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Cloud-Point Extraction for Selective Removal of Gd(III) and La(III) with 8-Hydroxyquinoline

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Abstract: A less-common extraction procedure, cloud-point extraction, is used with a lipophilic chelating agent (8-hydroxyquinoline) to extract and separate lanthanum(III) and gadolinium(III) ions from an aqueous solution. Surfactant solutions are used in conjunction with 8-hydroxyquinoline to form a lanthanide complex that is extracted into the micellar phase at a temperature above the cloud-point temperature. The structure of the lipophilic part of the nonionic surfactant, the chelating agent–metal molar ratio, and the cloud-point temperature are identified as factors determining the extraction efficiency and selectivity. With Triton X-114, a selectivity higher than 30 and a decontamination factor of 50 for Gd(III) indicate that micelle-mediated cloud-point extraction is promising for the specific separation of actinide ions from nuclear waste. Finally, a microwave procedure is proposed to decrease the duration of the experiment to less than 6 min.

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INTRODUCTION

Liquid–liquid extraction is widely used in the hydrometallurgy of base and strategic metals and, especially, for spent nuclear fuel reprocessing (1); however, this technique imposes important restrictions and presents drawbacks related to the use of expensive, toxic, and inflammable organic diluents. As a result, new separation methods based on innovative concepts are currently being developed (2). An interesting alternative to traditional liquid–liquid solvent extraction is the use of aqueous polymeric solutions as environmentally benign liquid–liquid extraction media. Many formulations for such systems are known, referred to as micellar extraction (3), aqueous biphasic systems (4), and cloud-point extraction (CPE) (5–8). Micelles have been accepted as a microscopic medium providing a new basis for development of separation techniques that lead to high extraction efficiencies and preconcentration factors and use inexpensive and reagents of low toxicity.

Surface-active agents can form microheterogeneous structures in solution referred to as micelles. During their formation, the surfactant micelles have been demonstrated to entrap several hydrophobic or slightly hydrophilic substances, isolating them from the bulk solution. The solubility of nonionic or zwitterionic surfactants in aqueous solution is dramatically depressed above a well-defined temperature called the cloud-point temperature (CPT). By settling the solution at a temperature above the CPT, the solution separates into a concentrated phase containing most of the surfactant, the surfactant-rich or coacervate phase, and a dilute aqueous phase (6, 7), in which the surfactant concentration is approximately equal to the critical micelle concentration (9). CPE arises from the partitioning of a solute between the two water-based phases, depending on its affinity for the surfactant. A high concentration of the target solute is then expected from a small volume of the surfactant-rich phase after phase separation. The phase separation is reversible, and CPE has been tentatively used to achieve the separation of different solutes for the extraction and preconcentration of molecules of biological interest (6, 7), for the preconcentration of analytes as a step prior to their determination (8, 10–12), or for the removal of pollutants from aqueous industrial streams and wastewaters (13, 14).

CPE has been successfully used in the absence of chelating agents (15, 16), but metal-ion separation could be improved by the formation of hydrophobic complexes in the surfactant micellar solution. Since Watanabe and Tanaka's pioneering work (17) on extraction of nickel and zinc cations, many chelating agents have been used to extract metal ions (18–20), such as the use of 8-hydroxyquinoline (8-HQ) derivatives for Cr^{3+} extraction (8, 20).

Among the most difficult of metal separations are the intra- and intergroup separations of lanthanides and trivalent actinides. The need to protect both society and the environment from the hazards associated with radioactive waste and new high-tech developments that have increased the demand for pure lanthanides have combined to promote a greater need for effective procedures to attain these separations. Taking full advantage of the attractiveness of the CPE approach, the concept of using this technique for the separation of lanthanides is investigated. In this paper, the separation of lanthanides is accomplished after formation of lipophilic complexes with 8-HQ. The influence of the nature of the surfactant, the CPT and the chelating agent–metal molar ratio on the extraction efficiency are studied. In addition, a microwave irradiation procedure is proposed to shorten the duration of the experiment.

