

Extraction behavior of actinides and lanthanides in a molten fluoride/liquid aluminum system

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Abstract

As one of the basic investigations on the group partitioning of actinides and lanthanides by a pyrochemical reductive extraction process, the distribution ratios of Pu, Am, Ce and Sm have been experimentally determined in the binary liquid LiF–AlF₃/Al–Cu system at the temperature of 830 °C. The distribution ratios of Pu and Am are much larger than those of Ce and Sm. They would allow a high recovery yield of the actinides and good separation factors with lanthanides. The influence of the salt composition (LiF/AlF₃ ratio) on the distribution coefficients has been investigated. Coupling the obtained experimental results and literature data, a thermodynamic model that describes the extraction in terms of Gibbs enthalpies of formation and the fluorobasicity of the melt (*pF*) has been developed. The activity coefficients of Sm(+II) et Ce(+III) versus the *pF* have been inferred: they clearly reveal the difference in solvation behavior between divalent and trivalent species.

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1. Introduction

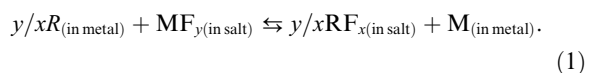
This work was undertaken to investigate the separation of the actinides from the lanthanides by reductive extraction in a molten fluoride/liquid metal medium which could be a promising technique for the treatment of spent nuclear objects (either irradiated targets coming from minor actinides transmutation or Generation IV reactor fuel) [1]. Previously published works in this area concern the LiF–BeF₂/Li–Bi [2,3] or LiF–CaF₂/Mg–Zn [4] systems. The purpose of this work is: (i) to evaluate the potentialities of liquid aluminum for actinides (An)/lanthanides (Ln) separation, (ii) to investigate the influence of the fluorobasicity (*pF* = $-\log a_{\text{LiF}}$) of the melt on the solvation (activity coefficients) of the solutes.

This study therefore addresses the distribution of actinides (Pu, Am) and lanthanides (Ce, Sm), in the LiF–AlF₃/Al–Cu (78–22 mol%) system at 830 °C.

2. Thermodynamic considerations

2.1. Reductive extraction: Principle

The reductive extraction consists in contacting a molten salt (here, a fluoride) which contains the elements (MF_y) that must be extracted with a liquid metallic phase containing a reductive agent (R). The solutes are reduced and transferred into the metal. The extraction can be described by the general following equation:



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The efficiency of the extraction of the solute MF_y is described by the distribution ratio $D_M = x_{M(\text{in metal})} / x_{MF_y(\text{in salt})}$ at the equilibrium (with x , the molar fraction).

The separation efficiency between two solutes M_1 and M_2 is described by the separation factor $S_{M_1/M_2} = D_{M_1} / D_{M_2}$.

2.2. Selection of the extracting system

Writing the mass action law for the standard thermodynamic constant (K_M^0) of the reaction (1) leads

$$K_M^0 = \frac{a_M \cdot a_{RF_x}^{y/x}}{a_{MF_y} \cdot a_R^{y/x}} \quad (2)$$

This can be rewritten with the distribution coefficient D_M and the activity coefficients $\gamma = a/x$

$$K_M^0 = \frac{D_M}{D_R} \cdot \frac{\gamma_M \cdot \gamma_{RF_x}^{y/x}}{\gamma_{MF_y} \cdot \gamma_R^{y/x}} \quad (3)$$

The activity coefficient terms reflect deviations from ideality in both phases. They can be expressed with respect to the variation of the excess Gibbs energy ΔG^{exc} of dissolution of the pure liquid using the relation $\Delta G^{\text{exc}} = RT \ln \gamma$. Thus, the separation factor between M_1F_y and M_2F_y can be expressed as

$$S_{M_1/M_2} = \frac{K_{M_1}^0 \gamma_{M_2} \gamma_{M_1F_y}}{K_{M_2}^0 \gamma_{M_1} \gamma_{M_2F_y}} \quad (4)$$

