ABSTRACT

Cadmium and bismuth metal are mostly used as solvent in nuclear pyrochemical processes and especially in actinides/lanthanides separations. Gallium metal has been chosen because no literature values are available with plutonium and its regeneration by refining at low temperature is possible. Electrochemical window of gallium metal and activity coefficient of plutonium in gallium have been determined by using potentiometric method. Secondly, the electrochemical properties of plutonium have been studied in molten equimolar NaCl/KCl and CaCl$_2$ at 1073K by cyclic voltammetry. The standard potentials of Pu(III)/Pu redox couple, respectively, -2.54 V and -2.51 V, led to the calculation of the activity coefficients of Pu(III). In CaCl$_2$ the complexation of Pu(III) ions is lower and the voltage gap between Pu(III)/Pu couple and the solvent limit is higher. The new data on plutonium electrochemistry in molten chlorides and liquid gallium media combined with literature data on lanthanides suggest that gallium can be a good solvent metal for pyrochemistry separation.

INTRODUCTION

Pyrochemical separations from molten salts media with metal solvent by liquid/liquid extraction or electrorefining are commonly used for the reprocessing of nuclear spent fuels [1, 2] and plutonium [3, 7]. A good knowledge of the molten salts plutonium chemistry is essential to develop separation process. Activity coefficients of the solute in liquid metal and salt phases are important thermochemical parameters for predicting separation efficiently and to assess the solvents influence. Plutonium activity coefficient in liquid gallium metal phase has been studied at CEA/Valduc in the frame of advanced pyrochemical process development for plutonium scraps recycling. Many studies have been carried out on the plutonium in molten chlorides salts (in particular in LiCl-KCl) by EMF measurements, chronopotentiometry and voltammetry [4-6]. Few studies have been performed on plutonium in NaCl [8], KCl [9] and in NaCl-KCl mixture [10]. In order to compare with previous results [10], we have determined the standard potential of Pu(III)/Pu in the equimolar NaCl-KCl at 1073K by cyclic voltammetry.
Then, a study of standard potential of Pu(III)/Pu in CaCl₂ has been performed at 1073K. The activity coefficients of plutonium in metal phase have been determined in several metals (Al, Bi, Zn, Cd) [11].

An electrochemical study has been performed on liquid gallium with dilute plutonium at 1073K to assess their behavior and to obtain activity coefficients. Then, a comparison of several metal phases based on activity coefficient of cerium and plutonium and consequences on separation efficiency is proposed.

**EXPERIMENTAL**

In all experiments, the feed chlorides, CaCl₂, NaCl and KCl (ACS reagents) were heated at 200°C under vacuum during 5 days to remove water [12]. Pure commercial gallium and cerium metal and plutonium metal pieces prepared at CEA/Valduc were used to prepare Ga/Pu or Ga/Ce alloys.

The chlorides, equimolar NaCl/KCl mixture or CaCl₂ 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 mol.kg⁻¹). Two 1 mm diameter tungsten wires were used as working and counter electrodes respectively. Electrode active surface was calculated after determination of the electrode immersion depth. Cyclic voltammograms were recorded using an AUTOLAB PGSTAT30 potentiostat coupled with a PC computer.

**RESULTS AND DISCUSSION**

Electrochemical window of chlorine solvent salt

The electrochemical windows in NaCl-KCl and CaCl₂ have been studied using metallic tungsten and vitreous carbon working electrodes. Cyclic voltammograms of equimolar NaCl-KCl at 1000K on tungsten and vitreous carbon electrodes are reported on Figure 1. On vitreous carbon, two redox systems (I and II) are observed at about 0 V and -2.8 V vs. chlorine reference electrode. These redox systems are respectively the oxidation of chlorine ion into chlorine gas and the sodium chloride reduction in carbon with depolarisation [13]. On tungsten electrode, the potential reduction of Na⁺ into Na is equal to -3.28 V (peak III’c). This potential is in good agreement with the decomposition potential of NaCl in NaCl-KCl at 1000K obtained from the standard free energy of NaCl formation (ΔG°(NaCl)=320.217 KJ.mol⁻¹) and the activity of NaCl in NaCl-KCl (aNaCl=0.65) [14] at 1000K.

