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Donatien Gomes Rodrigues, Sophie Monge, S Pellet-Rostaing, Nicolas Dacheux, Denis Bouyer, et al.. A new carbamoylmethylphosphonic acid-based polymer for the selective sorption of rare earth elements. *Journal Chemical Engineering*, 2019, 371, pp.857-867. 10.1016/j.cej.2019.04.026 . hal-02114899

HAL Id: hal-02114899

<https://hal.science/hal-02114899v1>

Submitted on 9 Oct 2023

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A new carbamoylmethylphosphonic acid-based polymer for the selective sorption of rare earth elements

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Abstract:

Sorption properties of a new hydrosoluble polymer containing carbamoylmethylphosphonic diacid (**hcmp**) moieties were investigated. This polymer was obtained by hydrolysis of the poly(diethyl-6-(acrylamido)hexylcarbamoylmethylphosphonate (P(CPAAm6C))). The study allowed the determination of an experimental maximum capacity Q_{\max} equal to 1.5 mmol.g^{-1} which is three times higher than the one obtained for P(CPAAm6C), as previously described (i.e. 0.6 mmol.g^{-1}). Experimental data were fitted with the Langmuir equation and parameters Q_{\max}^L and K_L , were found to be $1.72 \pm 0.067 \text{ mmol.g}^{-1}$ and $0.302 \pm 0.063 \text{ L.mmol}^{-1}$, respectively. Additionally, this capacity depends on different parameters (concentration of metals and sorbent, pH, and ionic strength). The study proved that the **hP**(CPAAm6C) was selective of gadolinium in Gd/Ni mixtures. Additionally, the precipitation of the polymer was observed simultaneously to the Gd complexation. The results described in this paper proved that the **hP**(CPAAm6C) is a very promising hydrosoluble material for the purification of lanthanide elements or in the field of nuclear fuel reprocessing by using new solvent free and low energy consuming processes.

Introduction

Rare earth elements (REEs) are composed of 17 elements in the periodic table including the 15 lanthanides, yttrium and scandium.[1], [2] REEs became more and more important because of the development of new technologies as wind turbines, hybrid cars, computer equipment, catalytic converters, photovoltaic thin films or energy-efficient lighting. Indeed, lanthanides are part of various compositions of magnets, catalysts compounds, batteries, metal alloys, glass additives, ceramics and luminophors.[1], [3] REEs are not as rare as their name suggests since their abundance is higher than that of metals such as copper, lead or silver.[4] Their historically name originates from the 18th and 19th centuries as “earth”, originally defined for refractory materials which could not be changed further by heat.[4] These elements can be supplied by two main routes, among which the more important is mining. REEs are extracted all over the world from different minerals which can contain other elements like transition metals or primary radioelements such as thorium (Th) and uranium (U).[5]–[9] After mechanical pre-treatments including crushing and grinding of minerals, the powders are dissolved in concentrated acids (HCl, HNO₃ or H₂SO₄) to recover metal ions in solution.[10] Significant amounts of REEs are found in Canada, Greenland, South Africa, Malawi, and Vietnam but half of all world stocks are located in China.[1], [2] Since few years, the Chinese production represents about 95 % of the REEs produced worldwide.[4], [11] For this reason, several industrials explored other routes to recover REEs coming from the recycling of electronic wastes named “E-waste” or “urban mining”. [2], [12], [13] After mechanical separation of metals, plastics and wirings [14], metallic materials are leached.[2], [15]–[17] Dissolution processes of minerals or wastes lead to acidic aqueous solution containing REEs mixed with others elements which must be separated by different processes like precipitation, solvent extraction or solid phase extraction.[7], [18] Although it is the most economical and simplest way to implement, precipitation process is not the most efficient. Indeed, the drawback of this process is mainly due to co-precipitation phenomena (precipitation of a part of untargeted cations), which make

this process less selective and can induce the use of many expensive successive steps to reach satisfying purification. Solvent extraction consists in using complexing entities (like cationic or anionic exchangers or neutral solvation extractants) solubilized in organic oil.[10], [19] This process is generally used to reach high degree of purity of each lanthanide element (between 96 and 99.999 % in the case of the Rhone Poulenc process).[10] The main drawback of the solvent extraction is the use of large volumes of solvent and the generation of large amounts of waste. Solvents are generally aliphatic (pure alkanes, kerosene, hydrogenated tetrapropylene (TPH)) harmful to the environment and health. An alternative way to proceed, which does not use any organic solvent, is the solid phase extraction process.[1], [2] It consists in contacting aqueous solution (containing metals) with solid material incorporated in a column or as particles in suspension subsequently filtered. Materials can be organic,[20]–[25] inorganic[26]–[29] or hybrid.[30]–[38] Organic and hybrid materials are usually functionalized with selective ion exchange or solvating sites as O-donor sites like amides, malonamides, phosphates, carbamoylmethyl-phosphine oxides, carbamoylphosphonates, and carbamoylmethylphosphonic acids.[20], [39]–[42] Unfortunately, in the case of solid sorbent (resin and inorganic materials), the accessible complexing groups are located on the contact porous surface of the materials. The total porous volume of the material being difficult to reach for all target elements, sorption capacity may be quite low with slow kinetics.

Side to solid sorbents, new recovery processes are emerging with the use of functionalized thermosensitive P(NnPAAm-*stat-h*MAPC1) copolymers [43]–[45] which enable the simultaneous selective sorption of Al³⁺ and their separation by precipitation.[45]

These materials allow obtaining high sorption capacities thanks to the increased accessibility to complexing groups when the polymer is in the soluble state and an easy separation by microfiltration after precipitation of the polymer above the cloud point (CP).

Previous work also showed the interest of P(CPAAm6C) homopolymers that combine selective sorption of Gd(III) in acidic conditions thanks to the carbamoylmethylphosphonate ester function (cmp), [46], [47] and thermosensitive properties used for the separation step of the process. It is important to note that thermosensitivity was dependent on the ionic species concentrations. As a result, the control of the cloud point value involved an excellent knowledge of the elements in solution. [46] The maximum sorption capacity of gadolinium on P(CPAAm6C) was evaluated to 0.6 mmol.g^{-1} at $\text{pH} = 1$, *i.e.* 86.6 mg of Gd per gram of polymer. According to literature, phosphonic acid moieties have good interactions with trivalent cations [45] and demonstrate good performances in the field of the lanthanides extraction. [31], [48] In order to increase the capacity of P(CPAAm6C), it has been proposed to hydrolyze the ester functions affording the diacid analogues. This modification was expected to induce the loss of the thermosensitive properties in favor of flocculation properties.

This paper deals with the synthesis and the study of the sorption properties of hydrolyzed carbamoylmethylphosphonate *hP*(CPAAm6C). In particular, the study was first dedicated to the sorption of gadolinium as a function of various parameters such as the amount of Gd(III) and *hP*(CPAAm6C), pH, and ionic strength. The gadolinium element was chosen in this study as a surrogate of all lanthanide since it is located in the middle of the series. Then, the understanding of the mechanism of ionic exchange/coordination (from sorption experiments and infrared characterization) was investigated. Finally, the evaluation of the selectivity properties of *hP*(CPAAm6C) regarding to gadolinium in Gd(III)/Ni(II) multicomponent solutions modeling recycling was performed.

1. Experimental

1.1. Materials

1.1.1. Chemical products

Synthesis of hydrolyzed *hP*(CPAAm6C), bromotrimethylsilane (TMSBr) ((CH₃)₃SiBr, Aldrich, 97%), sodium hydroxide (NaOH, Fisher Scientific) were used as received. P(CPAAm6C) used in this work was synthesized according to the procedure detailed in a previous paper.[46] Dichloromethane and methanol were purchased from Aldrich and were used without any further purification.

For sorption experiments, stock metal solutions were prepared with a final concentration of 0.5 mol.L⁻¹ by dissolving nitrate salts of the given elements in deionized water. Gadolinium(III) nitrate hexahydrate (Gd(NO₃)₃·6H₂O, Aldrich, metal basis trace, 99.99%), nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O, Aldrich, metal basis trace, 99.999%) and sodium nitrate (NaNO₃, Aldrich, metal basis trace, 99%) salts were used as received. Each concentration was checked by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES).