Also, the lower is $\frac{\gamma_{M_1}}{\gamma_{M_2}}$, the more selective is the separation of M_1 from M_2 . We have applied that consideration to An/Ln by calculating $\log \gamma_{Pu} - \log \gamma_{Ce}$ and $\log \gamma_U - \log \gamma_{Ce}$ versus T (°C) in various metal solvents. The source data have been compiled by Lebedev [5]. The results are given in Fig. 1. They show that, among the metals in which activity coefficients of Pu, U and Ce are known, aluminum seems to be the most promising metallic solvent for the An/Ln separation. Moreover, the ability of Al to reduce actinides fluorides is well known and has been used to elaborate Pu–Al fuel [6]. That is the reason why aluminum can be chosen as both solvent and reductive agent for our extraction experiments. But, Al is a light metal ($d \sim 2.3$ at 830 °C) and it seems suitable to alloy it with a heavier one to facilitate the decantation. An Al–Cu (78–22 mol%) alloy has been selected. Its density is about 3.3 at 830 °C and its melting point 570 °C. The selected fluoride melt is the LiF–AlF₃ binary which has two advantages: (i) its thermodynamic (activities of LiF and AlF₃) [7] and physical (density, viscosity) [8] properties are well known; (ii) it is possible to control the distribution ratios by changing x_{AlF_3} . At a temperature of 800 °C, the binary phase diagram of LiF–AlF₃ [9] shows that a composition range from 10 to 35 mol% AlF₃ can be investigated.

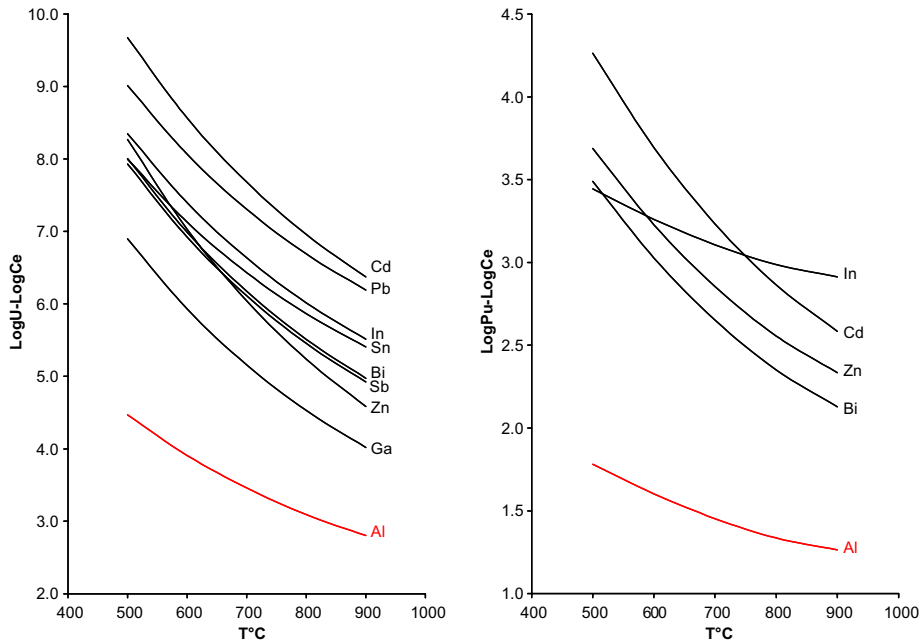


Fig. 1. Variation of $\log U - \log Ce$ and $\log Pu - \log Ce$ versus temperature for various metals. Liquid reference state for activity coefficients. Data from [3].

