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Activity coefficients of plutonium and cerium in liquid gallium at 1073 K: Application to a molten salt/solvent metal separation concept

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Abstract

Activity coefficients in liquid metal and salt phases are important parameters for predicting the separation efficiency of reductive extraction or electrochemical pyrochemical processes. The electrochemical properties of Ce and Pu in gallium metal and chlorides media – $CaCl_2$ and equimolar NaCl–KCl – have been studied at 1073 K. Cyclic voltammetry and chronoamperometry show the thermodynamic feasibility of using gallium as solvent metal for pyrochemical processes involving Pu and Ce. The activity coefficient of Pu in liquid Ga ($\log(\gamma_{Pu,Ga}) = -7.3 \pm 0.5$) is deduced from the results and is a basis of assessing the potential for using liquid metals in pyrochemical separation of actinides and lanthanides. Evaluation of literature data for Al, Bi and Cd suggests that Ga is most favorable for selective separation of Pu from Ce near 1073 K.

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1. Introduction

Pyrochemical separations, involving molten salt and molten metal media, by liquid/liquid extraction or electrorefining, are important for nuclear defence and civil applications [1–3]. Both are concerned with actinide separation. Lanthanides, such as cerium, are often used as surrogates. Early steps of a pyrochemical processes development consist of studying the molten salt chemistry of the elements to be separated. Activity coefficients of the solute in liquid metal and salt phases are important thermochemical parameters for predicting separation efficiency and assessing effects of the solvent. Plutonium and cerium activity coefficients in liquid gallium metal have been studied at CEA/Valduc in the frame of developing advanced pyrochemical process for recycling of scrap plutonium.

Many studies have been conducted on plutonium in molten chlorides salt by electrochemical methods [4–10] and activity coefficients in molten salts have been calculated. The activity coefficients of plutonium in metal phase have been determined in several metals (Al, Bi, Zn, Cd) [11].

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Electrochemical measurements have been performed on liquid gallium containing dilute metallic cerium and plutonium at 1073 K to study their behaviour and to obtain activity coefficients. Suitability of several metal phases is evaluated based on activity coefficient of cerium and plutonium and on consequences for separation efficiency.

2. Experimental

In all experiments, the feed chlorides, $CaCl_2$, NaCl and KCl (ACS reagents) were heated at 200 °C under vacuum during 5 days to remove water [12]. Pure commercial gallium and cerium metals and pure plutonium (>99.9%) metal pieces (prepared at CEA/Valduc) were used to prepare Ga/Pu or Ga/Ce alloys. Ce(III) was introduced in the molten salt in the form of $CeCl_3$ (MERCK). Pu(III) was introduced by anodic oxidation at applied potential of Pu metal.

The experimental cell is described in Fig. 1. The chlorides, equimolar NaCl–KCl mixture or $CaCl_2$ and the metal were melted in a magnesia crucible placed in a stainless steel inside a furnace under dry argon at atmospheric pressure. The reference electrode was made of a silver wire (1 mm diameter) dipped into a porous alumina tube containing a solution of silver chloride in the corresponding chloride ($0.75\ \mathrm{mol\,kg^{-1}}$). A tungsten wire was used as counter electrode. The working electrode is made of liquid gallium. Gallium is introduced in the bottom of the crucible and the contact is made with a tungsten wire isolated from the molten salt using an alumina tube and magnesia cement. Cyclic voltammograms were recorded using an AUTOLAB PGSTAT30 potentiostat coupled with a PC computer.

The potential of the redox system Cl_2/Cl^- was previously determined by cyclic voltammetry on a tungsten working electrode against the reference electrode (AgCl/Ag) and found equal to 1.05 V/Ref. Thus, all the potential values can be given against the redox system Cl_2/Cl^- in order to compare with the potentials given in the literature. Then, in this paper, all the potential values are related to the Cl_2 (0.1 MPa)/Cl^- redox system. Thermodynamic calculations of Gibbs enthalpy leading to standard redox potentials determination were performed using the database and software HSC Chemistry for Windows version 4.0 created by Woutokumpu (Finland).

3. Results and discussion

3.1. EMF measurements and activity coefficient of cerium in liquid gallium

A study of cerium in liquid gallium has been conducted in order to test the experimental set-up and compare our results with the literature values [11] before studies were conducted with plutonium. The activity coefficient of cerium in liquid gallium was determined by EMF measurements. This method was already implemented for the determination of the activity coefficient of gadolinium in liquid gallium [13]. ΔE_{exp} measurement (described in Fig. 1) is obtained by measuring the potential between the working electrode (liquid gallium containing various amounts of metallic Ce) and the reference electrode (AgCl/Ag). In the present purpose, the electrochemical cell (given in Fig. 1) is