1.2. Analysis and characterization

Bruker Advance DRX 300 (300MHz) was used to record ¹H NMR spectra with D₂O as deuterated solvent purchased from Eurisotop. Chemicals shifts were referenced to the corresponding hydrogenated solvent residual peak at 4.79 ppm for D₂O. Infrared spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer with an ATR sampling apparatus. Energy Dispersive X-Ray spectroscopy (EDX) analysis were performed with a FEI Inspect S50 Scanning Electron Microscope equipped with a Bruker nano Xflash detector 5010.

hP(CPAAm6C) (500 mg) was dissolved in water (50 mL). Titration of the resulting solution was achieved using a 0.1 N NaOH solution. pH values were plotted as a function of the volume of NaOH and pK_a values were determined at the half equivalence point for each titration curve.

The concentrations of metals were determined by ICP-OES with a SPECTRO ARCOS ICP spectrometer. The spectrometer was calibrated with 0; 0.5; 1; 5; 10 and 15 mg.L⁻¹ standard solutions (prepared by dilution of 1000 mg.L⁻¹ commercial standards of Gd and Ni (SCP Science, PlasmaCAL)).

1.3. Synthesis of *hP*(CPAAm6C) polymeric sorbent

Trimethylsilylbromide (TMSBr) (3.6 mL, 26.5 mmol) was added to a solution of poly(diethyl-6-(acrylamido)hexylcarbamoyl-methylphosphonate) (P(CPAAm6C)) (2.06 g, 5.74 mmol, 34600 g.mol⁻¹, $\bar{D} = 3.7$) in anhydrous dichloromethane (40 mL). After stirring for 3 hours at room temperature, the mixture was concentrated under reduced pressure to decrease the volume by about half. Methanol (100 mL) was added and the mixture was stirred for 4 hours at room temperature. Finally, the solvents and residues were fully evaporated and the powder was dried under vacuum.

¹H NMR (D₂O, 300MHz) δ (ppm): 1.16-1.57 (m, 4H, -CH₂-), 2.72-2.89 (m, 2H CO-CH₂-PO), 3.00-3.24 (m, 4H, NH-CH₂-).

1.4. Methodology for sorption studies

1.4.1 Sorption using dialysis methods

Sorption experiments were carried out using a dialysis tubular membrane as described in previous papers.[45], [47] 2kDa membrane cut-off was chosen to keep the polymer solution in the membrane tube which was dipped in cation solutions (see Supplementary Material). The temperature was controlled by a 6L Fisher Bioblock Scientific Cryothermostated bath. The cation solution was stirred during the sorption experiment by magnetic stirring. The “dialysis method” was selected for sorption isotherms in order to decouple sorption and separation phenomena and thus to overcome the polarization phenomena generally observed near the filtration processes. Concentration of cations was determined in bulk solution to overcome the pollution of the ICP-OES plasma by the organic polymer. When thermodynamic equilibrium was reached, the concentration of free ions in dialysis were considered to equal the concentration in the bulk, *i.e.* $C_{e, \text{bulk}} = C_{e, \text{dial}}$. The initial concentration of cation C_0 was considered in the total volume of the system and was calculated from equation 1:

$$C_0 = \frac{C_{bulk} \times V_{bulk}}{V_{bulk} + V_{dial}} \quad (1)$$

where C_{bulk} and V_{bulk} are the concentration and volume of the bulk solution (out of dialysis), respectively. V_{dial} is the volume of dialysis membrane containing the polymer solution.

1.4.2. Sorption kinetics

Four experiments were performed to study the kinetics and three samples of 1 mL were collected to keep the volume change negligible (max 3%) for each series of experiments. The sorption capacity at a given time t (Q_t , expressed in mmol.g^{-1}) was then calculated from the mass balance (equation (2)) where C_t (mmol.L^{-1}) is the elemental concentration of metal at the given time t (hours), V (L), C_0 (mmol.L^{-1}) and m (g) are the volume, the initial elemental concentration and the mass of P(CPAAm6C), respectively.

$$Q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

1.4.3. Sorption equilibrium experiments

Sorption equilibrium was studied by varying either the metal concentration for a given mass (or concentration) of polymer in the dialysis membrane or the mass of *h*P(CPAAm6C) for a constant metal concentration in the bulk. The effects the pH and ionic strength were investigated by addition of nitric acid and sodium nitrate solutions, respectively. The influence of the temperature was studied between 10 and 40 °C. After 24 hours of stirring (optimized from kinetic experiments), the concentration of metals in solution at equilibrium, C_e (mmol.L^{-1}) was measured and the sorption capacity at equilibrium Q_e (mmol.g^{-1}) was determined from the mass balance (Eq. 3).

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (3)$$

where C_0 (mmol.L^{-1}) is the initial concentration of the metal, m (g) is the mass of polymer and V (L) is the total volume of solution.

Sorption isotherms were described by the Langmuir and Freundlich equations (Eq. 4 and 5).

$$Q_e = Q_{max}^L \cdot \frac{K_L C_e}{(1 + K_L C_e)} \quad (4)$$

$$Q_e = K_F C_e^{\frac{1}{n}} \quad (5)$$

where Q_{max}^L is the maximum capacity (mmol.g⁻¹) determined from Langmuir model, K_L is the Langmuir constant related to the energy of sorption (L.mmol⁻¹), K_F (mmol^{1-1/n} g⁻¹ L^{1/n}) and n (dimensionless) are the Freundlich constants.

Each parameter was determined by linear regression from linearized Langmuir and Freundlich models described by Eq 6 and 7, respectively.

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_{max}^L} + \frac{1}{Q_{max}^L} C_e \quad (6)$$

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

1.4.4. Selective sorption studies

Sorption experiments were performed with solutions containing various initial amounts of targeted cations $\sum_{initial} C/cmp$ with mixtures containing equimolar quantities of Gd and Ni. Solutions were prepared with an initial pH value adjusted to 1 by addition of nitric acid (HNO₃). In order to quantify the separation efficiency between Gd and Ni from the binary systems, the separation factor $\alpha_{Gd/Ni}$ can be calculated from the ratio of the distribution constant K_d ($K_d = Q_e/C_e$) equation 8:

$$\alpha_{Gd/Ni} = \frac{K_d(Gd)}{K_d(Ni)} = \frac{Q_e(Gd) \cdot C_e(Ni)}{C_e(Gd) \cdot Q_e(Ni)} \quad (8)$$

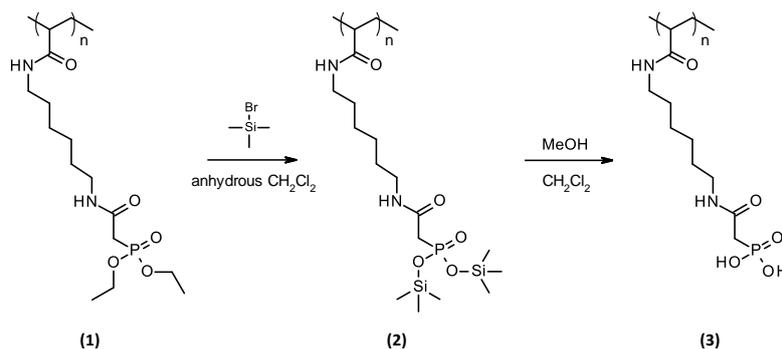
Values greater than 1 imply that gadolinium is more strongly sorbed compared to nickel. Also, the higher the $\alpha_{Gd/Ni}$ value, the better the efficiency of Gd (selective) sorption.

2. Results and discussion

2.1. Synthesis and characterization of the poly(diethyl-6-(acrylamido)hexylcarbamoyl-methylphosphonic diacid) (hP(CPAAm6C))

2.1.1. Synthesis of *hP*(CPAAm6C)

Synthesis of the poly(diethyl-6-(acrylamido)hexylcarbamoyl-methylphosphonic diacid) was achieved by hydrolysis of the phosphonated ester groups in two steps from P(CPAAm6C) **(1)** (Scheme 1) using the method described in the literature for the hydrolysis of simple phosphonate-based polyacrylate as P(MAPC1).[49]–[51]



Scheme 1 Reactional pathway describing the synthesis of the poly(diethyl-6-(acrylamido)hexylcarbamoylmethyl-phosphonic diacid) (*hP*(CPAAm6C)).