3. Experimental

Al, Cu, LiF, AlF_3 , CeF_3 and SmF_3 were purchased to Sigma-Aldrich with better than 99.99% purity. The fluorides were packaged by the supplier in ampoules under argon atmosphere with an initial water content of less than 100 ppm. AmF_3 was synthesized by precipitating Am(III) in a nitric acid medium using a 2 M hydrofluoric acid solution. The precipitate was successively washed with 0.1 M hydrofluoric acid, water and acetone, then dried in flowing air at room temperature, as for PuF_3 . Pu was in a nitric acid solution as Pu(IV), requiring prior reduction to Pu(III). This was achieved using ascorbic acid as a reducing agent and hydrazinium nitrate to control the nitrous acid concentration and prevent the oxidation of Pu(III) to Pu(IV) [10]. Thermogravimetric analysis of the PuF_3 precipitate showed that it included 4.1 wt% water and that drying for 4 h at 250 °C under argon atmosphere was sufficient to obtain the anhydrous product. The X-ray diffraction spectra of the PuF_3 powder before and after drying were similar to the spectrum of anhydrous PuF_3 synthesized by fluorination of PuO_2 with $\text{HF}(\text{g})$, indicating that water trapped during crystallization was not incorporated into the lattice. These observations confirm the possibility to dry PuF_3 by heating it in an inert atmosphere [10,11]. For lack of suitable instrumentation, a comparable study was not performed with AmF_3 . Nevertheless, considering the very similar crystalline and thermodynamic properties of PuF_3 and AmF_3 it can reasonably be assumed that the conditions necessary for dehydrating them will also be similar. Al–Cu alloy (78–22 mol%) was prepared by dissolving the suitable quantity of copper in liquid aluminum at 800 °C. This operation was performed under argon sparging in a

stainless steel reactor using a boron nitride crucible. The argon used to sparge the reactor was supplied by Air Liquid with very high purity: N60 grade, $\text{H}_2\text{O} < 0.6$ ppm and $\text{O}_2 < 0.1$ ppm. The experiments were carried out using the device (high-temperature liquid–liquid contactor: HTLLC) shown in Fig. 2. Two similar devices were used: one for the tests with Ce and Sm and another – in a glove box – for the tests involving Pu and Am. The HTLLC uses two crucibles: The metal is melted in the upper crucible, then poured through a stoppered orifice into the lower crucible. This system has two advantages: It accurately determines the starting time for kinetic studies and limits the entrainment of metallic oxides into the extraction crucible. Since all the liquid metal is not poured, the Al and Cu oxides in the film formed at the surface of the molten metal are not transferred into the lower crucible. This latter is the extraction vessel in which the two phases are contacted and stirred.

The salt mixture, 15–20 g of powder containing the solvent ($\text{LiF}-\text{AlF}_3$) and the solute CeF_3 (320 mg), PuF_3 (120 mg), SmF_3 (500 mg) or AmF_3 (20 mg), was thoroughly blended and placed in the extraction crucible. The LiF/AlF_3 ratio and the initial solute concentration are various for each test. About 45 g of solid Al–Cu alloy (78–22 mol%) were loaded into the upper crucible. The reactor was then sparged with argon and the temperature increased to 250 °C for 12 h to dehydrate the salt. The temperature was then increased to 830 °C to melt the two phases. While the melt was stirred at about 60 rpm, 15–25 g of alloy were poured by raising the stopper. The two phases were maintained in contact for 3 h, which was amply sufficient to reach equilibrium. Salt and liquid metal samples were then taken for analysis using quartz tubes and a syringe. The salt samples