EXPERIMENTAL

Chemicals and Reagents

The nonionic surfactants (Tween 80 and Triton X-114 from Aldrich, Simulsol OX 1006-L and Simulsol NW 900 from Seppic S.A., Paris, France), and 8-HQ (Aldrich) were used without further purification. All other reagents used were of analytical grade. Stock solutions of lanthanum and gadolinium nitrates (Aldrich) were prepared by dissolving appropriate amounts of their respective salts in doubly distilled water.

Determination of Lanthanide Concentrations

Concentrations of La^{3+} and Gd^{3+} in the solution were determined by inductively coupled plasma–atomic emission spectrometry (ICP-AES), using standard addition techniques. The system used for this work was the Spectro D system from Spectro Analytical Instruments.

CPE Procedure

In a thermostated bath, an appropriate amount of 8-HQ was dissolved in 450 mg of pure Triton X-114. An aliquot of 45 mL of a solution at 10°C that contained equimolar quantities of La^{3+} and Gd^{3+} (0.36 mM/L) was then added. The temperature of the homogeneous mixture thus obtained was increased to 60°C and left to stand for 1 h at this temperature in a thermostated bath (Haake CH, Fison). After centrifugation, the upper aqueous phase was removed and its lanthanide(III) concentration was determined by ICP-AES using standard-addition techniques. All values reported are the average of triplicate measurements.

In a microwave oven, an appropriate amount of 8-HQ was dissolved in 450 mg of pure Triton X-114. An aliquot of 45 mL of a solution at 10°C that contained equimolar quantities of La^{3+} and Gd^{3+} (0.36 mM/L) was then added. The homogeneous mixture was left to stand for 2–30 min before heating and for 30 sec (time required to reach 60°C) in an 800-W microwave oven (Daewoo). After 3 min of centrifugation, the upper aqueous phase was removed, and its lanthanides(III) concentration was determined by ICP-AES using standard-addition techniques. The final volume of the surfactant-rich phase was determined by measuring the phase after CPE. All values reported are the average of triplicate measurements.

The CPE of Ln(III) from micellar solutions was evaluated in terms of extraction efficiency $E_{Ln^{3+}}$, distribution ratio $D_{Ln^{3+}}$, selectivity $S_{Gd^{3+}/La^{3+}}$, and concentration factor $CF_{Ln^{3+}}$, which are defined as follows:

$$E_{Ln^{3+}} = \frac{C_i - C_f V_f}{C_i V_i} \times 100$$

$$D_{Ln^{3+}} = \left(\frac{C_i - C_f}{C_f}\right) \times \left(\frac{V_i}{V_{srp}}\right)$$

$$S_{Gd^{3+}/La^{3+}} = \frac{D_{Gd^{3+}}}{D_{La^{3+}}}$$

$$CF_{Ln^{3+}} = \frac{\text{total mass of } Ln^{3+} \text{in the surfactant rich phase}}{\text{total mass of } Ln^{3+} \text{in the aqueous phase}} = \frac{(C_i \times V_i) - (C_f \times V_f)}{(C_f \times V_f)}$$

where C_i is the initial concentration of metal ion in the micellar solution, C_f is the concentration of metal ion in the aqueous phase after CPE, V_i is the volume of the micellar solution (in mL), V_f is the volume of aqueous phase after CPE (in mL), and V_{srp} is the volume of the surfactant-rich phase after CPE (in mL).