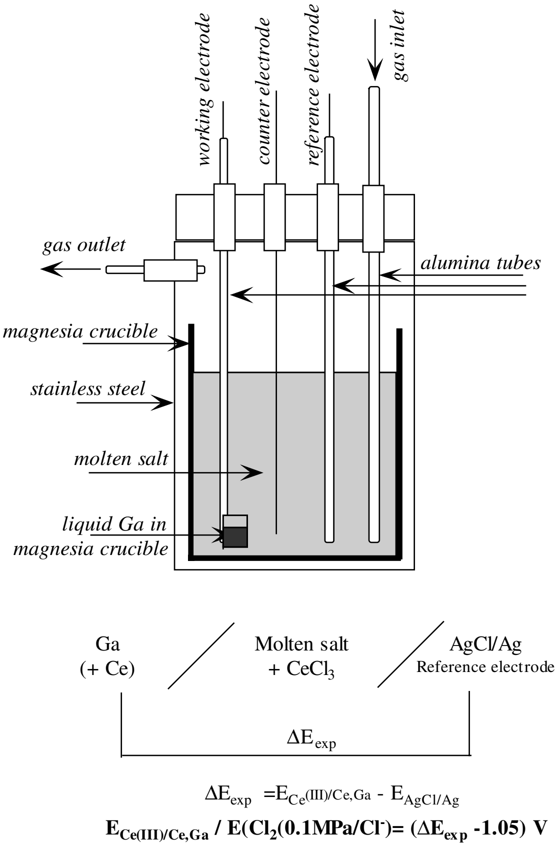

Fig. 1. Electrochemical cell scheme.

Ce (in Ga)/$CeCl_3$ (in NaCl–KCl)||Ag–AgCl
(in NaCl–KCl)

The corresponding potential expression is

$$E_{\mathrm{Ce(III)/Ce,Ga}} = E^{\circ}_{\mathrm{Ce(III)/Ce}} + 2.3 * \frac{RT}{3F}\log\frac{a_{\mathrm{Ce(III)}}}{a_{\mathrm{Ce,Ga}}}. \tag{1}$$

$E^{\circ}_{\mathrm{Ce(III)/Ce}}$ is the standard redox potential of Ce(III)/Ce system, $a_{\mathrm{Ce(III)}}$ is the activity of Ce(III) dissolved in the molten salt and $a_{\mathrm{Ce,Ga}}$ the activity of metallic cerium in liquid gallium ($R = 8.32\ \mathrm{J\,mol^{-1}\,K^{-1}}$, $T = 1073$ K and $F = 96\,500\ \mathrm{°C\,mol^{-1}}$).

Since $a(i) = \gamma(i) * x(i)$ with $\gamma(i)$ defining the activity coefficient and $x(i)$ defining the mole fraction of element (i), (1) becomes

$$E_{\mathrm{Ce(III)/Ce,Ga}} = E^{\circ}_{\mathrm{Ce(III)/Ce}} + 2.3 * \frac{RT}{3F} \log \frac{\gamma_{\mathrm{Ce(III)}} * x_{\mathrm{Ce(III)}}}{\gamma_{\mathrm{Ce,Ga}} * x_{\mathrm{Ce,Ga}}}. \tag{2}$$

The standard redox potential value of Ce(III)/Ce and the activity coefficient of Ce(III) have been previously determined by Levelut [14] in equimolar NaCl–KCl.

$E^{\circ}_{\mathrm{Ce(III)/Ce}} = -2.748$ V and $\log(\gamma_{\mathrm{Ce(III)}}) = -3.7$. Since the experimental mole fraction of Ce(III) is 7.14×10^{-3}, the potential depends only on the activity of Ce in liquid gallium

$$E_{\mathrm{Ce(III)/Ce,Ga}} = -3.163 - 2.3 \frac{RT}{3F} \log(\gamma_{\mathrm{Ce,Ga}} * x_{\mathrm{Ce,Ga}}). \tag{3}$$

Electrochemical measurements have been performed with various amounts of cerium metal in liquid gallium at 1073 K. Cerium metal was adding in liquid gallium by coulometry at applied potential according to the voltammetric measurements. The voltammogram given Fig. 2 was obtained in equimolar NaCl–KCl at 1073 K before and after addition of Ce(III). The description of the curve recorded without Ce(III) is given Section 3.2. After addition of Ce(III), a current increase characterizing an electrochemical reaction, is observed at −2.7 V (II′c) and, during the reverse scan, at −2 V (II′a). Comparison the curves (a) and (b) leads us to conclude that the phenomena II′c and II′a are characteristic of the redox system Ce(III)/Ce. The oxidation limit indicated Ia is due to gallium oxidation and the cathodic limit Ic corresponds to the reduction of sodium ions into Na metal.

Additions of Ce metal in liquid gallium were performed by coulometry applying −2.4 V at the gallium working electrode in the equimolar NaCl–KCl at 1073 K containing Ce(III) ions. Two additions of metal cerium were realized and after each addition the potential of liquid Ga, $E_{\mathrm{Ce(III)/Ce,Ga}}$ was recorded to reach steady state. $\mathrm{Log}(\gamma_{\mathrm{Ce,Ga}})$ is deduced from gallium working potential measurements (3). The results are reported in Table 1 and compared to Lebedev's results [11]. The slope of $E_{\mathrm{Ce(III)/Ce,Ga}}$ vs. $\log(x_{\mathrm{Ce,Ga}})$ – equal to −0.086 – indicates that the variation obeys to the relation (3) (the theoretical value being 0.071). Our activity coefficients results of metal Ce in liquid Ga are of the same order than Lebedev's results and the small difference on $\gamma_{\mathrm{Ce,Ga}}$ corresponds to a difference of potential equal to 25 mV.