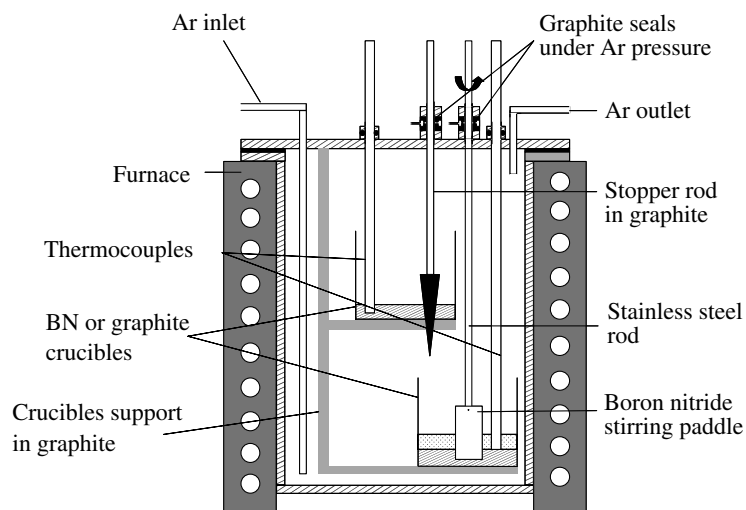


Fig. 2. Schematic cross section through the high-temperature liquid–liquid contactor (HTLLC).

were dissolved at 90–100 °C in a solution of HNO₃ (3 M) and Al(NO₃)₃ (1 M) [10]. The metal samples were dissolved in a mixture of HNO₃ (4 M) and HF (0.7 M). The Ce and Sm concentrations in solution were determined by ICP-AES. Pu and Am were analyzed by combining α counting and α spectrometry.

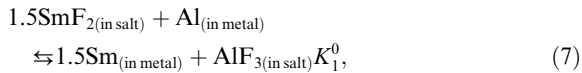
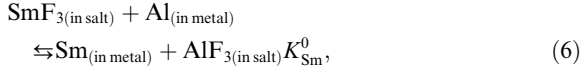
4. Results and discussion

4.1. Thermodynamic expression of distribution coefficients

Applying Eq. (3) to the extraction of CeF₃, PuF₃ and AmF₃ leads

$$D_M = K_M^0 \cdot \frac{a_{Al}}{x_{AlF_3} \cdot \gamma_{AlF_3}} \cdot \frac{\gamma_{MF_3}}{\gamma_M} \quad \text{with} \quad M = \text{Ce, Pu or Am.} \quad (5)$$

The K_M^0 thermodynamic constant of this reaction can be calculated from the Gibbs enthalpy of formation of the pure species involved (Table 1). The reference state in this study is the pure compound in the liquid state, except for AlF₃, which sublimates, and for which the reference state is the pure solid. In the case of Sm extraction, allowance must be made for its oxidation state II, which is stable in fluoride media. Two reduction equations must be thus considered



with $K_{\text{Sm}}^0 = 2.8 \times 10^{-8}$ and $K_1^0 = 7.38 \times 10^{-13}$ at 830 °C. The distribution ratio of samarium is defined by

$$D_{\text{Sm}} = \frac{x_{\text{Sm}}}{x_{\text{Sm(II)}} + x_{\text{Sm(III)}}} = \frac{D_{\text{Sm(III)}} \cdot D_{\text{Sm(II)}}}{D_{\text{Sm(III)}} + D_{\text{Sm(II)}}}, \quad (8)$$

where

$$D_{\text{Sm(II)}} = \frac{x_{\text{Sm}}}{x_{\text{Sm(II)}}} = K_1^{0.2/3} \frac{\gamma_{\text{SmF}_2}}{\gamma_{\text{Sm}}} \left(\frac{a_{\text{Al}}}{x_{\text{AlF}_3} \cdot \gamma_{\text{AlF}_3}} \right)^{2/3} \quad (9)$$