P(CPAAm6C) was synthesized according to the procedure detailed on the previous work.[46]. Its characterization by SEC using triple detection allowed to determine the molecular weight ($M_n = 36400 \text{ g}\cdot\text{mol}^{-1}$) and the dispersity ($D = 3.77$) (see Supplementary Material).

The first step of the synthesis dealt with the formation of a disilylated derivative (compound **(2)**) by two successive attacks of the oxygen of the phosphonated ester function on the bromotrimethylsilane (TMSBr). To perform this step, the bromotrimethylsilane (TMSBr) addition in excess in DCM was chosen because it was easy to remove by distillation and it allowed the solubilization of the P(CPAAm6C). To avoid the reaction between water and TMSBr, the first step was performed in an anhydrous DCM. After three hours of reaction at room temperature, the mixture was concentrated by distillation of half DCM and the derivative **(2)** was kept in anhydrous environment to keep it stable. Then, the second step consisted in the hydrolysis of the disilylated derivative by addition of a large

excess of methanol. After hydrolysis, all the solvents and volatile residues were removed by reduced pressure distillation and dried in vacuum.

2.1.2. Structural characterization

Chemical structure of *hP*(CPAAm6C) (**3**) was confirmed by ^1H NMR in deuterated water and infrared spectroscopy characterizations. The comparison between ^1H NMR spectra of *hP*(CPAAm6C) and non-hydrolyzed P(CPAAm6C) (Fig. 1) showed the disappearance of the triplet (k) and quadruplet (j) located at 1.34 and 4.18 ppm, corresponding to the resonance signal of the protons of $-\text{CH}_3$ and $-\text{CH}_2-$ associated to the phosphonated ester groups. Protons of the methylene in the α -position (h,i) shifted from 3.05-2.97 ppm for the diethylphosphonate form to 2.85-2.69 ppm in the resulting phosphonic diacid form. Other chemical shifts remained unchanged.

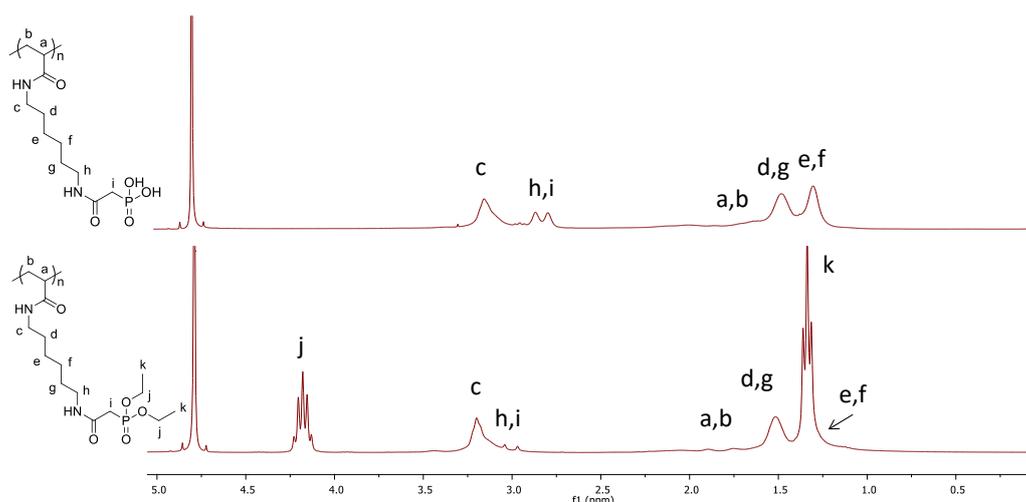


Fig. 1 ^1H NMR spectra in deuterium oxide (D_2O) of: (below) the poly(diethyl-6-(acrylamido)hexylcarbamoylmethyl-phosphonate) (P(CPAAm6C)) (**1**) and (top) the resulting poly(diethyl-6-(acrylamido)hexylcarbamoylmethylphosphonic diacid) *hP*(CPAAm6C) (**3**).

IR spectroscopy spectra shown in Fig. 2 highlight changes on the P=O and P-O stretching. The vibration associated to the symmetric stretching mode of P-O edge is shifted from 960 cm^{-1} (intense band) to 929 cm^{-1} (more intense band) whereas that associated to the antisymmetric stretching mode is shifted from 1019 cm^{-1} to a weaker band at 994 cm^{-1} .

The large band located between 2499 and 3487 cm^{-1} was assigned to O-H edge and confirmed the modification of the P-O-CH₂-CH₃ group onto the P-O-H group.[52] Indeed in the case of one P-OH with one P=O group as in mono-phosphonic acid, an additional broad band should have been observed at 1700-1640 cm^{-1} . Here the absence of this absorption band proved that the phosphonic diacid form was obtained.[52] The disappearance of the band assigned to the P=O bond and located at 1243 cm^{-1} is related to the existence of a charge delocalization in phosphonic diacid form. The shifts of the band assigned to C=O from 1643 to 1623 cm^{-1} and the shifts observed for methylene in α -position on ¹H NMR spectra are due to the increase of the electron density in the phosphonic diacid form compared to diester form. To conclude, ¹H NMR and IR analysis confirm that the hydrolysis of P(CPAAm6C) was complete, which led to the formation of *hP*(CPAAm6C).

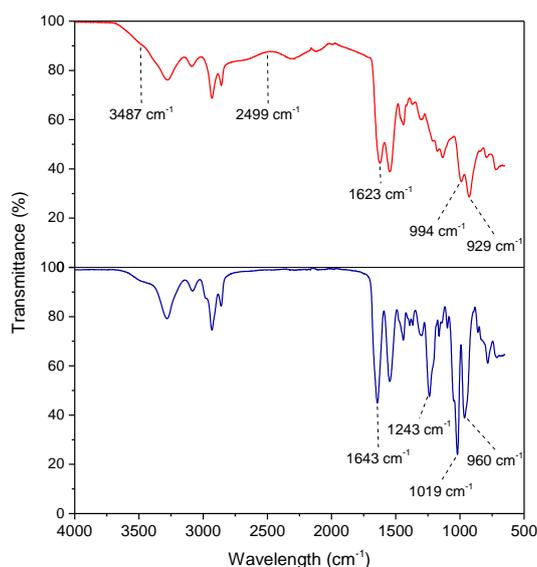


Fig. 2 Infrared spectra of: (bottom) dried P(CPAAm6C) (blue line), and (top) *hP*(CPAAm6C) (red line).

2.1.3. pK_a determination

Titration of *hP*(CPAAm6C) allowed the establishment of the speciation diagram and of the determination of dissociation constants pK_{a1} and pK_{a2} associated to *hcmp* (Fig. 3) The pK_{a1} and pK_{a2} values were found to be equal to 2.2 and 7.6, respectively. For pH < 1, *hcmp* was thus mainly found in the fully protonated form (95%) whereas at pH = 2.2, the two forms (fully and monoprotonated forms)

were found in equimolar proportions. At pH = 7.6, equimolar proportions of monoprotinated and totally dissociated forms were obtained. The pK_{a1} and pK_{a2} values, determined for *hP*(CPAAm6C), were slightly lower than that determined for polymer containing simple phosphonic diacid function [49], [53] which shows that the amide function of *hcmp* favors the dissociation of the phosphonic diacid.

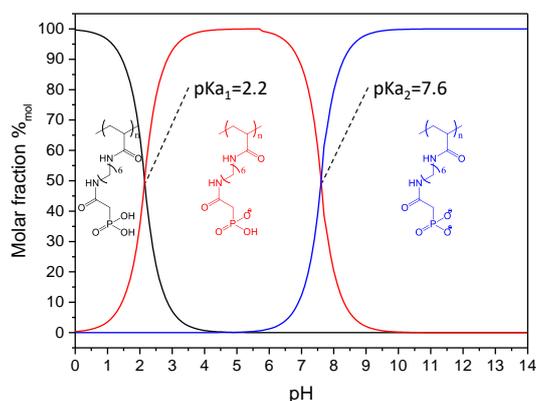


Fig. 3 Speciation diagram of the different species of carbamoylmethylphosphonic acid forms vs the pH.