3.2. Electrochemical study of plutonium in liquid gallium at 1073 K in chloride melts

Cyclic voltammograms were recorded in $CaCl_2$ and NaCl–KCl molten salt at 1073 K containing Pu(III) at a working electrode made of liquid gallium containing Pu metal. The curves are reported respectively on Figs. 3 and 4 with the corresponding cyclic voltammograms recorded without plutonium in gallium and in molten salt.

Fig. 3 (curve (a)) presents the electrochemical window on gallium metal in $CaCl_2$ media. The limits of the electrochemical window Ia and IIc are attributed, respectively, to the oxidation of gallium metal into gallium chloride (mono or tri-chloride) and to the reduction of Ca^{2+} into calcium metal in liquid gallium. By

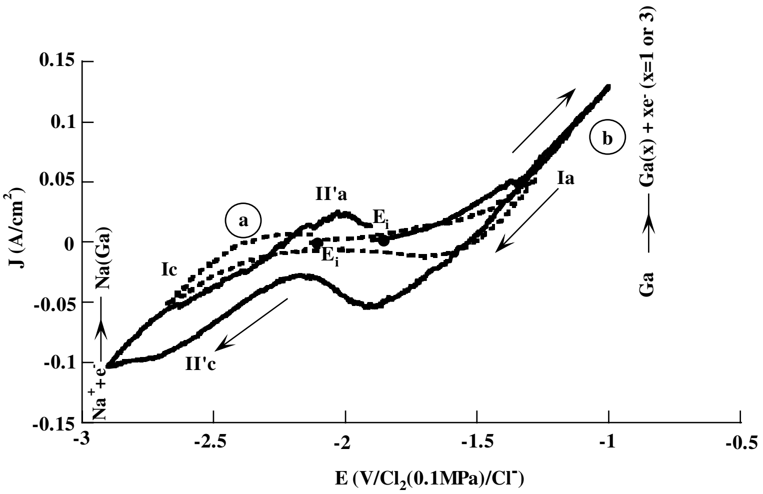

Fig. 2. Cyclic voltammograms obtained on liquid gallium working electrode at 100 mV/s in NaCl–KCl molten salt at 1073 K. Curve (a): $x_{\mathrm{Ce(III)}} = 0$. Curve (b): $x_{\mathrm{Ce(III)}} = 7.14 \times 10^{-3}$. E_i indicates the sweep initial potential value and the arrows indicate the sweep directions.

Table 1
Activity coefficient values of cerium in liquid gallium at 1073 K calculated by measuring the equilibrium potential of liquid gallium $E_{Ce(III)/Ce,Ga}$ in NaCl–KCl containing $x_{Ce(III)} = 7.14 \times 10^{-3}$ and using Eq. (3)

Molar fraction of Ce in Ga: $x_{Ce,Ga}$	$E_{Ce(III)/Ce,Ga}$ (V/Cl$_2$ (0.1 MPa)/Cl$^-$)	log($\gamma_{Ce,Ga}$)	log($\gamma_{Ce,Ga}$) Lebedev et al. [11]
6.6×10^{-3}	-2.42 ± 0.01	-8.29 ± 0.15	-7.9
8.39×10^{-3}	-2.43 ± 0.01	-8.26 ± 0.15	

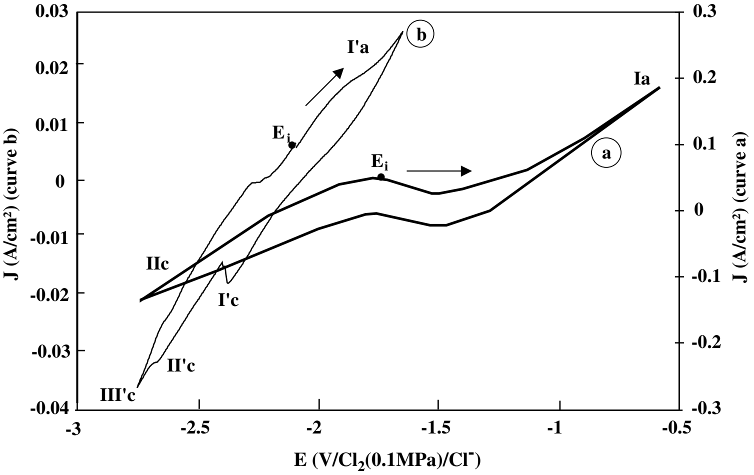

Fig. 3. Cyclic voltammograms recorded at 100 mV/s on liquid gallium in CaCl$_2$ at 1073 K. Curve (a): $x_{Pu,Ga} = 0$; $x_{Pu(III)} = 0$. Curve (b): $x_{Pu,Ga} = 0.0129$; $x_{Pu(III)} = 0.0011$. E_i indicates the sweep initial potential value and the arrows indicate the sweep directions.