RESULTS AND DISCUSSION

Experiments in a Thermostated Bath

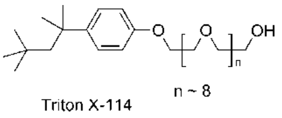
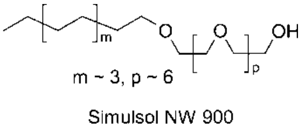
Ligand and Surfactant Selection

Lanthanide complexes with 8-HQ are characterized by a high thermodynamic stability [$\mathrm{Log}\beta_2^{(La)} = 25.23$ and $\log\beta_2^{(Gd)} = 27.04$, T = 35°C, 75% v/v dioxin, 0.2 M sodium percholate (21)]. The ratio of the formation constant of La^{3+} to

Gd^{3+} with 8-HQ is about 65, so the use of CPE could take advantage of such a difference, making this system highly efficient for lanthanide(III) intragroup separation. The CPE of lanthanide with 8-HQ was investigated, using a 1 wt% nonionic surfactant solution in a neutral aqueous solution (pH ~ 5.5). The cloud point depends on the structure of the nonionic surfactant. For a homologous series of nonionic surfactants, the cloud point increases with decreasing length of the hydrocarbon chain and the increasing length of the oxyethylene chain (5). In this work, four nonionic surfactants were tested: polyoxyethylated alcohols (Simulsol OX1006L and Simulsol NW 900), polyoxyethylene sorbitan monooleate (Tween 80), and polyethoxylated alkylphenol (Triton X-114). The structures and properties of Triton X-114 and Simulsol NW 900 are shown in Table 1.

When working with the nonionic surfactants Simulsol OX1006L, Simulsol NW 900, or Tween 80, for which the lipophilic part is aliphatic, 8-HQ is sparingly soluble in the initial micellar solution. Furthermore, the lanthanide complexes of these surfactants precipitate in the micellar solution. On the other hand, 8-HQ and its lanthanide complexes are soluble in the micellar solution of Triton X-114. A possible explanation is that the solubilization behavior of the micellar system formed with Triton X-114 arises from the aromatic structure of the lipophilic part of the Triton X-114. The solubilization of both 8-HQ and its lanthanide complexes is directly related to the existence of microscopically ordered structures of aromatic nuclei in the micelle. The CPT of the studied system using Triton X-114 is near room temperature, offering advantages in terms of experimental procedure, since the settling temperature was 60°C. Furthermore, the surfactant-rich phase is the heaviest, allowing an easier workup: the upper aqueous phase could be easily removed by suction.

Table 1. Structure and potential hazards of the surfactants used

Surfactant	Flash point (°C)	LD_{50} oral, rat (mg/kg)	Biodegradation	Carcinogenicity
 n ~ 8 Triton X-114	>93	3,800	Low	Not listed
 m ~ 3, p ~ 6 Simulsol NW 900	>149	8,600	High	Not listed

Influence of 8-HQ on CPT of 1 wt % Triton X-114 Solutions

The effect of experimental variables on CPT and CPE parameters has been previously studied (11, 13). The cloud point of a given nonionic surfactant can be increased or decreased by the presence of additives. In particular, the addition of polar organic compounds like phenols depresses the cloud point (22). Because solutes that make up the solution can affect the cloud point, the influence of the concentration of 8-HQ on CPT was studied. Figure 1 shows the influence of the concentration of 8-HQ on CPT. For 0 to ~8 mM/L of 8-HQ, CPT decreases linearly from 26 to 10°C, at which point a plateau is reached.

Effect of pH

The pH is a critical parameter for CPE of Ln^{3+} with 8-HQ. Figure 2 shows the distribution of La^{3+} and Gd^{3+} complexes as a function of pH with an excess of 8-HQ. The Ln^{3+}/8-HQ complexes dominate the system above pH 5.5. At pH 2, La^{3+} and Gd^{3+} are not complexed by 8-HQ and Ln^{3+} cations are free in solution. Lanthanide(III) intragroup separation was then evaluated at pH 5.5, where Ln^{3+}/8-HQ complexes dominate. Back extraction of both La^{3+} and Gd^{3+} should be performed at a lower pH (i.e., 2).