2.2. Sorption properties study

2.2.1. Determination of equilibrium time

The time needed to reach the equilibrium associated to sorption experiments by dialysis method was determined by monitoring the amount of cations sorbed *versus* time. The kinetic curve (Fig. S3) showed that equilibrium was reached after only 12 hours and led to a sorption capacity of 1.5 mmol of Gd ion per gram of *hP*(CPAAm6C). It is important to note this time is not only representative of the complexation of gadolinium on *hcmp* since it cumulates the complexation and dialysis equilibria. Hence, all sorption experiments were carried out during 24 hours in order to ensure that the sorption equilibrium was reached.

2.2.2. Sorption isotherm of Gd(III)

A first investigation aimed to determining the maximum experimental sorption capacity $Q_{max}(Gd)$ in acidic conditions defined in this work as the sorption capacity reached at the plateau of the sorption isotherm at 25 °C and pH = 1 (Fig. 4). This latter was chosen to study the sorption in acidic media and to prevent any potential precipitation of gadolinium hydroxide. The sorption isotherm (Fig. 4A) can be divided in two parts. First, the amount of Gd(III) trapped

by the *hP*(CPAAm6C) slowly increased when increasing the free gadolinium equilibrium concentration $C_e(\text{Gd})$ up to 3.5 mmol.L^{-1} then tended toward a first inflection corresponding to a sorption capacity about 0.65 mmol.g^{-1} . In the second part observed for $C_e(\text{Gd}) > 3.5 \text{ mmol.L}^{-1}$, the sorption capacity of gadolinium increased again to tend experimentally towards the $Q_{\text{max}}(\text{Gd})$ value about 1.5 mmol.g^{-1} . The presence of these two parts on the isotherm highlighted that there is not only one mechanism implied during the gadolinium sorption.

In order to better understand the sorption mechanism from experimental isotherm, Freundlich and Langmuir sorption models were applied. Due to the particular isotherm shape, two assumptions were considered. The first was to neglect the first part of the isotherm to focalize on the average curve and the plateau. The second assumption was to consider that the ions were adsorbed on a surface which was related to the molecular area of complexing groups on the polymer chain.[54] Linearized models clearly showed that the empirical Freundlich model could not be used over the whole concentrations range ($R^2 < 0.8$, Fig 4B). On the contrary, the Langmuir linearization led to an acceptable adjustment with correlation coefficient R^2 of 0.9895. Associated Q_{max}^L and K_L parameters were found to $1.72 \pm 0.07 \text{ mmol.g}^{-1}$ and $0.302 \pm 0.063 \text{ L.mmol}^{-1}$, respectively. It was thus possible to assume that only polymer-cation interactions occurred, assimilated to the monolayer coverage hypothesis from the Langmuir theory.

Associated with both parts of the isotherm different chemical mechanisms of Gd-sorption could be assumed for low and high concentrations of Gd. Indeed, at $\text{pH}=1$, the carbamoylphosphonic diprotonated form is favored (95%) and it could imply different sorption mechanisms: coordination (with C=O and P=O functions) and/or ion exchange (with P-O-H functions). The sorption of Gd(III) by ion exchange would imply the release of protons which should result in the modification of the pH in the solution, and thus in the Gd speciation (Gd^{3+} and $\text{Gd}(\text{NO}_3)_2^{2+}$). The study of both chemical mechanisms depending on the Gd and *hcmp* ratio will be described in more details later.

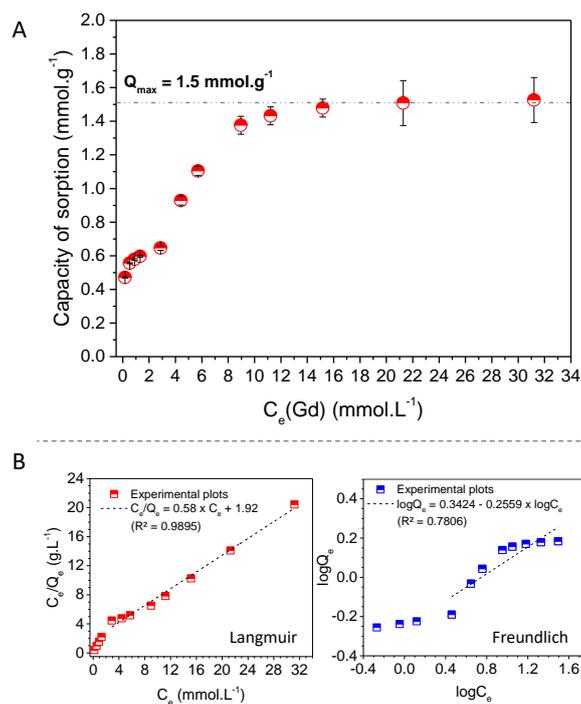


Fig. 4 A) Sorption isotherm of Gd obtained for 50 mg of *hP*(CPAAm6C) at pH = 1 and T = 25 °C. B) Linearization with Langmuir (left) and Freundlich (right) equations

Table 1 further evidences that the *hP*(CPAAm6C) exhibited higher sorption capacity for lanthanides compared with other solid sorbent or the hydrosoluble P(CPAAm6C).

Table 1 Comparison of gadolinium sorption capacity of different solid sorbents and hydrosoluble polymers at acidic pH.

Materials	Targeted	Experimental conditions		Maximum capacity (mmol.g ⁻¹)	Ref.
		pH	T (°C)		
Diglycol amic acid functionalized silica	Gd(III)	1	25	0.14	[38]
Silica-based bis(2-ethylhexyl)phosphoric acid impregnated	Gd(III)	1	25	0.32	[55]
Ion imprinted mesoporous silica	Dy(III)	2	25	0.137	[56]

(N-methyl-N-phenyl-1,10-phenanthroline-2-carboxamide) functionalized silica	Eu(III)	4	25	0.83	[57]
ZSM-5 zeolite	Eu(III)	3.6	25	0.016	[27]
Hydrosoluble and thermosensible carbamoylmethylphosphonate polymer	Gd(III)	1	25	0.60	[47]
Hydrosoluble carbamoylmethylphosphonic acid polymer	Gd(III)	1	25	1.5	Present work

2.3. Influence of operating conditions on Gd(III) sorption

2.3.1. *hP*(CPAAm6C) concentration influence

The sorption ratio of Gd(III) was optimized through the modifications of various parameters including the concentration of polymer, the ionic strength, and the pH of the solution. The variations of the sorption capacity $Q_e(\text{Gd})$ (expressed in $\text{mmol}\cdot\text{g}^{-1}$, red round) and of corresponding gadolinium sorption efficiency $\eta(\text{Gd})$ (expressed in %, blue square) as a function of the polymer concentration at $\text{pH} = 1$ are shown in Fig. 5.

The sorption capacity decreased from 1.9 to 0.8 $\text{mmol}\cdot\text{g}^{-1}$ when increasing the concentration of polymer in the dialysis tube from 0.25 to 15 $\text{g}\cdot\text{L}^{-1}$. The increase of the polymer concentration implied closer polymer chains promoting hydrogen interactions between protons and oxygen atoms of amides and phosphonic acids and reducing the gadolinium-*hcmp* interactions. Maximum gadolinium sorption rate of 87 % was observed for a polymer concentration of *hP*(CPAAm6C) equal to 15 $\text{g}\cdot\text{L}^{-1}$. This plateau highlighted that the complexing functions became less and less accessible because of polymer-polymer interactions in the polymer solution.

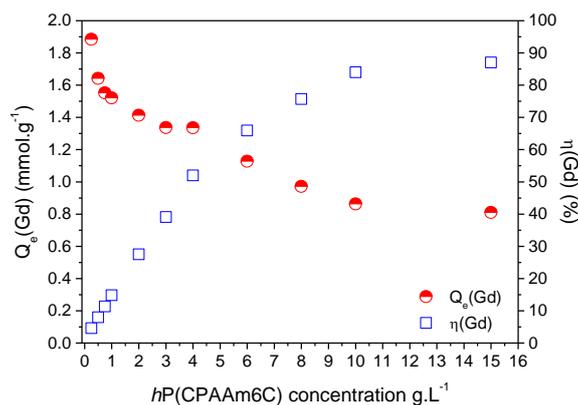


Fig. 5 Variation of Gd sorption ratio vs the concentration of **hP**(CPAAm6C) with $C_0(\text{Gd}) = 1.03 \times 10^{-3} \text{ mol.L}^{-1}$, $V = 100 \text{ mL}$ and $T = 25 \text{ }^\circ\text{C}$.