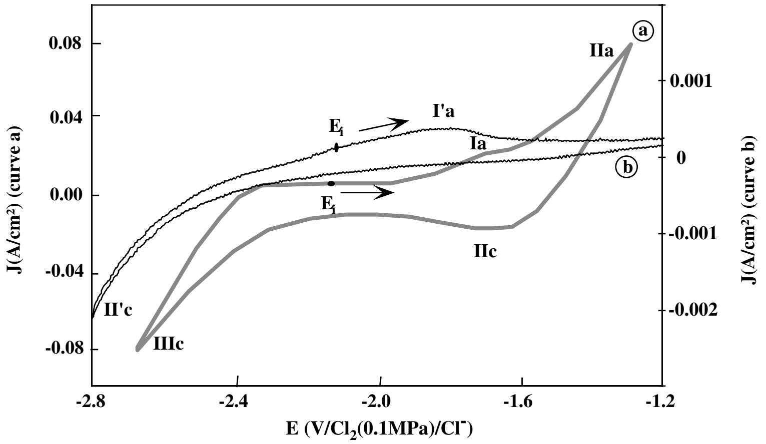

Fig. 4. Cyclic voltammograms recorded on liquid gallium at 100 mV/s in equimolar NaCl–KCl molten salt at 1073 K. Curve (a): $x_{Pu,Ga} = 0$; $x_{Pu(III)} = 0$. Curve (b): $x_{Pu,Ga} = 1.37 \times 10^{-2}$; $x_{Pu(III)} = 6.65 \times 10^{-4}$. E_i indicates the sweep initial potential value and the arrows indicate the sweep directions.

comparing curves (a) and (b), the current increases at −2 and −2.4 V indicated by I′a and I′c, were attributed, respectively, to the oxidation of plutonium metal (dissolved in liquid gallium) into plutonium trichloride and to the reduction of Pu(III), dissolved in the melt, into Pu(Ga). Another electrochemical system noted II′c, observed before the cathodic limit of the molten salt, is attributed to the formation of intermetallic Pu–Ga solid compounds on the electrode because this peak intensity is independent of plutonium trichloride concentration.

In Fig. 4, where the salt is equimolar NaCl–KCl, two anodic systems are evidenced with pure gallium (curve (a)), Ia and IIa which are attributed respectively to the oxidation of gallium metal into an adsorbed gallium mono-chloride and into gallium trichloride [15]. The system characterized by a current increase and indicated by IIIc is the reduction of sodium chloride into sodium in liquid gallium. The conditional standard potentials of the redox systems $CaCl_2$/Ca (in pure $CaCl_2$) and NaCl/Na (in equimolar NaCl–KCl media) are calculated equal to −3.28 V for the two media from thermochemical data of pure compounds and considering an activity of 0.65 for NaCl in NaCl–KCl salt [16]. By comparing these values to the reduction potentials of sodium chloride and calcium chloride into liquid gallium, we can note that the anodic depolarisation is more important with calcium chloride than for sodium chloride. This phenomenon is due to the different (Na, Ca)/Ga metal interactions in the gallium solvent described by their activity coefficients values ($\log(\gamma_{\mathrm{Ca,Ga}}) = -4.95$, $\log(\gamma_{\mathrm{Na,Ga}}) = 0.175$) [11].

In Fig. 4, in presence of plutonium dissolved in the molten salt (Pu(III)) and in the liquid gallium (Pu metal) (curve (b)), the electrochemical system, I′a, characterizes the oxidation of dissolved plutonium in gallium into plutonium trichloride. After this oxidation, gallium metal is not oxidized into gallium chloride and this is probably due to the precipitation of the plutonium chloride into plutonium sesquioxide at the surface of the liquid electrode and the formation of an oxide phase. This fact has been evidenced after the cooling by the presence of a black oxide phase on the top of gallium metal electrode. The cathodic limit of the molten salt II′c is due to the reduction of NaCl into Na.

The cyclic voltammograms obtained with Pu(III) dissolved in melt cannot be used for potential determination of the redox system Pu(III)/Pu. In $CaCl_2$ melt, the difference between the anodic and cathodic systems (I′a and I′c) is very large, indicating a no reversible system. The same observation is made in NaCl–KCl melt in which the cathodic system does not even appear in the electrochemical window. So we can not deduce some characteristic potential values from these voltammograms.

In order to obtain equilibrium potential values, current–potential steady state were deduced from chronoamperograms measurements. The potential domain considered is ranging between −2.2 and −1.6 V. Measurements are performed every 50 mV. A constant potential is applied at the working electrode during 20 s. During the same time, the current response is recorded corresponding to chronoamperogram curves. For one potential value, several current values can be obtained from the chronoamperogram curves at various sample times (for instance 1, 2, 10 and 20 s). The current–potential curves deduced from these measurements so obtained are reported in Fig. 5 for $CaCl_2$ at 1073 K and in Fig. 6 for the equimolar NaCl–KCl at 1073 K. The sample time for current measurement do not modify the shape of the curves. The difference between long and short sample times is the current intensity which decreases when the time increases. Steady state is reached for the longer sample times. The curves in Figs. 5 and 6 present an anodic wave Ia before the anodic limit IIa. These redox systems are attributed to the oxidation of plutonium metal (dissolved in liquid gallium) into plutonium trichloride and to the oxidation of gallium metal into gallium mono or tri-chloride. In

