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# Sorption properties of carbamoylmethylphosphonated-based polymer combining both sorption and thermosensitive properties: New valuable hydrosoluble materials for rare earth elements sorption



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GRAPHICAL ABSTRACT

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### HIGHLIGHTS

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- Sorption using a new polymer combining both sorption and thermosensitive properties.
- Investigation of sorption efficiency for gadolinium ions in various operating conditions.
- Mechanism of extraction by solvation effect with amido-phosphonate sites.
- Selective sorption of Gd(III) ions in Gd/Ni mixtures.



### ABSTRACT

The sorption properties of gadolinium (Gd) by an original carbamoylmethylphosphonate (cmp)-based acrylamide polymer combining both chelating and thermosensitive properties namely poly(diethyl-6-(acrylamido)hexylcarbamoyl-methylphosphonate) (P(CPAAm6C)) are presented for the first time. For pH = 1 and at 20 °C, the maximum sorption capacity reached 0.6 mmol·g<sup>-1</sup> for the highest Gd concentrations. Different parameters influencing the sorption of Gd were studied as pH, ionic strenght and temperature. The temperature was shown to influence both the sorption and the stability of the complex cmp-Gd formed by coordination mode with C=O and P=O functions. The selectivity of the cmp group for Gd was demonstrated in Gd/Ni mixture and shows its thermosensitive polymer is very promising for the development of selective sorption processes.

# 1. Introduction

Rare earth elements (REE) are a group of elements including lanthanides (Ln), scandium (Sc) and yttrium (Y) [1]. They are used in various applications in high technology as magnets, catalytic converters, battery, optical lenses, phosphors or electronic compounds [2,3]. Most of REE are not rare as suggested by their name. Except promethium which isotopes are radioactive with short life decay period, all of REE are found all over the world and, are more abundant in the Earth's crust than silver, gold, nickel, lead or platinum. Since their supply risk was pointed out in 2010 and because of their economic importance, these metals are considered as critical [3,4].

Despite REE are produced in many countries (Australia, Russia, USA), about 86% of them are still produced in China [5–7]. This situation of quasi-monopoly leads the European industry to develop alternative separation processes to obtain REE, and more particularly

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lanthanide elements, by recycling or exploitation of new mineral deposits. REEs are present in numerous minerals such as monazite (phosphates, (Ce,La,Nd,Sm,Gd,Y,Th)PO<sub>4</sub>) [8,9], samarskite (oxides, (Y,Fe<sup>3+</sup>,Fe<sup>2+</sup>,U,Th,Ca)<sub>2</sub>(Nb,Ta)<sub>2</sub>O<sub>8</sub>) [2,10], bastnaesite (carbonate-fluorides, REECO<sub>3</sub>F) [11] and allanite (oxide, Ca,REE,Fe<sup>2+</sup>,Al<sub>2</sub>(SiO<sub>7</sub>)) [12]. These minerals usually contain lanthanides (Ln), transition metals and small amounts of natural radioelements such as uranium (U) and thorium (Th) and can be exploited.

Another means of supply can be the exploitation of the "urban mine" *ie.* the Waste Electronic and Electrical Equipment (WEEE) recycling which contains lanthanides and transition metals [7]. For example lamp phosphors, Nickel-Metal-Hybrid batteries (NiMH) and catalysts can contain 20, 10 and 3.5% of REE respectively combined with transition metals. But nowadays < 1% of REE used are recycled from WEEE [13].