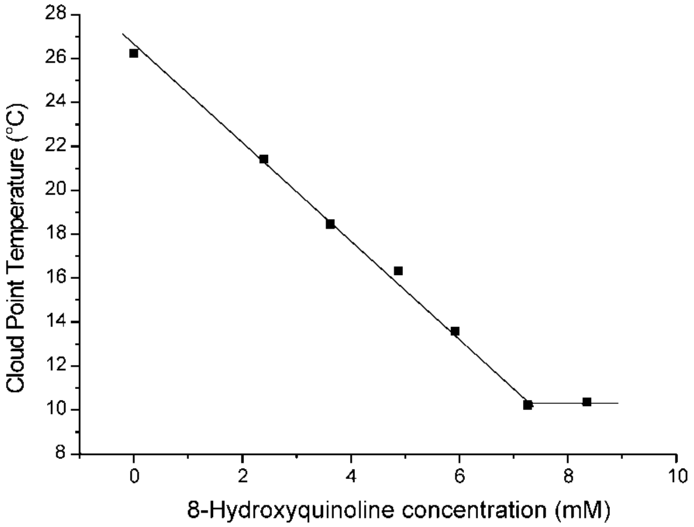


Figure 1. Cloud-point temperature (°C) vs. 8-hydroxyquinoline concentration (mM).

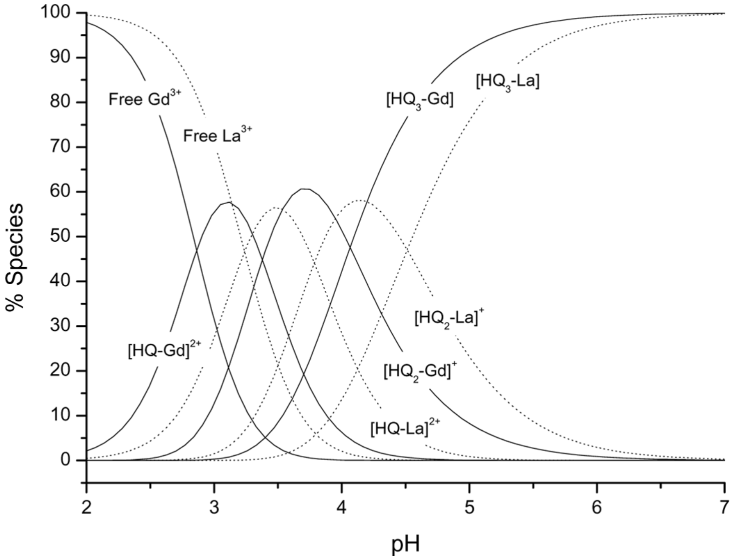


Figure 2. Calculated speciation for La^{3+} and Gd^{3+} complexes with 8-hydroxyquinoline (Q) calculated as a function of the pH for molar ratio of $[Ln^{3+}] = [Q]/5$ build using Hyperquad Simulation and Speciation (HySS) 2003.
($pKa_{1HQ} = 10.6$ and $pKa_{2HQ} = 14.6$, $\text{Log } K_1 = 9.728$, $\text{Log } \beta_2 = 17.71$, $\log\beta_3 = 25.23$ for La^{3+} and $\log K_1 = 90.94$, $\log\beta_2 = 18.99$, $\log\beta_3 = 27.04$ for Gd^{3+}).

Influence of Time and Temperature on Gd^{3+}/La^{3+} Extraction Selectivity

Table 2 summarizes the influence of temperature and equilibration time on Gd^{3+}/La^{3+} extraction selectivity for a period from 0.5 to 8 hr at a settling temperature of 40–80°C. As seen in Table 2, from 40–60°C, Gd^{3+}/La^{3+}

Table 2. Effect of temperature and equilibration time on Gd^{3+}/La^{3+} selectivity[a]

Settling temperature time (h)	S Gd^{3+}/La^{3+}, 40°C	S Gd^{3+}/La^{3+}, 60°C	S Gd^{3+}/La^{3+}, 80°C
0.5	17 ± 3.0	30 ± 6.0	31 ± 7.0
1	20 ± 3.5	33 ± 7.5	31 ± 8.0
2	20 ± 3.5	32 ± 7.5	24 ± 6.0
6	22 ± 4.0	28 ± 6.5	18 ± 5.5
8	19 ± 3.5	32 ± 12.0	22 ± 6.4