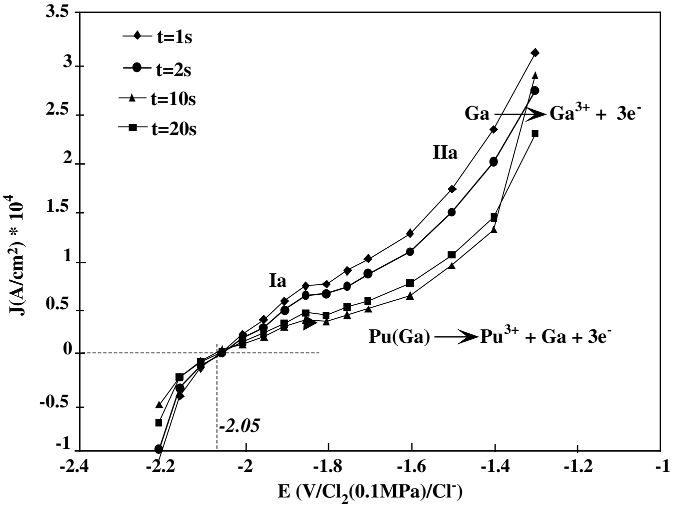

Fig. 5. Steady-state current–potential curves deduced from chronoamperograms realized in $CaCl_2$ at 1073 K. $x_{\mathrm{Pu,Ga}} = 0.0129$; $x_{\mathrm{Pu(III)}} = 0.0011$.

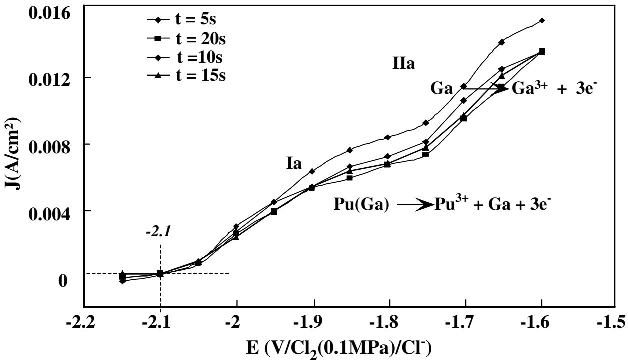

Fig. 6. Steady-state current–potential curves deduced from chronoamperograms realized in equimolar NaCl–KCl at 1073 K. $x_{\mathrm{Pu,Ga}} = 0.0137$; $x_{\mathrm{Pu(III)}} = 6.65 \times 10^{-4}$.

this case, no plutonium oxide was observed at the gallium surface.

The equilibrium potential at zero current $E_{\mathrm{Pu(III)/Pu,Ga}}$ can be deduced from these measurements (as indicated Figs. 5 and 6). This potential is fixed by the redox system Pu(III)/Pu, Ga and its expression is

$$E_{\mathrm{Pu(III)/Pu,Ga}} = E^{\circ}_{\mathrm{Pu(III)/Pu}} + \frac{2.3RT}{3F}\log\frac{a_{\mathrm{Pu(III)}}}{a_{\mathrm{Pu,Ga}}}, \tag{4}$$

with $a_{\mathrm{Pu(III)}}$ defining the activity of Pu(III) in the molten salt and $a_{\mathrm{Pu,Ga}}$ the activity of Pu metal in Ga metal. The activity coefficient of plutonium in gallium metal can be expressed by the following relation:

$$E_{\mathrm{Pu(III)/Pu,Ga}} = E^{\circ\prime}_{\mathrm{Pu(III)/Pu}} + \frac{2.3RT}{3F}\log\frac{x_{\mathrm{Pu(III)}}}{x_{\mathrm{Pu,Ga}}} - \frac{2.3RT}{3F}\log\gamma_{\mathrm{Pu,Ga}}. \tag{5}$$

In this expression, $E^{\circ\prime}_{\mathrm{Pu(III)/Pu}}$ is the conditional standard potential of plutonium chloride in chloride media and its expression is

$$E^{\circ\prime}_{\mathrm{Pu(III)/Pu}} = E^{\circ}_{\mathrm{Pu(III)/Pu}} + \frac{2.3RT}{3F}\log\gamma_{\mathrm{Pu(III)}}. \tag{6}$$

$E^{\circ\prime}_{\mathrm{Pu(III)/Pu}}$ was previously calculated by experimental measurements [17] and is equal to −2.51 V in CaCl$_2$ and −2.54 V in NaCl–KCl molten salt at 1073 K. Then, the activity coefficient of plutonium in liquid gallium can be calculated using relation (5). The equilibrium potential $E_{\mathrm{Pu(III)/Pu,Ga}}$ is measured on the current–potential curves given Figs. 5 and 6. Uncertainties sources on measured voltages are due to potentiostat precision (1 mV) and graph measurement accuracy. We estimate the total uncertainties on measurement voltage equal to 0.01 V. The obtained results are reported on Table 2. The activity coefficients of plutonium obtained with two different molten chlorides are of the same order and that shows that the coefficient activity of plutonium in gallium is independent of selected molten chlorides.

3.3. *Influence of metal phase*

In order to point out the influence of metal solvent in a separation process and especially on the difference of potential (i.e. electrochemical selectivity) between an actinide and a lanthanide (for example plutonium and cerium), we have calculated the consequence on the electrochemical selectivity by using our present results on plutonium and cerium in liquid gallium and the published values for aluminium, bismuth and cadmium.