2.3.2. Ionic strength influence

The effect of the ionic strength (I) on the sorption of Gd was investigated by adding sodium nitrate to the initial solution which already contained nitrate ions (consequently to the introduction of gadolinium nitrate solution and of nitric acid). The amount of sorbed Gd increased from 0.4 mmol.g^{-1} to a maximum value equal to 1.4 mmol.g^{-1} when increasing the ionic strength from 0.1 to 0.3 mol.L^{-1} . Then, for an ionic strength ranging from 0.3 to 1.1 mol.L^{-1} , the sorption capacity decreased to 0.75 mmol.g^{-1} (Fig. 6). The increase of the ionic strength in the range of $0.1 - 0.3 \text{ mol.L}^{-1}$ (corresponding to $0 - 0.2 \text{ mol.L}^{-1}$ of NaNO_3) led to some changes in the Gd speciation (see Electronic Supplementary Information), especially to the decrease of Gd^{3+} in favor to $\text{Gd}(\text{NO}_3)^{2+}$ ion. The decrease of the charge of gadolinium species would allow the phosphonic diacid to sorb more $\text{Gd}(\text{NO}_3)^{2+}$ than Gd^{3+} by ion exchange and therefore would increase the sorption capacity. On the other hand, the decrease of the sorption ratio between 0.3 mol.L^{-1} and 1.1 mol.L^{-1} ionic strength could be related to the loss of solubility of the polymer as NaNO_3 concentration increases. Fig. 7 shows that the **hP**(CPAAm6C) is soluble until the NaNO_3 concentration reaches 1 mol.L^{-1} ($I = 1.1$). Above this concentration, the sorbent solution becomes cloudy, which traduces the presence of a high concentration of insoluble aggregates. However, above 2.0 mol.L^{-1} ($I = 2.1$) the polymer was found to be totally insoluble and was

precipitating. Due to a partial or total insolubility, the sorption sites became less accessible and so the sorption capacity should decrease.

When ionic strength ranged between 0.3 and 1.1 mol.L⁻¹ solution were clear but $Q_e(\text{Gd})$ decreased (Fig. 6). The decrease of $Q_e(\text{Gd})$ could be explained by the partial solubility of the polymer *ie.* the chains formed soluble aggregates and induced a partial accessibility of the complexing sites.

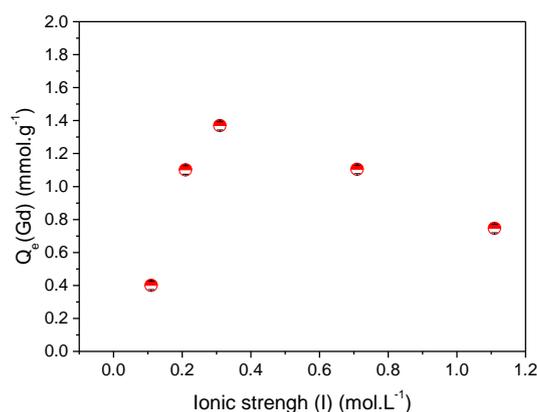


Fig. 6 Variation of the Gd sorption capacity as a function of the ionic strength for 50 mg of *hP*(CPAAm6C), $[\text{Gd}(\text{NO}_3)_3] = 0.013 \text{ mol.L}^{-1}$, $V = 100 \text{ mL}$, $\text{pH} = 1$ and $T = 25 \text{ }^\circ\text{C}$.



Fig. 7 Solutions of *hPCPAAm6C* obtained for various concentrations of NaNO_3 , for $C_{hP(\text{CPAAm6C})} = 5 \text{ g.L}^{-1}$ and $\text{pH} = 1$.

2.3.3. pH influence

Due to the use of carbamoylmethylphosphonic diacid function (showing two characteristic dissociation constants pK_{a1} and pK_{a2}), the sorption properties were expected to depend on the initial pH of the solution. As already mentioned, at $\text{pH} = 1$, 95% of *hcmp* groups were fully protonated. The nature of the function (deprotonated, monoprotated or fully protonated

form) may have a significant influence on the sorption mechanism either by coordination or ion exchange mode. Additionally, the competition between protonation and ion exchange could affect the sorption capabilities of the polymer. The sorption capacity at the equilibrium is represented in Fig. 8 as a function of the pH (between 1 and 3.25, which was chosen according to the pH used during dissolution processes). It exhibits two trends. First, the amount of trapped gadolinium decreased from 2.1 to 1.1 mmol.g⁻¹ when decreasing the pH value from 3.5 to 2. This trend was associated to the first acidity constant (pK_{a1} = 2.15). Indeed, the fraction of the mono-dissociated form of the *hcmp* groups (Fig. 3) was lower as the pH value decreased. Simultaneously, the sorption of Gd(III) ions by ion exchange decreased. For pH < 2, di-protonated species predominated according to the speciation of diphosphonic acid. A small increase of the sorption capacity from 1.1 to 1.25 mmol.g⁻¹ was observed, which may be connected to more Gd-*hcmp* interactions by coordination mode due to the increase of the ionic strength (thanks to the higher proton and nitrate ions concentrations). Gd ions were thus complexed by C=O or P=O functions of the ligand.

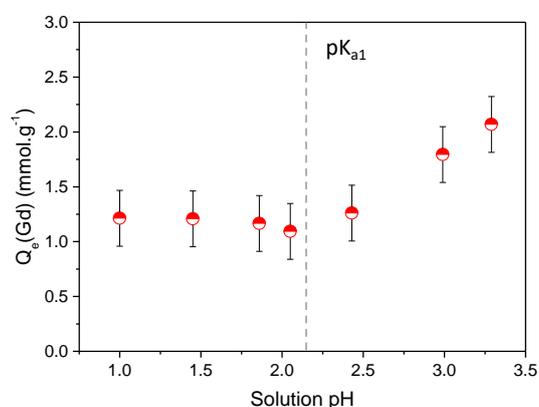


Fig. 8 Variation of the Gd sorption capacity vs the pH of the solution obtained in nitric media for 50 mg of *hP*(CPAAm6C), C₀(Gd) = 4.56×10⁻³ mol.L⁻¹, V = 100 mL and T = 25 °C.

2.4. Study of the complexation mechanism

As previously described, two trends were observed on the Gd-sorption isotherm. It led to the hypothesis that different sorption mechanisms may be involved for low and high Gd concentrations in solution (Fig. 5). In order to confirm this assumption, different approaches were used to determine whether the sorption mechanism between carbamylmethylphosphonic diacid groups and Gd ions was mainly driven by coordination and/or by ion exchange. It required the study of the number of Gd sorbed per *hcmp* sites, the determination of the number of protons released and infrared study. Because the goal was to highlight the different types of mechanisms and since the variation of proton concentration was difficult to evidence for initial pH value of 1 (very low pH variation), the experiments were performed at pH = 6 (mono protonated form of the phosphonic acid groups favored).

2.4.1. Determination of the maximum stoichiometry of complexation

The first step of the study was to determine the maximum *hcmp* groups involved in the complexation mechanism. The protocol used to evaluate the sorption of Gd(III) (expressed in mol of Gd per mol of *hcmp*) vs. Gd/*hcmp* initial ratio (Fig 9) consisted in keeping the Gd concentration constant and equal to 1×10^{-3} mol.L⁻¹ for various *hP*(CPAAm6C) amounts (from 0.25 to 10 g.L⁻¹). The comparison of the Gd_{sorbed}/*hcmp* vs the Gd_{initial}/*hcmp* ratios allowed the determination of a maximum stoichiometry around Gd/*hcmp* = 0.5 when the plateau was reached. As a consequence, it was expected that complexation of gadolinium involved a maximum of one cation for two complexing *hcmp* sites.

Phosphonic acid could interact with cations either by electrostatic interaction (ion exchange) or by electronic interaction (coordination).[45] Because of the multidentate character and the presence of labile protons and electro donor functions, the *hcmp* group could also interact through two ways: (i) acidic protons of the phosphonic diacid could be exchanged with the gadolinium ion (ion exchange mechanism), or (ii) exceeding electron of C=O and P=O could coordinate the gadolinium which is deficient in electron (solvation mechanism).