[a] $[La(NO_3)_3] = [Gd(NO_3)_3] = 0.36$ mm; pH = 5.5; 1 wt% Triton X-114; 8-hydroxyquinoline/Ln(III) molar ratio = 10; volume of the micellar phase = 45 mL; volume of the surfactant-rich phase after CPE = 1.2 mL.

extraction selectivity increases to a maximum of 33. Above 60°C, temperature does not affect extraction selectivity. In general, the settling temperature time has no effect on Gd^{3+}/La^{3+} extraction selectivity, which is optimal at 60°C.

Effect of 8-HQ–Lanthanide(III) Molar Ratio on Extraction Efficiency

Figure 3 shows results obtained for the CPE of lanthanides with Triton X-114 as surfactant with increasing 8-HQ concentrations after 1 h at a 60°C CPT.

In the absence of chelating agent, a weak extraction (less than 15%) of La^{3+} and Gd^{3+} is observed. The low value for Gd^{3+}/La^{3+} selectivity that is observed can be explained by the difference in hydration enthalpy between lanthanum and gadolinium (23). When increasing the 8-HQ–lanthanide(III) molar ratio from 2 to 14 (i.e., 1.44–10.08 mM), extraction efficiency increases more rapidly for Gd^{3+} than for La^{3+}; this result is in accordance with the stability constants, leading to a high Gd^{3+}/La^{3+} selectivity (Table 3).

When using high 8-HQ–lanthanide ratios, high distribution coefficients and selectivities for gadolinium are obtained. When using an 8-HQ–lanthanide(III) molar ratio of 14, a Gd^{3+}/La^{3+} selectivity of 32 is obtained with a concentration factor of 57 for Gd^{3+}. Nevertheless, the process is quite time-consuming, requiring more than 1 h to complete. In order to improve the process, we set up an experiment using a microwave oven instead of the thermostated bath.

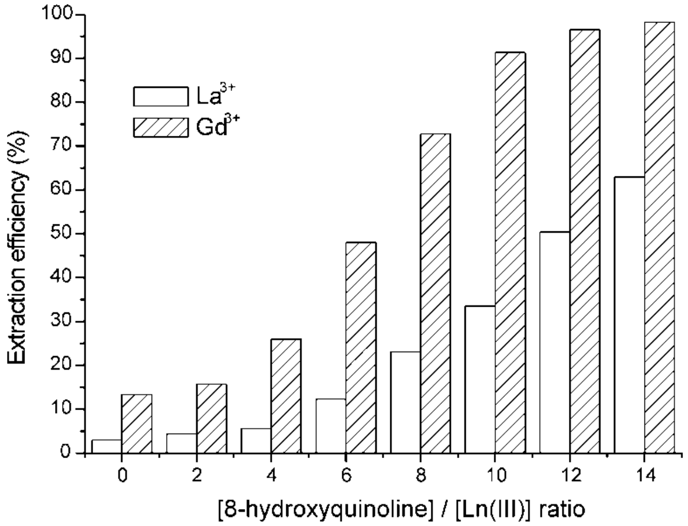


Figure 3. Effect of 8-hydroxyquinoline/lanthanide molar ratio on Gd(III) and La(III) extraction efficiency. $[La(NO_3)_3] = [Gd(NO_3)_3] = 0.36$ mm; pH = 5.5; 1 wt% Triton X-114; settling temperature = 60°C; equilibration time = 1 h.