In the case of both supply routes, after an initial grinding step, minerals or WEEE are leached with concentrated solutions of hydrochloric, sulfuric or nitric acids to increase the recovery of metals in solution [14]. After filtration, each element is subsequently separated and pre-concentrated using different processes such as precipitation (or fractioned crystallization), solvent extraction [5,14] or solid phase extraction [15,16]. Although it is the most economical and the simplest process to implement, precipitation is not always the most efficient. The disadvantage of this type of process is mainly due to co-precipitation phenomena (precipitation of a part of non-targeted cations) that makes sometimes this process poorly selective and complicated due to the presence of many successive steps. Solvent extraction or liquid-liquid extraction is usually applied to obtain high degree of purity of each elements [14]. For example, the Rhône Poulenc process had the capability of producing a purity grade about 96% in the case of praseodymium (Pr), neodymium (Nd) and samarium (Sm). A higher purity was obtained for the other lanthanides with a grade higher than 99.5%. This high selectivity is obtained by using selective extractants such as cationic or anionic exchangers, or chelating extractant. Concerning the selective separation of lanthanide and actinide elements, the main part of chelating functional groups contains O-donor sites like, amides [17,18], malonamides [18-20], phosphates [21,22], carbamoylmethylphosphine oxides [21], carbamoylmethyl-phosphonate, and carbamoylmethyl-phosphonic acids [23,24]. However, despite its high efficiency and excellent selectivity, solvent extraction requires a large amount of aliphatic solvents (heptane, kerosene...), which are generally carcinogenic compounds and make them harmful for health and environment. An alternative process consists in using extraction on solid phase, which doesn't need any organic solvent. Lanthanide/actinide sorbents could be organic (resins) [25-35], inorganic [36,37], or hybrid (organic/inorganic) [35,38-40] materials. Organic or hybrid materials are generally functionalized with ion exchange or solvating sites with similar complexing motifs than those used in solvent extraction [25,27,29,33–35]. However, these materials are generally designed in eluting column and thus they are difficult to industrialize in a continuous process, on the one hand and, energy consumer on the other hand [38]. New recovery processes are now emerging such as polymer enhanced ultrafiltration or polymer assisted ultrafiltration (PEUF/ PAUF), which associates a functionalized polymer (soluble or insoluble) in order to complex metals with a membrane ultrafiltration step to recover the polymer after complexation [41,42]. For example, Ricoux et al. reported the development of a recovery process for palladium using an insoluble phosphine oxide functionalized polymer [43,24]. Another more interesting example is the Graillot et al. TEMF process (Thermosensitive Enhanced MicroFiltration) that allowed to eliminate metals from water by using water soluble P(NnPAAm-stat-hMAPC1) copolymers [44]. The NnPAAm showed thermosensitive properties whereas the MAPC1 monomers enabled the metal complexation [45,46]. The use of this kind of complexing-thermosensitive polymer has two advantages: (i) the thermosensitive polymer is soluble in solution at temperature lower than the cloud point (CP) thus favoring the



**Scheme 1.** Chemical structure of the poly(diethyl-6-(acrylamido)hexylcarbamoyl-methylphosphonate) (P(CPAAm6C) obtained by free radical polymerization.

complexation of metals and (ii) the polymer becomes insoluble at temperature above the CP, leading to the increase of particle sizes and thus to an easier filtration step which allows energy savings [47–49].

In a previous work, the first thermosensitive-complexing homopolymer (P(CPAAm6C)) was reported [50]. The possibility to obtain both properties from a single monomer would be advantage an for industry. The homopolymerization of the CPAAm6C enabled to obtain a functional rate of 100% by free radical polymerization (chemical structure represented in Scheme 1), which was not reached by using copolymerization of two monomers. Furthermore the distribution of functional sites remained unclear in the case of P(NnPAAm-stat-MAPC1) or P(NnPAAm-stat-DAAmEP) copolymerization (thermosensitive monomer vs. complexing monomer) as observed by Graillot [51]. With its carbamoylmethylphosphonate esters function (cmp), the P(CPAAm6C) could be used for lanthanide recovery using a process involving three successive steps: (i) complexation of lanthanide elements at a temperature lower than CP by the carbamoylmethylphosphonate (cmp) function, (ii) increase of temperature above the CP to get an insoluble polymer of higher particle size and finally (iii) filtration of the insoluble polymer complexing lanthanides. In this work, the multiparametric study of gadolinium sorption (chosen as model of lanthanides series) by P(CPAAm6C) was investigated by varying several parameters as the amounts of Gd(III) and P(CPAAm6C), pH, ionic strength and temperature during the extraction step. Thereafter, some informations about the extraction mechanism were obtained by infrared spectroscopy and the selectivity of P(CPAAm6C) regarding to gadolinium was studied in synthetic solutions containing Gd(III)/Ni(II) mixtures to mimic REE/transition metals mixtures encountered in the recycling steps consequently to the treatment of solutions coming from WEEE recycling or mining.

# 2. Experimental

# 2.1. Materials

## 2.1.1. Polymeric sorbent

Polymeric sorbent used in this study is the poly(diethyl-6-(acrylamido)hexylcarbamoyl-methylphosphonate) homopolymer (P (CPAAm6C)) obtained from the free radical polymerization of CPAAm6C as described in a previous work [50]. All details concerning the synthesis and the main characteristics of the polymer are reported in Supplementary Data.

## 2.1.2. Synthetic solutions

 $0.5 \text{ mol} \cdot \text{L}^{-1}$  stock metal solutions were prepared by dissolution of gadolinium(III) nitrate hexahydrate (Gd(NO<sub>3</sub>)<sub>3</sub>, 6H<sub>2</sub>O, Aldrich, metal basis trace, 99.99%) or Nickel(II) nitrate hexahydrated (Ni(NO<sub>3</sub>)<sub>2</sub>,

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