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Photochemical separation and co-precipitation of lanthanides in nitric acid solution

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Abstract

Mutual separation of lanthanide elements was carried out using photochemical techniques. Light from an ultrahigh pressure mercury lamp was used to irradiate a nitric acid solution containing fourfold mixtures of lanthanide elements (Nd, Sm, Eu and Gd), $(NH_4)_2SO_4$ and isopropyl formate. Nd, Sm and Eu formed precipitates as a function of the irradiation time, but Gd did not co-precipitate. It was concluded that ligand photosubstitutional reactions can be initiated by f-state excitation provided that the reduction potential of the target element is sufficiently low. When La was introduced instead of Gd, La co-precipitated together with Nd, Sm and Eu. To explain these results, Nd–Gd and Nd–La systems were photolysed for comparison, and the difference in precipitation behaviour between these two systems was explained by the different sizes of the ions of these elements. © 1997 Elsevier Science S.A.

Keywords: Co-precipitation; Lanthanides; Nitric acid solution; Photochemical precipitation

1. Introduction

The lanthanides (Ln) display line-like absorption features due to inner f-shell transitions in the near-UV to near-IR spectral regions. Furthermore, some Ln display broader absorption peaks in the UV (350 nm or less), which have been assigned to 4f–5d transitions (resulting in photo-oxidation) or charge transfer transitions (resulting in photo-reduction) [1].

As expected from the formally non-bonding character of f electrons, relatively few photochemical studies have involved excited 4f- or 5f-electron states. Photosubstitutions in lanthanide β-diketonate were demonstrated as early as 1978 [2]. Polymerization of vinyl compounds via ligand sensitization (i.e. transfer of energy from a metal ion excited f state to a ligand) has been cited as an example of photochemistry involving f-electron states [3]. In a review of applied laser photochemistry, Donohue [4] cites another example: a Sm^{3+} ligand photosubstitution reaction initiated by f-state excitation. Recently, Kusaba et al. [5] reported that two-photon absorption induces the photoreduction of Eu^{3+} to Eu^{2+} in a methanol solution of $EuCl_3$ and that the excitation spectra clearly indicate that the photoreduction occurs via 4f transitions.

In previous work, we performed experiments to investigate the photochemically induced precipitation behaviour of lanthanides [6]. On irradiation of $LnCl_3$–$(NH_4)_2SO_4$–HCl and $Ln(NO_3)_3$–$(NH_4)_2SO_4$–HNO_3 (Ln ≡ Nd, Sm, Eu and Gd) solutions, Eu, Sm and Nd were precipitated, but Gd was not. Therefore the selective separation of Gd from Nd, Sm and Eu in hydrochloric acid and nitric acid solution was carried out effectively. The reason for this observation was not clear at that point.

We assumed that precipitation was followed by ligand photosubstitution reactions by f-shell transitions. In this study, the photochemical behaviour of La, in addition to Nd, Sm, Eu and Gd, was examined by irradiation of $Ln(NO_3)_3$–$(NH_4)_2SO_4$–HNO_3 (Ln ≡ Nd, Sm, Eu, Gd and La) solution. The results, including our previous work [6], were interpreted considering the separation and co-precipitation behaviour as well as the reduction potentials. All irradiation experiments were carried out as a function of time under given HNO_3 concentrations.

2. Experimental details

A trial to examine the photochemical behaviour of some of the lanthanide elements was carried out in aqueous solution using an ultrahigh pressure mercury lamp. An equimolar mixture (0.1 M) of lanthanide nitrate was dissolved in 0.5 N

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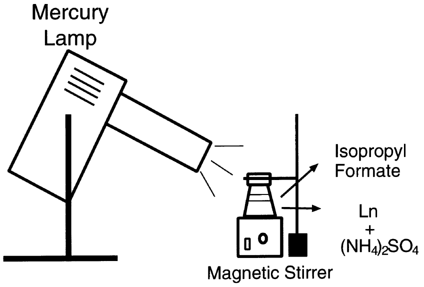

Fig. 1. Schematic view of apparatus.

HNO_3 solution containing 0.5 M $(NH_4)_2SO_4$. Isopropyl formate was added to the aqueous solution as a scavenger of $^{\cdot}OH$ radicals. Alcohols such as 2-propanol and esters such as isopropyl formate are effective radical scavengers. The volumes of HNO_3 solution and isopropyl formate were 20 ml and 4 ml respectively unless otherwise noted.

Aqueous (HNO_3 solution) and organic (isopropyl formate) phases were continuously homogenized using a magnetic stirrer, and irradiated with an ultrahigh pressure mercury lamp (Wacom model BMD-500 D, 500 W) (Fig. 1). The light from the mercury lamp was cut off with a filter and adjusted so that only lines around 350–410 nm were used for irradiation. For reference, we also studied Ln precipitation in $LnCl_3$–$(NH_4)_2SO_4$–HCl (Ln ≡ Nd, Sm, Eu, Gd, La) solution.