Table 3. Effect of 8-Hydroxyquinoline/Lanthanide ratio on distribution coefficient and Gd^{3+}/La^{3+} selectivity[a]

8-HQ/Ln(III) molar ratio	D La^{3+}	D Gd^{3+}	S Gd^{3+}/La^{3+}
0	1.1 ± 0.3	5.9 ± 0.3	5.4 ± 1.4
2	1.7 ± 0.3	6.9 ± 0.3	4.0 ± 0.8
4	2.2 ± 0.3	13.2 ± 0.4	6.0 ± 0.9
6	5.3 ± 0.3	32.6 ± 0.6	6.1 ± 0.5
8	11.3 ± 0.4	100 ± 1	8.8 ± 0.3
10	18.9 ± 0.5	394 ± 4	20.8 ± 0.6
12	38.1 ± 0.7	1059 ± 10	27.8 ± 0.6
14	63.8 ± 0.9	2067 ± 20	32.4 ± 0.6

[a] $[La(NO_3)_3] = [Gd(NO_3)_3] = 0.36$ mm; pH = 5.5; 1 wt% Triton X-114; settling temperature = 60°C; equilibration time = 1 h; micellar-phase volume = 45 mL; surfactant-rich-phase volume after CPE = 1.2 mL.

Experiments in a Microwave Oven

Figure 4 shows the results obtained for the CPE of lanthanides with Triton X-114 as surfactant and with an 8-HQ–lanthanide(III) molar ratio of 10,

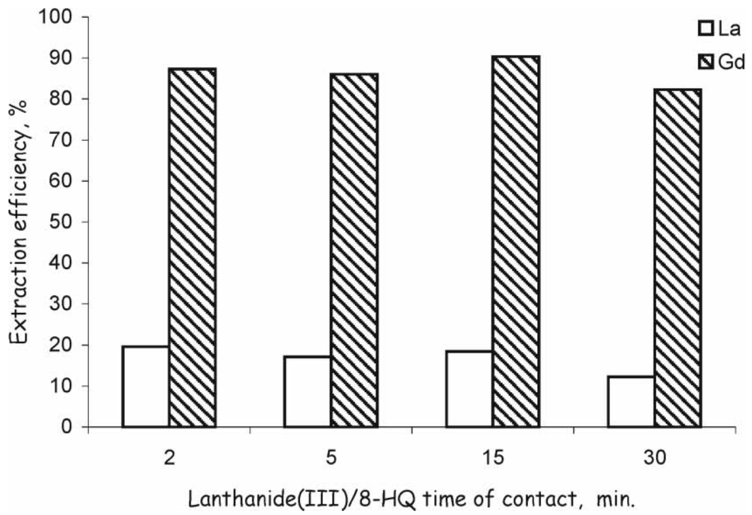


Figure 4. Effect of lanthanide(III)/8-hydroxyquinoline time of contact before heating on lanthanide(III) extraction efficiency. $[La(NO_3)_3] = [Gd(NO_3)_3] = 0.36$ mm; pH = 5.5; 1 wt% Triton X-114; settling temperature = 60°C; equilibration time = 30 sec.

after 2–30 min of 8-HQ–lanthanide(III) contact before heating and 30 sec at a 60°C settling temperature in a microwave oven.

An increase in the lanthanide/8-HQ time of contact before heating does not affect Gd^{3+} extraction efficiency and its selectivity toward La^{3+}. After 2 min of lanthanide/8-HQ contact before heating and 30 sec of equilibration time at a 60°C settling temperature, Gd^{3+} extraction efficiency is maximum (90%) and Gd^{3+}/La^{3+} extraction selectivity is comparable to that obtained for the experiments in a thermostated bath.

CONCLUSIONS

A promising liquid–liquid procedure based on the CPE concept has been developed for the separation of lanthanides without the use of organic diluents. The extent of extraction is markedly influenced by the nature of the nonionic surfactants and the molar ratio of 8-HQ to Ln(III). In addition, it has been demonstrated that the use of microwaves shortens the process. The results of this study clearly demonstrate the usefulness of this new type of micelle-mediated extraction technique to selectively extract, preconcentrate, and separate lanthanides.

Presently, back-extraction experiments and multistep extractions are in progress to evaluate the possibility of using this micelle-mediated extraction technique for lanthanide intragroup separation. The use of organophosphoric acid extractants (22–24) is also considered in order to process solutions of lower pH and to enhance the selectivity of lanthanide extraction.

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