The equilibrium potentials of a redox couple Me(III)/Me (Pu(III)/Pu or Ce(III)/Ce) in a molten salt with a metallic solvent (M) can be written as follows:

$$E_{\mathrm{Me(III)/Me,M}} = E^{\circ}_{\mathrm{Me(III)/Me}} + \frac{b}{3}\log\left(\frac{\gamma_{\mathrm{Me(III)}}\cdot x_{\mathrm{Me(III)}}}{\gamma_{\mathrm{Me,M}}\cdot x_{\mathrm{Me,M}}}\right). \tag{7}$$

Table 2
Values of activity coefficient of plutonium metal in liquid gallium calculated from measurements performed in CaCl$_2$ and in equimolar NaCl–KCl mixture at 1073 K using the equilibrium potential deduced from the chronoamperometry study and Eq. (5)

Molten salt	Molar fraction of Pu(III) in the molten salt: $x_{\mathrm{Pu(III)}}$	Molar fraction of Pu in Ga: $x_{\mathrm{Pu,Ga}}$	(V/Cl$_2$ (0.1 MPa)/Cl$^-$)		Activity coefficient of Pu in liquid Ga: log($\gamma_{\mathrm{Pu,Ga}}$)
			$E_{\mathrm{Pu(III)/Pu,Ga}}$	$E^{\circ\prime}_{\mathrm{Pu(III)/Pu,Ga}}$	
CaCl$_2$	1.1.10^{-3}	0.0129	−2.05 ± 0.01	−2.51 ± 0.01	−7.5 ± 0.3
NaCl–KCl	6.65.10^{-4}	0.0137	−2.12 ± 0.01	−2.54 ± 0.01	−7.2 ± 0.3

$E^{\circ}_{\mathrm{Me(III)/Me}}$ is the standard potential (deduced from the standard free energy of formation), b is the constant 2.3(RT/F), $\gamma_{\mathrm{Me(III)}}$ and $x_{\mathrm{Me(III)}}$, respectively, are the activity coefficient and the molar fraction of dissolved metal chloride in the melt and $\gamma_{\mathrm{Me,M}}$ and $x_{\mathrm{Me,M}}$, respectively, are the activity coefficient and the molar fraction of metal in the metallic solvent.

The potential value of $E_{\mathrm{Me(III)/Me,M}}$ depends on the ratio of mole fractions of Me(III) in molten salt over Me in liquid metal. In the same way, this ratio will be fixed under applied potential according to relation (7). Then, we can calculate as a function of potential, the extraction efficiency, μ(Me) defined as the ratio $\frac{x_{\mathrm{Me,M}}}{x_{(\mathrm{Me})_i}}$ for Pu and Ce in several metal solvents, $x_{(\mathrm{Me})_i}$ being the initial molar fraction of Me(III) in the molten salt. The following relation is derived from (7):

$$\log\frac{x_{\mathrm{Me(III)}}}{x_{\mathrm{Me,M}}} = \frac{3}{b}\left(E_{\mathrm{Me(III)/Me,M}} - E^{\circ\prime}_{\mathrm{Me(III)/Me}}\right) + \log\gamma_{\mathrm{Me,M}} = \varphi(\mathrm{Me}). \tag{8}$$

$E^{\circ\prime}_{\mathrm{Me(III)/Me}}$ is the conditional standard potential of Me(III)/Me redox system in the molten salt considered

$$E^{\circ\prime}_{\mathrm{Me(III)/Me}} = E^{\circ}_{\mathrm{Me(III)/Me}} + \frac{2.3RT}{3F}\log\left(\gamma_{\mathrm{Me(III)}}\right). \tag{9}$$

If we consider an extraction cell containing quantities of molten salt and liquid metal chosen to have $n_{\mathrm{MS}} = n_{\mathrm{LM}}$, n_{MS} being the number of mole of molten salt and n_{LM} the number of mole of liquid metal.

In these conditions, $x_{(\mathrm{Me})_i} = x_{\mathrm{Me(III)}} + x_{\mathrm{Me,M}}$, and we have

$$\frac{x_{(\mathrm{Me})i} - x_{\mathrm{Me,M}}}{x_{\mathrm{Me,M}}} = \frac{x_{(\mathrm{Me})i}}{x_{\mathrm{Me,M}}} - 1 = 10^{\varphi(\mathrm{Me})} \tag{10}$$

and then

$$\mu(\mathrm{Me}) = \frac{x_{\mathrm{Me,M}}}{x_{(\mathrm{Me})i}} = \frac{1}{10^{\varphi(\mathrm{Me})} + 1}. \tag{11}$$

When the ratio μ(Me) is equal to 1, the extraction is complete. The selectivity α(Me1/Me2) is defined as

$$\alpha(\mathrm{Me1/Me2}) = \frac{x_{\mathrm{Me1,M}}/x_{\mathrm{Me1(III)}}}{x_{\mathrm{Me2,M}}/x_{\mathrm{Me2(III)}}} = \frac{\mu(\mathrm{Me1})/(1-\mu(\mathrm{Me1}))}{\mu(\mathrm{Me2})/(1-\mu(\mathrm{Me2}))}. \tag{12}$$