The concentrations of lanthanide in the HNO_3 or HCl solution before and after irradiation were determined using a UV–visible–near-IR scanning spectrophotometer (Shimadzu, UV-3100PC) [7]. Prior to the measurements, the solutions containing these elements were spun at 3000 rev min^{-1} for 10 min to separate the precipitates.

3. Results and discussion

Solutions containing Eu, Sm, Nd, Gd and La chlorides were photolysed. Eu, Sm and Nd precipitate, whereas Gd and La do not, when each lanthanide is photolysed separately. When Gd and La are photolysed in binary or fourfold mixtures of lanthanides, they show different behaviour. La co-precipitates together with Eu, Sm and Nd, whereas Gd does not. Table 1 shows the concentrations of lanthanides in the chloride solutions after 48 h of irradiation.

Table 1
Concentration of lanthanides in liquid phase after irradiation in chloride system

Lanthanide in liquid phase	Concentration (C/C_0) (%)				
	Eu	Sm	Nd	Gd	La
Eu	4.7	–	–	–	–
Sm	–	3.8	–	–	–
Nd	–	–	3.2	–	–
Gd	–	–	–	99.5	–
La	–	–	–	–	93.1
Eu, Sm	4.7	3.2	–	–	–
Eu, Nd	5.2	–	6.1	–	–
Nd, Gd	–	–	3.8	92.3	–
Nd, La	–	–	8.9	–	11.2
Eu, Sm, Nd, Gd	6.7	5.8	5.2	94.2	–
Eu, Sm, Nd, La	5.3	5.2	7.6	–	8.2

C_0, initial concentration of lanthanides; C, concentration after irradiation.

In the experiments on $Ln(NO_3)_3$, the lanthanides exhibit the same precipitation behaviour as in the chloride experiments. Nd, Sm and Eu precipitate. However, the yield of precipitation is not as great as when $LnCl_3$ is photolysed. Table 2 shows the concentrations of lanthanides in the nitrate solutions after 48 h of irradiation of various lanthanide mixtures. The acidity of the solutions is 0.5 N. Fig. 2 and Fig. 3 show the concentration profiles of Nd–Gd and Nd–La systems as a function of the irradiation time. Fig. 2 shows that the concentration of Nd decreases to about 60%, whereas

Table 2
Concentration of lanthanides in liquid phase after irradiation in nitrate system

Lanthanide in liquid phase	Concentration (C/C_0) (%)				
	Eu	Sm	Nd	Gd	La
Eu	54.8	–	–	–	–
Sm	–	54.3	–	–	–
Nd	–	–	60.2	–	–
Gd	–	–	–	98.7	–
La	–	–	–	–	94.2
Eu, Sm	57.8	59.2	–	–	–
Eu, Nd	58.2	–	62.5	–	–
Nd, Gd	–	–	63.2	97.5	–
Nd, La	–	–	69.6	–	72.3
Eu, Sm, Nd, Gd	60.5	62.3	67.3	96.2	–
Eu, Sm, Nd, La	62.2	63.2	65.3	–	71.6

C_0, initial concentration of lanthanides; C, concentration after irradiation.

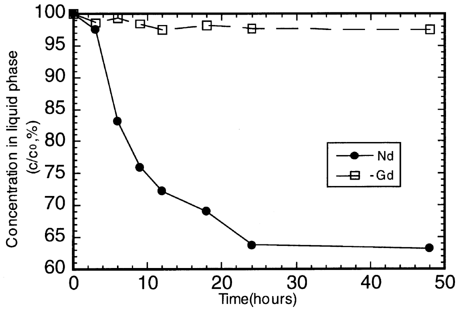

Fig. 2. Concentration profile of Nd–Gd system.

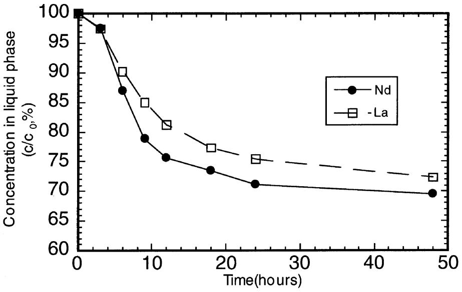

Fig. 3. Concentration profile of Nd–La system.

that of Gd shows no significant change during 48 h of photolysis. Isopropyl formate (ester) is decomposed by nitric acid, causing the yield of precipitation to be lower in the nitrate system than in the chloride system. The addition of 4 ml of isopropyl formate causes further precipitation, resulting in a decrease in the concentration of Nd to nearly 0%. This leads to the complete separation of Nd and Gd in 0.5 N nitric acid by the ultrahigh pressure mercury lamp. Precipitation does not occur in the absence of radical scavenger, irradiation or $(NH_4)_2SO_4$. In contrast, Fig. 3 shows that the photolysis of the Nd–La system does not lead to the separation of these elements and La co-precipitates together with Nd.