Table 1
Gibbs enthalpy of formation at 830 °C of Sm, Ce, Pu and Al fluorides

| Compound | ΔG_f° (kJ mol ⁻¹) | Reference |
|----------------------|--|-----------|
| SmF ₃ (l) | -1380.6 | [14] |
| SmF ₂ (l) | -984.4 | [13] |
| CeF ₃ l) | -1394.9 | [14] |
| PuF ₃ (l) | -1283.5 | [14] |
| AlF ₃ (s) | -1222.9 | [12] |
| Sm(l) | 1.7 | [12] |

and

$$D_{\text{Sm(III)}} = \frac{x_{\text{Sm}}}{x_{\text{Sm(III)}}} = K_{\text{Sm}}^0 \frac{\gamma_{\text{SmF}_3}}{\gamma_{\text{Sm}}} \left(\frac{a_{\text{Al}}}{x_{\text{AlF}_3} \cdot \gamma_{\text{AlF}_3}} \right). \quad (10)$$

4.2. Variation of distribution coefficients with x_{AlF_3}

Any variation in the AlF₃ concentration will directly influence the distribution coefficients by modifying x_{AlF_3} in Eqs. (5), (9) and (10), but also indirectly by modifying γ_{AlF_3} , γ_{MF_3} and γ_{SmF_2} . In a binary mixture such as LiF–AlF₃, the notion of fluoroacidity accounts for the major variation of the activity coefficients [7,15]. It is characterized by the activity of the F⁻ ions in solution, which depends on the LiF/AlF₃ ratio. LiF is highly dissociated in the melt and can be considered as a fluorobase (F⁻ donor). Conversely, AlF₃ is known to be a strong F⁻ acceptor, forming AlF_{3+x}⁻ anions (where x = 1, 2 or 3), making it a fluoroacid.

The Pu, Am, Ce and Sm distribution coefficients were measured at 830 °C for various initial AlF₃ concentrations. As the quantities of the element to be extracted were very small compared with Al, the AlF₃ concentration at equilibrium was virtually the same as the initial value. The initial CeF₃, PuF₃, AmF₃ and SmF₃ concentrations in the salt were: 3.7×10^{-1} , 9.4×10^{-2} , 1.5×10^{-2} and 5.5×10^{-1} mol% (2.1, 0.8, 0.1, 3.2 wt%) respectively. The Ce and Sm distribution coefficients were determined with about 10% uncertainty. The results for Pu and Am were of lower precision, mainly because of their low concentrations (between 10⁻² and 10⁻³ wt%) in the salt at the equilibrium. The results (Fig. 3) show that the logarithm of the distribution coefficients of these elements decreases with the increase of the AlF₃ concentration. For Sm and Ce, this can be described by the linear relations $\log D_{\text{Sm}} = -7.02x_{\text{AlF}_3} + 0.17$ and $\log D_{\text{Ce}} = -4.76x_{\text{AlF}_3} + 0.21$. The fact that the two slopes are different reveals two different extraction behaviors and probably the presence of Sm(+II) species

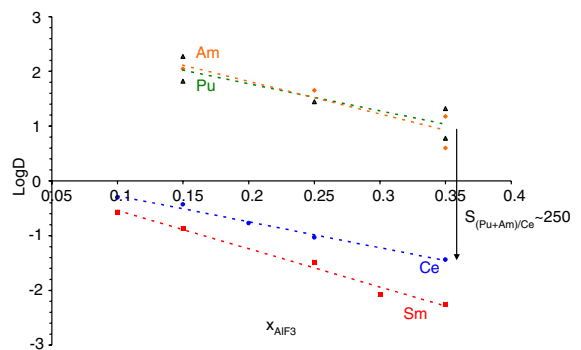


Fig. 3. Pu, Am, Ce and Sm partitioning in the LiF–AlF₃/Al–Cu system: effect of the salt composition.

in the salt at the equilibrium. It is confirmed by the purple colour of Sm containing salts after contact with the Al–Cu alloy.

Selective extraction of Pu and Am was effective over the full composition range investigated. For example, with a 15 mol% AlF_3 composition – corresponding to a binary LiF– AlF_3 eutectic melting at 710 °C – and for a metal/salt molar ratio of about 1:1, over 99% of the Pu and Am can be extracted in a single stage with separation factors (ratio of the distribution coefficients) of about 250 versus Ce and about 500 versus Sm.