We have studied the possibility of an electrochemical separation and extraction of Pu from a molten chloride salt containing both Pu(III) and Ce(III). To do that, we have calculated the values of μ(Pu), μ(Ce) and the selectivity α(Pu/Ce) considering several metallic solvents (Ga, Cd, Al and Bi). The data used for calculations are given in Table 3. Fig. 7 presents the variation of μ(Pu) and μ(Ce) as a function of applied potential. In all cases, Pu(III) is reduced at a potential higher than Ce(III) making possible the extraction of Pu. The selectivity depends on the potential difference between the two redox systems. Increasing the difference increases the selectivity. We have calculated the gap ΔE_{M} between plutonium and cerium potentials for each metal solvent corresponding to an extraction of 50% (or μ(Me) = 0.5) as indicated in Fig. 7. In this case, the term φ(Me) is equal to zero and the relation used for ΔE_{M} calculation is

$$\Delta E_{\mathrm{M}} = E_{\mathrm{Pu(III)/Pu,M}} - E_{\mathrm{Ce(III)/Ce,M}}, \tag{13}$$

$$\Delta E_{\mathrm{M}} = E^{\circ\prime}_{\mathrm{Pu(III)/Pu,M}} - E^{\circ\prime}_{\mathrm{Ce(III)/Ce,M}} + \frac{b}{3}\log\frac{\gamma_{\mathrm{Ce,M}}}{\gamma_{\mathrm{Pu,M}}}. \tag{14}$$

The results of these calculations are presented in Table 4. It appears that the highest selectivity can be obtained by the use of a solid cathode (in which the activity of the extracted metal is equal to one). By comparing liquid metals, the best results are obtained using liquid gallium and the worst ones using liquid cadmium. Fig. 8 (left scale) which shows the selectivity α(Pu/Ce) calculated for the four liquid metals confirms this conclusion and we can sort the different liquid metal by the $\alpha(\mathrm{Pu/Ce})_{\mathrm{M}}$ value such as

$$\alpha(\mathrm{Pu/Ce})_{\mathrm{Ga}} > \alpha(\mathrm{Pu/Ce})_{\mathrm{Al}} > \alpha(\mathrm{Pu/Ce})_{\mathrm{Bi}} > \alpha(\mathrm{Pu/Ce})_{\mathrm{Cd}}. \tag{15}$$

Besides its high selectivity, the use of liquid gallium is very interesting because the difference between reduction

Table 3
Activity coefficient values of Pu and Ce in various liquid metals used in the calculation of the extraction efficiency and selectivity

	Pu	Ce	Na
$\log\gamma_{\mathrm{Me(III)}}$ in NaCl–KCl at 1073 K	−0.507 [17]	−3.7 [12]	0.121 [16]
$E^{\circ\prime}_{\mathrm{Me(III)/Me}}$	−2.54 ± 0.01 [17]	−3.01 [12]	−3.20 [16]
$\log\gamma_{\mathrm{Me,Ga}}$ in Ga	−7.3 ± 0.3*	−8.27*	0.268 [11]
$\log\gamma_{\mathrm{Me,Bi}}$ in Bi	−6.24 [11]	−8.3 [11]	−0.0105 [11]
$\log\gamma_{\mathrm{Me,Al}}$ in Al	−4.94 [11]	−6.27 [11]	
$\log z\gamma_{\mathrm{Me,Cd}}$ in Cd	−1.74 [11]	−4.6 [18]	−2.7 [11]

∗: this work.

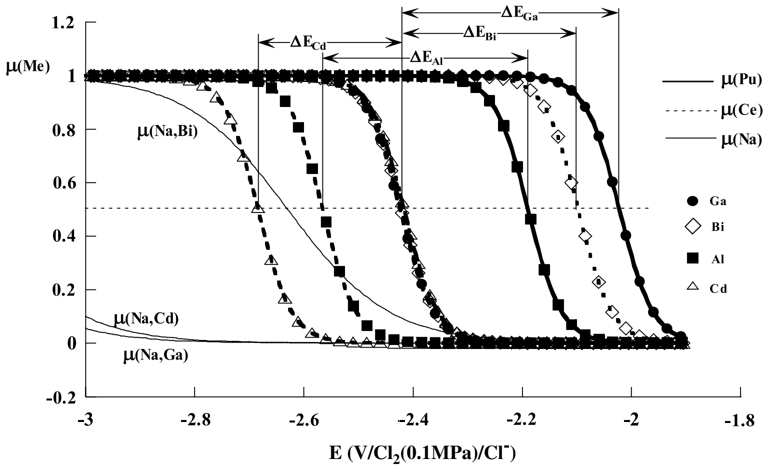

Fig. 7. Extraction efficiency $\left(\mu(\mathrm{Me}) = \frac{x_{\mathrm{Me,M}}}{x_{(\mathrm{Me})i}}\right)$ of plutonium, cerium and sodium calculated for various metal solvents (Ga, Al, Bi and Cd) in NaCl–KCl at 1073 K as a function of potential.