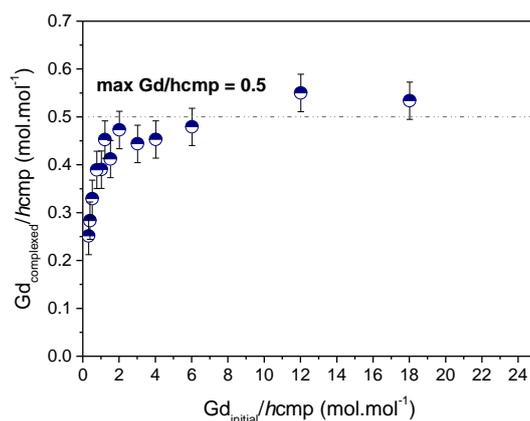


Fig. 9 Variation of the amount of Gd sorbed per mol of hcmp group as a function of the initial ratio obtained for $C_0(\text{Gd}) = 1 \times 10^{-3} \text{ mol.L}^{-1}$ and $\text{pH}_0 = 6$.

2.4.2. Characterization of the ion exchange mechanism through protons release

It was shown when drawing the isotherm that the sorption capacity increased when decreasing the initial pH from 2 to 1 due to protons release, which could affect the mechanism through a change of the gadolinium speciation. In order to assume this hypothesis and to approach the ion exchange mechanism, the $\text{H}^+/\text{Gd}_{\text{sorbed}}$ and the pH value at equilibrium (pH_{eq}) were studied for various initial Gd/hcmp mole ratios. With this objective, the starting gadolinium constant, $C_0(\text{Gd})$, was kept constant and the mass of **hP**(CPAAm6C) was varying between 2.5 and 100 mg corresponding to Gd/hcmp initial ratios ranging from 12 to 0.3 (Table 2). The pH was measured in the bulk solution (out of dialysis) to follow the proton release at the equilibrium from the mass balance. The pH_0 value corresponded to the pH value obtained without any polymer in the dialysis tube at the equilibrium. It represented the pH value in the absence of ion exchange. This method was chosen to study the impact of the proton release on the evolution of ion-exchange mechanism. The obtained $\text{Gd}_{\text{sorbed}}/\text{hcmp}$ mole ratio was varying from 0.25 to 0.49 for initial Gd/hcmp mole ratio ranging from 0.3 to 12, respectively (Table 2). During the sorption process, it appeared that the pH decreased from 6 (pH_0) to a pH_{eq} value between 2.70 to 3.95. pH_{eq} value depended on the $\text{Gd}_{\text{sorbed}}/\text{hcmp}$ mole ratio, which gave information on the amount of proton released. Also, it appeared that the pH_{eq} increased from 2.70 to 3.95 when the $\text{Gd}_{\text{sorbed}}/\text{hcmp}$ mole ratio increased from 0.25 to 0.49.

Focusing on the $H^+_{\text{released}}/Gd(III)_{\text{sorbed}}$ mole ratio, the results obtained showed that the number of protons exchanged increased from 2.5 to 3 when increasing the $Gd_{\text{sorbed}}/hcmp$ mole ratio from 0.25 to 0.39. When the $Gd_{\text{sorbed}}/hcmp$ mole ratio reached approximately the maximum stoichiometry (*i.e.* 0.5 mol.mol⁻¹), the corresponding number of protons released by *hcmp* was about 3 per gadolinium and the pH became higher than 3. These results clearly showed different ion-exchange mechanisms depending on the pH obtained at equilibrium. Above $pH_{\text{eq}} = 2.96$, the number of exchanged proton per sorbed gadolinium ranged from 2.5 and 3.0 showing the simultaneous sorption of trivalent Gd^{3+} and divalent $Gd(NO_3)_2^{2+}$ species. For higher pH_{eq} values, 3 protons were exchanged per gadolinium atom, showing the sorption of only Gd^{3+} .

Table. 2 Release of H^+ vs. Gd sorption for various experiments with $C_0(Gd) = 1 \times 10^{-3}$ mol.L⁻¹ and $pH_0 = 6$

<i>hP</i> (CPAAm6C) mass (mg)	$\frac{Gd_0}{hcmp}$	$\frac{Gd(III)_{\text{sorbed}}}{hcmp}$	pH_{eq}	$\frac{H^+_{\text{released}}}{Gd(III)_{\text{sorbed}}}$
100	0.3	0.25	2.70	2.5
60	0.5	0.33	2.78	2.7
30	1	0.39	2.96	3.0
15	2	0.47	3.19	2.9
7.5	4	0.45	3.51	3.0
2.5	12	0.49	3.95	3.1

2.4.3. Characterization of the coordination mechanism

In order to highlight the coordination mode, the Gd-*hP*(CPAAm6C) precipitates obtained after reaching the sorption equilibrium were filtered, dried then finally characterized by infrared spectroscopy. FTIR spectra are represented in Fig 10 for different $Gd/hcmp$ molar ratio. As observed for the esterified group,[47] the infrared spectra for different $Gd_{\text{sorbed}}/hcmp$ mole ratios showed a shift of the carbonyl bond of the amide (C=O) when increasing the $Gd_{\text{sorbed}}/hcmp$ mole ratios. The band corresponding to the C=O edge of *hcmp* shifted from 1623 cm⁻¹ to 1611 cm⁻¹ when $Gd_{\text{sorbed}}/hcmp$ increased from 0 to 0.48. Additionally, the band assigned to the N-H vibrations (located at 1546 cm⁻¹) disappeared as the sorption capacity of Gd

increased. The progressive shift of the C=O bands showed that the amide function was involved in the complexation mechanism through the metal coordination.

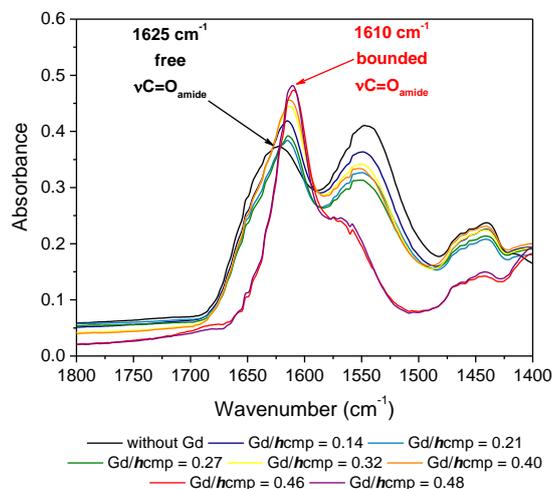
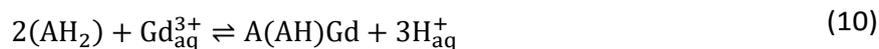
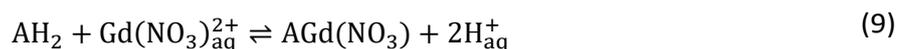


Fig. 10 Normalized IR spectrum of *hP*(CPAAm6C) with different Gd/*hcmp* ratios loaded

2.4.4. Proposed mechanism of gadolinium sorption

By considering all the information obtained, it was possible to propose mechanisms associated to the sorption of Gd on *hP*(CPAAm6C) (Fig. 11). The study of ion exchange mechanism showed that the pH was modified during the sorption process by the release of protons. The number of protons exchanged was found between 2 and 3, which modified the initial pH value from 6 to 2.70 - 3.95 when equilibrium was reached. For $1 < \text{pH} < 3$, two forms of gadolinium ions, $\text{Gd}(\text{NO}_3)_2^{2+}$ and Gd^{3+} , coexisted in aqueous solution (see Supplementary Material). Therefore, two balances had to be considered for the overall description of the sorption of gadolinium by ion exchange (equations (9) and (10)) in which 2 and 3 protons were salted out).



where AH_2 , AH^- and A^{2-} correspond to the diprotonated, monoprotonated and fully deprotonated forms, respectively.

For $C_0(\text{Gd}) = 1 \times 10^{-3} \text{ mol.L}^{-1}$, various amounts of *hP*(CPAAm6C) and pH_{eq} ranging from 2.70 and 2.9, the number of released protons was between 2.5 and 3 demonstrating at these pH values, there is coexistence of $\text{Gd}(\text{NO}_3)_2^{2+}$ and Gd^{3+} sorption. As shown in Fig. 11, $\text{Gd}(\text{NO}_3)_2^{2+}$ can be exchanged by two protons coming from one or two *hcmp* groups whereas Gd^{3+} can be exchanged by 3 protons coming from two *hcmp* groups. These exchange ratio corresponded to the maximum stoichiometry observed in Fig. 9. For $\text{pH}_{\text{eq}} > 3$, 3 protons were always exchanged per gadolinium cation Gd^{3+} which was the lonely species in solution. Then, only one kind of ion-exchange mechanism could be considered in these conditions. Also, in all cases, it was shown that ion exchange was associate with Gd complexation mechanism by coordination with C=O groups (Fig. 11).