Eu^{3+} is photoreduced by electron transfer from a binding ligand, such as H_2O or SO_4^{2-}, in its charge transfer (CT) band (188 nm) [8]

$$Eu^{3+}(H_2O)\xrightarrow{h\nu}Eu^{2+}+H^{+}+{}^{\cdot}OH \qquad (1)$$

A radical must be scavenged to avoid the reverse reaction. Water is a poor radical scavenger, but alcohols such as 2-propanol and esters such as isopropyl formate are effective radical scavengers

$$(CH_3)_2CHOH+{}^{\cdot}OH\rightarrow H_2O+(CH_3)_2COH \qquad (2)$$

The chemical properties of Eu^{2+} are similar to those of the alkaline earth ions, so that separation can be achieved by precipitation with sulphate by the formation of $EuSO_4$, since $EuSO_4$ is insoluble in water and media of low acidity.

Clear evidence for the two-photon reduction of Eu^{3+} to Eu^{2+} in solution has been presented [5]. The first photon is absorbed in an $f' \leftarrow f$ transition band of Eu^{3+} and the second photon is absorbed in a transition band of an intermediate level relative to the CT level.

The light from the ultrahigh pressure mercury lamp used in this study was cut off with a filter, so that lines around 350–410 nm were used for irradiation. Irradiation at this wavelength is effective for the initiation of the photosubstitutional reaction of Nd^{3+} which has an absorption peak at 354.0 nm due to inner f-shell transitions. Sm (401.5 nm) and Eu (394.2 nm) are also photosubstituted, but Gd (272.8 nm) and La (no f electron) are not, and do not form precipitates on irradiation with this mercury lamp. 4f transitions and charge transfer are effective in bringing about ligand photosubstitution reactions.

The difference in co-precipitation behaviour between Gd and La strongly suggests that photoreduction occurs. This can be explained by lanthanide contraction: a progressive decrease in the ionic radius of Ln^{3+} as the atomic number increases. When reduced to divalent form, the lanthanide ion becomes much larger, so that the radius of Eu^{2+} is somewhat larger than that of Pr^{3+}. It can be assumed that, because trivalent Nd, Sm and Eu are photoreduced to the divalent form, their ionic sizes become closer to that of La^{3+} than to that of Gd^{3+}. The more similar the size of the ions, the more tendency there is for co-precipitation [9].

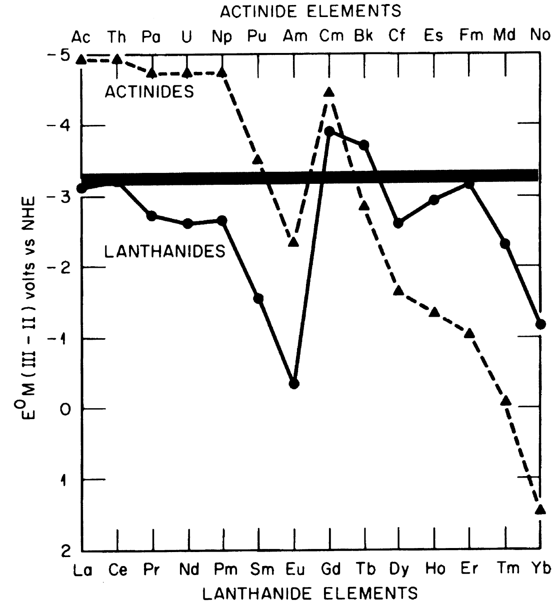

Fig. 4. Reduction potentials for M^{3+}/M^{2+} couples. Reprinted from K.A. Gschneidner, Jr., L. Eyring, G.R. Choppin and G.H. Lander (eds.), Handbook on the Physics and Chemistry of Rare Earths, Vol. 18, Lanthanides/Actinides: Chemistry, Elsevier, Amsterdam, 1994, 481 pp.

The relative stabilities of the lanthanide elements were examined to compare their reduction potentials and the energies required for photoreduction. If the reduction potential of the target element is larger than the energy provided, photosubstitutional reaction through single photon absorption is negligibly small, so that photoreduction cannot be carried out effectively.

Fig. 4 shows the reduction potentials of the lanthanides and the actinides for the M^{3+}/M^{2+} couples ($M \equiv Ln, An$). The shaded area in this figure represents the energy provided by one-photon absorption from the ultrahigh pressure mercury lamp used in this study. Although, as in the case of electronic configurations, these potentials must be used cautiously, since many other factors play a role in determining the compounds formed, Fig. 4 shows that Eu^{3+}, Sm^{3+} and Nd^{3+} are more likely to be reduced to the divalent form than Gd^{3+} and La^{3+}.

4. Conclusions

Ligand photosubstitutional reactions can be initiated for lanthanide elements by f-state excitation if the reduction potential of the target element is sufficiently low. Nd, Sm and Eu were precipitated by photolysis. The co-precipitation behaviour of Gd^{3+} and La^{3+} with these three elements strongly suggests the occurrence of photoreduction.

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