functionalized organophosphorus compounds in SC-CO<sub>2</sub> was studied at 25 MPa and 318 K ( $\rho_{\text{CO}_2} = 0.879 \text{ g.mL}^{-1}$ ) (see Table 1). These operating conditions allow a good solubilization of most of similar extractants (such as TBP-HNO<sub>3</sub><sup>2</sup>). When the length of the linear alkyl chain decreases (hexyl versus butyl), the solubility of the molecule increases. This may be explained by a decrease of the molecular weight, which is in agreement with the literature<sup>3</sup>. An increase in the branching of equivalent molecular weight induces a small increase of the solubility, as described in the literature in the case of polyvinyl ester<sup>4</sup>. While the use of branched chains instead of linear chains may improve the solubility of organic molecules in SC-CO<sub>2</sub>, it seems that the molecular weight (or the length chain) have a higher impact on the solubility. Secondly, the solubility and extraction capacity towards cerium of the most soluble extractant has been determined as a function of CO<sub>2</sub> density.

Chemical name of group R	$y \cdot 10^3 \text{ (mol.mol}^{-1}) \pm u(y)$	$\overline{\Delta m}_{\text{extractant}}$ (%)	$\overline{\Delta m}_{\text{CO}_2}$ (%)
Isobutyl	$2.47 \pm 3.02 \cdot 10^{-3}$	3.3	10.1
Butyl	$2.41 \pm 2.62 \cdot 10^{-3}$	1.8	10.3
Hexyl	$2.14 \pm 2.62 \cdot 10^{-3}$	2.9	10.5
2-ethylhexyl	$1.56 \pm 1.93 \cdot 10^{-3}$	0.8	9.6

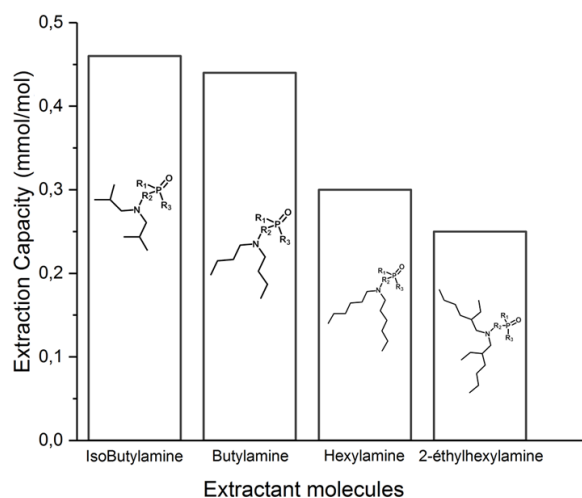
**Table 1.** Solubility of organophosphorous in SC-CO<sub>2</sub> at 25 MPa and 318 K ( $\overline{\Delta m}_{\text{extractant}}$  and  $\overline{\Delta m}_{\text{CO}_2}$  are the mass deviation of extractant and CO<sub>2</sub>)

The extractant with a CO<sub>2</sub>-philic chain comprising four branched carbons called "Isobutyl" has been chosen for investigating the role of pressure and temperature on solubility and cerium extraction. Solubility measurements have been carried out for temperatures ranging from 313 to 331 K and pressures ranging from 13 to 28 MPa. SC-CO<sub>2</sub> feed flow rate has been set to 1 mL/min to reach thermodynamic equilibrium. For both conditions at 313 K and 320 K, the solubility  $y$  (mmol of molecule in SC-CO<sub>2</sub> per mol of SC-CO<sub>2</sub>) increases up to a limit corresponding to a minimum pressure of 25 MPa (see Figure 1). A similar phenomenon has already been demonstrated by Ghaziaskar *et al.*<sup>5</sup> in the case of hexanoic acid in SC-CO<sub>2</sub>, due to dimerization phenomenon. For the 331 K isotherm, the solubility is much lower regardless of the solubilization pressure. Chimowitz *et al.*<sup>6</sup> showed the existence of a transition temperature from which the solubility depends either more or less on the solute vapor pressure or on the SC-CO<sub>2</sub> density. Indeed, as the temperature increases, the solute vapor pressure increases whereas the SC-CO<sub>2</sub> density decreases both effects playing an opposite role in the solubility. In our case, the extractant solubility increases with temperature up

to 320 K which seems that the temperature transition is between 320 and 330 K. Below this, the vapor pressure dominates and above the SC-CO<sub>2</sub> density takes prevalence over the extractant vapor pressure and consequently the solubility decreases.



**Figure 1.** Solubility of selected extractant (R = Isobutyl) as a function of (a) pressure at 313 K, 320 K and 331 K and (b) temperature between 13 MPa and 28 MPa.



**Figure 2.** Cerium extraction capacity of organophosphorus molecules in function of their structure.

A first series of liquid-liquid extraction in dodecane and hexane showed that this type of molecule didn't allow the cerium extraction. A second series of SC-CO<sub>2</sub> extraction were carried out (25 MPa, 314 K) on a porous cotton matrix (94% cellulose) on the surface of which cerium ( $1.4 \pm 0.05$  mg) was deposited by drying an aqueous solution containing cerium nitrate. Here, we introduce the extraction capacity towards cerium (in mmol of cerium per mol of extractant) which makes it possible to determine the necessary quantity of extractant. Figure 2 shows us that extraction capacity increases with extractant solubility. It confirms that the solubility of the extractant is a key parameter in SC-CO<sub>2</sub> extraction processes.

### 3. Conclusions

The solubility measurements of an organophosphorus cerium extractant in SC-CO<sub>2</sub> have been carried out using a gravimetric method. Thus, the structures of the CO<sub>2</sub>-philic chain, the pressure and the temperature conditions have been tuned to determine the most suitable conditions for extraction. Extractant solubility has been shown to increase with branching and decreasing with alkyl chain length. Preconized temperature and pressure are 25 MPa and 313 K. Indeed, an inversion of solubility trend may occur depending on the predominance of vapor pressure or the CO<sub>2</sub> density for temperatures higher than 320 K. Finally, we show that this process using an extractant solubilized in SC-CO<sub>2</sub> can extract cerium directly from a solid matrix, that can't be the case by a liquid-liquid process. We also show that cerium extraction capacity of synthesized molecules have been determined and allows to distinguish this or that extractant in addition to solubility values.

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