As it was shown previously (Part 2.3.3.), the pH of the solution drastically affected the sorption capacity for constant gadolinium and polymer amounts. A link with the dissociation constant of the polymer can confirm the sorption mechanism by information on competition between protonation of *hcmp* groups and sorption by ion-exchange. For pH values ranging from 2.5 to 4, the monoprotonated form of *hcmp* was favored and for $\text{pH} < 2.15$, the di-protonated form of *hcmp* was favored. The two acidic equilibria (see 2.1.3.) could be in competition with the ion exchange mechanism, thus explaining the decrease of sorption capacity with the pH.

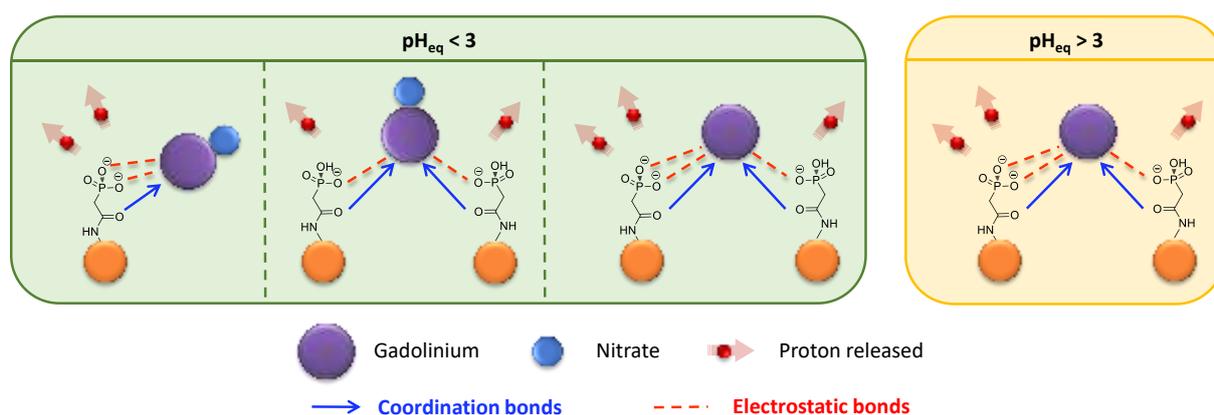


Fig. 11 Proposed mechanism describing the sorption of gadolinium by *hP*(CPAAm6C) in the presence of Gd^{3+} and $\text{Gd}(\text{NO}_3)_2^{2+}$ species.

2.5. Sorption selectivity towards a Gd/Ni mixture

In previous works, because Ni is a transition metal which may be encountered in the recycling process of electronic compound, it was shown that the P(CPAAm6C) was selective for Gd in Gd/Ni mixtures. The modification of the phosphonated ester to phosphonic acids could change the selectivity and efficiency of the sorbent. In order to compare the selectivity between P(CPAAm6C) and *h*P(CPAAm6C), the affinity of the *h*cmp group for Gd cation was studied in the presence of Ni using an equimolar mixture of gadolinium and nickel. The global cationic concentration *C* was adjusted to reach a global *C/h*cmp ratio ranging from 0.6 to 24. As this global *C/h*cmp ratio took into account all the cationic species in solution, it will be called $\sum_{\text{initial}} C/h\text{cmp}$ thereafter.

The molar distribution (expressed in mol.%) of Gd(III) and Ni(II) ions loaded on the *h*P(CPAAm6C) when equilibrium was reached is reported in Fig. 12. Increasing the $\sum_{\text{initial}} C/h\text{cmp}$ value showed a modification of the cations distribution on the polymer. Indeed, the molar fraction of loaded gadolinium reached 83% for $\sum_{\text{initial}} C/h\text{cmp} = 0.6$, 88% for $\sum_{\text{initial}} C/h\text{cmp} = 1$ and about 93% for $\sum_{\text{initial}} C/h\text{cmp} = 4$ and 24. Simultaneously, the proportion of complexed Ni(II) decreased from 17% to 6% when increasing the $\sum_{\text{initial}} C/h\text{cmp}$ value. These results were similar to those observed for the sorption of Gd/Ni mixtures on carbamoylmethylphosphonate (cmp) group on the P(CPAAm6C)[47] and suggest that increasing the cations concentration in solution led to the increase of Gd(III) ratio loaded on the *h*cmp site. As for previous works, the *h*cmp group is a hard Lewis base (*i.e.* with a strong electron density) which preferentially complexes the hard Lewis acids such as lanthanide at the expense of lowest Lewis acid as nickel, as described in the Pearson's classification. [58]–[60]

To study the effect of hydrolysis on the selective separation of Gd from Gd-Ni mixtures, separation factor $\alpha_{\text{Gd/Ni}}$ were determined for *h*P(CPAAm6C) and compared to that obtained for P(CPAAm6C) (Fig. 12B).

In case of **hP**(CPAAM6C), separation factor increased from 12 to 68 when $\sum_{\text{initial}} C/\text{phosphonated group}$ increased from 0 to 4. Beyond an initial ratio of 4, $\alpha_{\text{Gd/Ni}}$ decreased to reach 18. Whatever the $\sum_{\text{initial}} C/\text{hcmp}$ range, the $\alpha_{\text{Gd/Ni}}$ values were much higher than 1, demonstrating a strong selectivity of **hP**(CPAAM6C) for Gd compared to Ni. The change observed at $\sum_{\text{initial}} C/\text{hcmp} = 4$ corresponded to **hP**(CPAAM6C) saturation, when no additional ion can be sorbed onto the the polymer (plateau being reached in the isotherm). Then, lower distribution coefficient of Gd ($K_d(\text{Gd})$) leads to the decrease of the separation factor $\alpha_{\text{Gd/Ni}}$. Thereby, among these four operating conditions, the best efficiency in terms of Gd/Ni separation was obtained for $\sum_{\text{initial}} C/\text{phosphonated group} = 4$.

In comparison, $\alpha_{\text{Gd/Ni}}$ values obtained for **P**(CPAAM6C) increased from 5 and 57 when $\sum_{\text{initial}} C/\text{phosphonated group}$ ranged between 0.33 and 19 and does not decreased in the range of study. Also, the **hcmp** group showed better selectivity than **cmp** for $\sum_{\text{initial}} C/\text{phosphonated group} < 4$ while for $\sum_{\text{initial}} C/\text{phosphonated group} > 4$, **cmp** group are associated to higher $\alpha_{\text{Gd/Ni}}$ values.

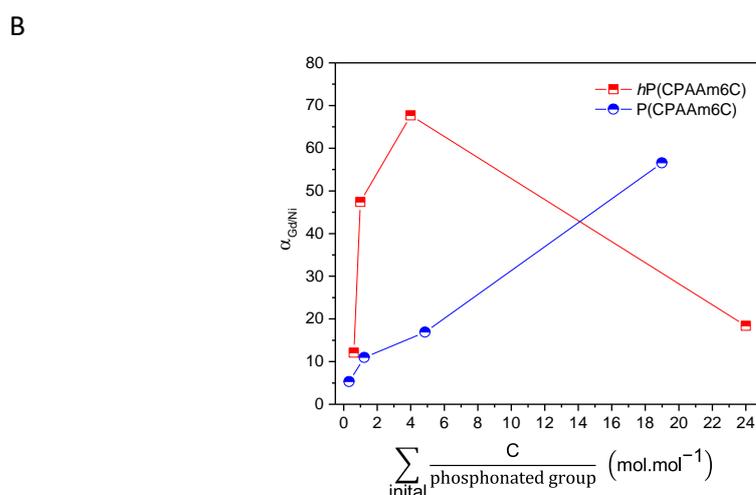
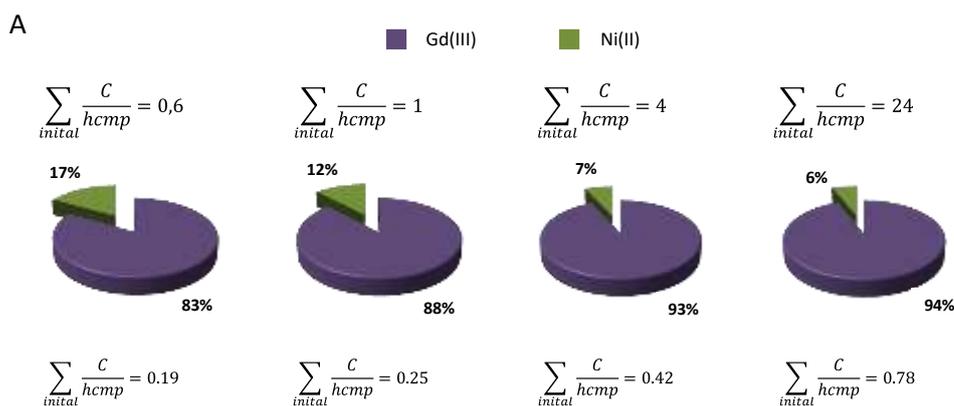