Table 4
Calculation (using relation (14)) of ΔE_{M} potentials corresponding to an extraction of Pu and Ce equal to 50% in different metal solvents and on solid electrode

	Electrode material	$E_{\mathrm{Pu(III)/pu,M}}$	$E_{\mathrm{Ce(III)/Ce,M}}$	ΔE_{M}
Liquid metal electrodes	Ga	−2.02 ± 0.01	−2.42 ± 0.01	0.40 ± 0.01
	Al	−2.19 ± 0.01	−2.56 ± 0.01	0.37 ± 0.01
	Bi	−2.10 ± 0.01	−2.42 ± 0.01	0.32 ± 0.01
	Cd	−2.42 ± 0.01	−2.68 ± 0.01	0.26 ± 0.01
Solid electrode	W	−2.54 ± 0.01	−3.01 ± 0.01	0.47 ± 0.01

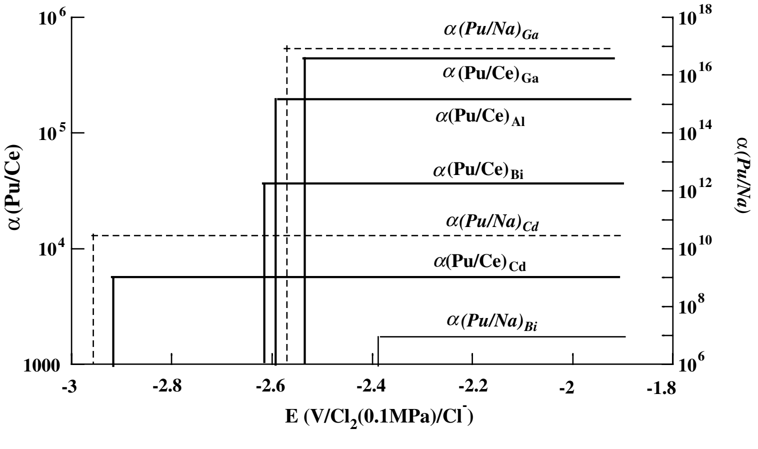

Fig. 8. Extraction selectivity calculated for various metal solvents (Ga, Al, Bi and Cd) in NaCl–KCl at 1073 K as a function of potential. Left scale: α(Pu/Ce). Right scale: α(Pu/Na).

potentials of Pu(III)/Pu and Na(I)/Na redox systems which is higher than in the other liquid metals. That can be calculated using activity coefficients of NaCl in NaCl–KCl molten salt at 1073 K [16] and activity coefficients of metallic Na in Ga, Cd and Bi determined by Lebedev [11] (Table 3). To our knowledge, the value in

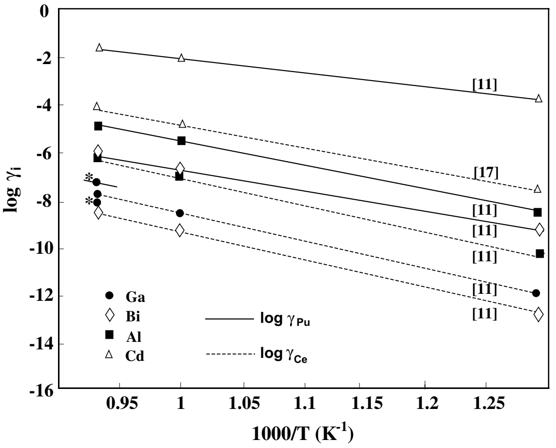

Fig. 9. Temperature dependence of activity coefficients of Pu in Bi, Cd, Al and Ga. ∗: this work.

Al has never been reported in the literature. The variations of μ(Na) and α(Pu/Na) in Ga, Cd and Bi reported respectively in Figs. 7 and 8 (right scale) as a function of potential, show the possibility to use Ga to extract Pu from NaCl–KCl at 1073 K with a potential control to prevent extraction of Ce and Na. Bi and Cd are not good candidates because sodium is extracted in Bi and Ce is extracted in Cd at too high potential values to obtain extraction of pure Pu.

Fig. 9 shows the reported activity coefficients of plutonium and cerium in different metals as a function of temperature. The dependence of the activity coefficients of plutonium and cerium in each metal is important. The selectivity depends on the gap between activity coefficients: the selectivity increases as the gap decreases. For a high temperature, the use of liquid gallium is better than aluminium, bismuth, or cadmium. At a low temperature (around 873 K) we can see that the electrochemical selectivity between plutonium and cerium in cadmium and in bismuth decreases, for aluminium it is slightly the same. The activity coefficient of plutonium in liquid gallium at low temperature is not available yet, so we can not conclude for gallium at this temperature.

These assessments of the separation efficiency show the importance of knowing fundamental data such as activity coefficients and standard redox potential values. These results permit thermodynamic evaluation of separation process before experiments are made.

4. Conclusion

Electrochemical investigations on plutonium and cerium in liquid gallium molten chlorides have been carried out. Gallium can be used as solvent metal for pyrochemical process involving these two elements at 1073 K. The extraction of plutonium in a liquid gallium cathode is possible with a careful control of cathode potential to prevent metal chloride melt reduction.

Activity coefficients of cerium and plutonium in gallium have been deduced from these electrochemical studies. By comparing with other solvent liquid metal such as Cd, Bi, Al, gallium seems to be the most favorable for Pu/Ce separation. For economic reasons, aluminium appears to be good choice for large-scale applications.

In fact, as the gap between plutonium and cerium redox couples is smaller in presence of a solvent metal than without, none of these solvent metals is a real asset for the selectivity of their separation on the thermochemical point of view. Because the melting points of plutonium and cerium are respectively 914 and 1071 K, it is not realistic to use a solid cathode for a separation process achieved at 1073 K, because electrodeposited Pu (or Ce) will probably flow in the bottom of the cell. For these elements, the use of liquid solvent metal is very interesting to trap the elements in a liquid phase.

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