4.3. CeF_3 and SmF_2 activity coefficient variation versus fluoroacidity pF

Eq. (5) allows us to write

$$\log \gamma_{\text{CeF}_3} = -\log K_{\text{Ce}}^0 + \log D_{\text{Ce}} + \log a_{\text{AlF}_3} - \log a_{\text{Al}} + \log \gamma_{\text{Ce}}, \quad (11)$$

K_{Ce}^0 and D_{Ce} are respectively the standard thermodynamic constants and experimental values quoted previously. The activity coefficients of Ce in pure Al is available in the literature [15]: at 830 °C, using the pure liquid as the reference state, $\gamma_{\text{Ce/Al}} = 9.2 \times 10^{-7}$. The value of γ_{Ce} in Al–Cu alloy (78–22 mol%) used here can be obtained by experimentally determining their distribution coefficients in pure Al and applying the relation based on Eq. (5):

$$\gamma_{\text{Ce/(Al-Cu)}} = \frac{D_{\text{Ce/Al}}}{D_{\text{Ce/(Al-Cu)}}} \cdot \gamma_{\text{Ce/Al}} \cdot \frac{a_{\text{Al/(Al-Cu)}}}{a_{\text{Al}}}, \quad (12)$$

where $a_{\text{Al}} = 1$.

In LiF– AlF_3 (85–15 mol%), $D_{\text{Ce/Al}} = 0.50$, $D_{\text{Ce/(Al-Cu)}} = 0.37$ and $a_{\text{Al/(Al-Cu)}} \sim 0.78$; hence $\gamma_{\text{Ce/(Al-Cu)}} = 9.7 \times 10^{-7}$. In our operating conditions, adding 22 mol% Cu to the Al thus does not significantly modify the Ce activity coefficient.

The relations between x_{AlF_3} , $pF = -\log a_{\text{LiF}}$ and a_{AlF_3} were electrochemically determined by Dewing [7]; the variation of the activity coefficients for CeF_3 can thus be determined according to the fluorobasicity of the medium.

As seen previously, it is more difficult in the case of Sm, because Sm(+II) and Sm(+III) species can coexist. There are two unknown quantities (γ_{SmF_2} and γ_{SmF_3}) and only one equation (12). To go further on thermodynamic discussion, it is necessary to make two assumptions: (i) The activity coefficients of SmF_3 are close to those of CeF_3 . Indeed, the complexation power strongly depends on the charge of the cation and its ionic radius and, according to Shannon, Sm^{3+} and Ce^{3+} have comparable ionic radii, respectively 102 and 96.8 pm [16]. (ii) As in the case of Ce, the activity of Sm in Al–Cu (78–22 mol%) is not significantly different that the one in pure Al. This last one has been reported to be 3.5×10^{-7} , with a pure liquid reference state [5].

Using Eq. (10) and previously determined activity coefficients of CeF_3 , it is possible to estimate the equilibrium values of $x_{\text{Sm(III)}}$

$$x_{\text{Sm(III)}} \cong x_{\text{Sm(in metal)}} \frac{\gamma_{\text{Sm}} \cdot a_{\text{AlF}_3}}{K_{\text{Sm}}^0 \cdot \gamma_{\text{CeF}_3} \cdot a_{\text{Al}}}, \quad (13)$$

$$x_{\text{Sm(II)}} = x_{\text{Sm(in salt)}} - x_{\text{Sm(III)}}. \quad (14)$$

The calculations show that the ratio Sm(II)/Sm(III) increases from 16, for a salt containing 10 mol% AlF_3 , to 63, for 35 mol% AlF_3 . Also, on the basis of our hypothesis, experimental and literature data (+II), oxidation number of Sm can be considered as predominant in the salt at the equilibrium. Thus, according to Eq. (7)