Fig. 12 A) Distribution of cations (Gd(III) and Ni(II)) sorbed on *hP*(CPAAm6C) for different initial $C^{n+}/hcmp$ ratios at 20 °C, 10 mL of 5 g.L⁻¹ of *hP*(CPAAm6C) immersed in 100 mL of cation solution, pH = 1 and [NaNO₃] = 0 mol.L⁻¹, starting from equimolar quantities of Gd and Ni. B) Comparison of separation factor between Gd/Ni cations $\alpha_{Gd/Ni}$ for sorption experiments with *hP*(CPAAm6C) and P(CPAAm6C) polymers.

2.6 Selective flocculation

In the presence of gadolinium, precipitation was observed during the sorption process. Graillot reported that strong flocculation occurred when phosphonic acid based thermosensitive polymer sorbed trivalent aluminium whereas in the presence of divalent cation such as Ni, Ca, or Cd, this flocculation was not observed.[61] This difference was attributed to the positive surface charge in the case of the polymer-Al and to Al species ability to bridge polymer chains. In order to study this property, some experiments were performed with gadolinium and nickel put separately and then mixed together. In this field, 10 mL of 5 g.L⁻¹ of *hP*(PCPAAm6C) solution was contacted with 10 mL of solution containing 0.1 mol.L⁻¹ of cations and then was vigorously stirred. The obtained mixtures at equilibrium

(Fig. 13 (a), (b) and (c)) revealed that the polymer precipitation occurred after sorption in presence of Gd (i.e. for Gd(III) and Gd(III)/Ni(II) mixtures whereas no precipitation was observed in the case of Ni(II) lonely). The obtained precipitates were filtered, dried and analyzed by energy dispersive X-ray spectroscopy (EDX) (Fig (d)) at low energy because the polymer was very sensitive to the electron beam despite the metallization performed with platinum. Although the EDX results were not quantitative due to the acquisition conditions, they showed the absence of nickel in the polymers precipitated from Gd/Ni mixtures.

Such results showed that in addition to its selective sorption property, *hP*(CPAAm6C) allowed the selective precipitation of gadolinium, which appears to be very important in the field of gadolinium separation. Indeed, after the selective sorption of gadolinium, it would possible to perform its recovery by using filtration step.

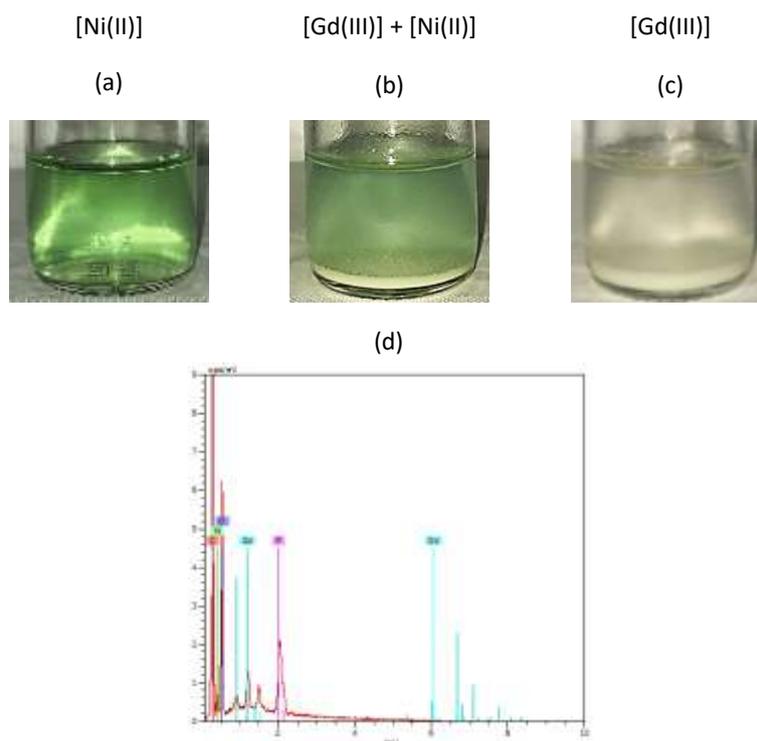


Fig. 13 Polymer solutions after sorption of (a) $[\text{Ni(II)}] = 0.05 \text{ mol.L}^{-1}$, (b) equimolar Gd/Ni mixture with $[\text{Gd(III)}] + [\text{Ni(II)}] 0.05 \text{ mol.L}^{-1}$ and (c) $[\text{Gd(III)}] = 0.05 \text{ mol.L}^{-1}$. ($C_{\text{polym}} = 2.5 \text{ g/L}$, $\text{pH} = 1$, $T = 25^\circ\text{C}$, $\sum_{\text{initial}} C/h_{\text{cmp}} = 6$)

Conclusion

A new promising water soluble polymeric sorbent bearing carbamoylmethylphosphonic diacid groups (**hP**(CPAAM6C)) was studied for the recovery of lanthanide elements. Experimental data enabled determining an experimental maximum sorption capacity Q_{\max} of about 1.5 mmol per gram of polymer at pH = 1 and T = 25°C; this maximum capacity being three times higher than that obtained for P(CPAAM6C) (carbamoylphosphonated ester form). Sorption isotherm was adjusted by the Langmuir equation and allowed to determine Q_{\max}^L and K_L parameters, which were found to equal $1.72 \pm 0.067 \text{ mmol.g}^{-1}$ and $0.302 \pm 0.063 \text{ L.mmol}^{-1}$, respectively. It was also demonstrated that the sorption capacities were improved by the increase of pH and of the ionic strength. A complexation mechanism was proposed. It suggests that both functions of the carbamoylmethylphosphonic acid were involved in distinct sorption mechanisms: the amide through coordination mode and the phosphonic acid through ion exchange mode. Additionally, the ion-exchange mechanisms were strongly dependent on the pH variation induced by complexation, as the protons release during the sorption process led to modifications in the gadolinium speciation in solution. The selectivity of **hP**(CPAAM6C) at pH = 1 with respect to Gd(III) was also demonstrated in mixtures containing gadolinium and nickel. Comparison with P(CPAAM6C) showed that **hP**(CPAAM6C) provides better selective separation properties for $\sum_{\text{initial}} C/h_{\text{cmp}} < 4$ while P(CPAAM6C) is better for $\sum_{\text{initial}} C/h_{\text{cmp}} > 4$ at pH = 1. Finally, gadolinium sorption induced the precipitation of the **hP**(CPAAM6C) in water allowing its specific precipitation, even in the presence of nickel. All these results show that the material developed could be used in new solvent free and low energy consuming process combining two main steps: (i) sorption/flocculation followed by (ii) filtration or centrifugation. Complementary studies dealing with the influence of pH, nature of competitive cation (other lanthanides and metals) and all process dimensioning developments should lead to a new process that may be considered as well as for the treatment of Waste Electronic and Electrical Equipment (WEEE)

as for other applications such as treatment of radioactive liquid waste in the field of the nuclear fuel cycle.

Acknowledgements

The authors acknowledge the LabEx Chemistry of Molecular and Interfacial Systems (LabEx CheMISyst) and the “Institut Carnot CED2” for financial support (ANR-10-LABX-05-01) for this works.

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