$$\gamma_{\text{SmF}_2} \cong D_{\text{Sm/(AlCu)}} \cdot \gamma_{\text{Sm/(AlCu)}} \cdot \frac{1}{K_1^{0/2/3}} \left(\frac{a_{\text{AlF}_3}}{a_{\text{Al}}} \right)^{2/3} \quad (15)$$

with

$$\gamma_{\text{Sm/(AlCu)}} = \gamma_{\text{Sm/(Al)}} \cdot \frac{D_{\text{Sm/(Al)}}}{D_{\text{Sm/(AlCu)}}} \cdot \left(\frac{a_{\text{Al/(AlCu)}}}{a_{\text{Al}}} \right)^{2/3}. \quad (16)$$

Eq. (16) yields $\gamma_{\text{Sm/(AlCu)}} = 3.4 \times 10^{-7}$. This value is very close to the one in pure Al, which agrees with our second hypothesis. Thus, using Eq. (15), and in the same manner than with CeF_3 , it is possible to calculate the activity coefficients of SmF_2 as a function of the fluorobasicity (pF) of the salt. The results, related to both CeF_3 and SmF_2 , are given in Fig. 4. They show that CeF_3 and SmF_2 are solvated in very different ways in fluoride media. The activity coefficients for CeF_3 increase with the acidity of the medium, which is characteristic of an acidic compound. CeF_3 can thus be expected to be solvated in the form of CeF_{3+x}^{-x} complexes in fluoride media, like AlF_3 . Conversely, the activity coefficient of SmF_2 diminishes only very slightly when the acidity increases, making it a neutral or very slightly basic compound. It can thus be expected to be present as Sm^{2+} , SmF^+ or SmF_2 in fluoride media. A similar reasoning could be used for predicting Eu(+II), Ln(+III) or An(+III) solvation behavior in salt as a function of fluorobasicity. This is due to the fact that all the Ln(+III) and An(+III) have

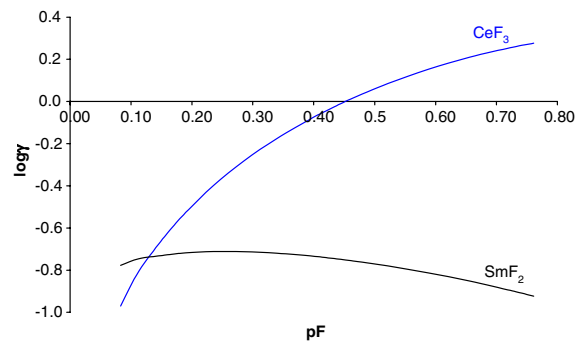


Fig. 4. CeF_3 and SmF_2 activity coefficients versus the fluoroacidity of the medium at 830 °C.

close ionic radii. The general tendency can be stated as follows: In basic medium (low pF values), the trivalent species are more stabilized than the divalent ones. On the contrary, the divalent species are more stabilized in acidic medium (high pF values) than the trivalent ones.

5. Conclusion

An experimental device and protocol have been developed to study the distribution of actinides and lanthanides in molten fluoride/liquid metal medium.

The results obtained with plutonium, americium, cerium and samarium in the $(\text{LiF}-\text{AlF}_3)/(\text{Al}-\text{Cu})$ medium revealed the potential of the system for separating the actinides from the lanthanides. More exactly, with a salt composition corresponding to the basic eutectic ($\text{LiF}-\text{AlF}_3$, 85–15 mol%), up to 99% of the Pu and Am could be recovered in a single stage, with cerium and samarium separation factors exceeding 250.

The effect of the AlF_3 concentration in the salt has been investigated. The distribution coefficients logically diminish as the initial AlF_3 concentration rises (AlF_3 is a reduction reaction product). A thermodynamic model of extraction versus fluoroacidity has been developed on the basis of the experimental results for cerium and samarium. The model clearly reveals the difference in solvation between divalent and trivalent lanthanides in fluoride media.

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