Figure 2 exhibits a cyclic voltammogram obtained in the molten CaCl₂ on tungsten electrode. In the anodic side, redox systems Ia and IIa correspond respectively to the oxidation of tungsten electrode and the oxidation of chlorine ion in chloride gas. The potential of tungsten electrode oxidation in NaCl-KCl and CaCl₂ are quite similar and is equal to -0.5 V/Cl₂(1atm),Cl⁻ (peak II’a on Figure 1 and peak Ia on Figure 2). In the...
cathodic region, two peaks I\'c and II\'c are observed. They can be attributed to the reduction of Ca\(^{2+}\) into an intermediate specie (Ca\(^+\) or Ca\(^{2+}\)) and into metallic calcium. Several authors have mentioned the existence of this phenomena [15, 16, 17]. Recently, G. Chen and D. Fray have attributed the intermediate reduction wave to the reduction of Ca\(^{2+}\) into CaC\(_2\) on a carbon electrode [18]. In molten CaCl\(_2\) at 1000K, the electrochemical window is equal to 3.1 V. This value is of the same order that G. Chen results [18] but is smaller than the value obtained from the standard free potential of formation of CaCl\(_2\) (3.27 V).

Figure 1: Cyclic voltammograms in equimolar NaCl-KCl at 1000K, scan rate: 0.1 V/s.

Figure 2: Cyclic voltammograms in CaCl\(_2\) at 1000K scan rate: 0.1 V/s.
Cyclic voltammograms of plutonium trichloride in equimolar NaCl-KCl and CaCl₂ at 1073K were recorded on tungsten electrode (Figure 3 and Figure 4). In NaCl-KCl, Figure 3 shows two cathodic peaks Ic and Iic at potential respectively equal to -2.8V and -2.9V. Many studies have demonstrated the plutonium (III) reduction into plutonium metal in one step. So, the cathodic peaks Ic and Iic have been attributed respectively to the reduction of Pu(III) into Pu and the reduction of Na⁺ into Na. The reduction potential of Na⁺ (peak Iic) is higher than without Pu(III) (Figure 1). This potential increase can be attributed to the presence of plutonium metal on the electrode before the Na⁺ reduction (aNa is not equal to 1) or to the presence of a complex anion in the melt, eg PuCl₆³⁻, that changes the acidity of the melt and probably the activity of the NaCl. In NaCl-KCl, the reduction potential of Pu(III) is near the reduction of Na⁺. This fact confirms the observation of L. McCurry et al. [19] that addition of sodium chloride (6 %mol) in a KCl melt decreases the voltage separation between plutonium reduction and melt limit (sodium reduction). The voltage separation between the plutonium (III) reduction and the KCl reduction is equal to 0.4 V and in KCl-NaCl (6% mol.), this difference is about 0.2 V (with the sodium chloride reduction). Consequently, it is difficult to distinguish the plutonium trichloride reduction and the sodium reduction.

Figure 4 shows a typical cyclic voltammogram of Pu(III) in CaCl₂ at 1073K on tungsten electrode. With the background cyclic voltammogram, we can see that one well-defined system (Ia/Ic) appears near the calcium chloride reduction (IIC). In this case, the difference between the plutonium trichloride reduction and the calcium chloride reduction allowed us to distinguish the two phenomena.

The value of the Pu(III)/Pu redox potential has been estimated from the results of cyclic voltammetric studies in equimolar NaCl-KCl and CaCl₂ at 1073K. The equilibrium potential, $E_{eq}$ was approximated from the zero current intercepts of the reverse scans of the cyclic voltammetry [20] and led us to calculate the standard potential $E^{0}_{Pu(III)/Pu}$ (using the relation $E_{eq} = E^{0}_{Pu(III)/Pu} + \frac{RT}{2F} \ln [Pu(III)]$). The obtained results have been summarized in Table 1 and compared to those previously determined. We can see that our potential determination of Pu(III)/Pu in NaCl-KCl is of the same order as that of O. Skiba et al. results [10]. In order to compare the standard potential in the NaCl-KCl and CaCl₂ melt, we have calculated the activity coefficient of Pu(III).
Figure 3: Cyclic voltammogram for plutonium trichloride in equimolar NaCl-KCl at 1073K, scan rate 0.1V/s, S=0.31 cm², $X_{PuCl3}=1.05 \times 10^{-3}$

Figure 4: Cyclic voltammogram for plutonium trichloride in CaCl₂ at 1073K, scan rate 0.1V/s, $X_{PuCl3}=1.1 \times 10^{-3}$, surface area=0.31 cm²
Table 1: Values of standard potential of Pu(III)/Pu in various molten chloride mixture at 1073K, (V/Cl₂⁻/Cl⁻, mole fraction scale)

| Molten chlorides | Skiba et al. | R. Benz et al. | This work |
|------------------|--------------|----------------|-----------|
| NaCl-KCl         | -2.585 [10]  | -2.54          |           |
| NaCl             | -2.513 [10]  | -2.393 [8]     |           |
| KCl              | -2.605 [10]  | -2.381 [9]     |           |
| CaCl₂            | -2.51        |                |           |

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

Cyclic voltammetry of plutonium metal dissolved in liquid gallium with CaCl₂ and NaCl/KCl are reported respectively on Figure 5 and Figure 6 with their corresponding cyclic voltammetry background (without plutonium in gallium). The figure 5 (curve (a)) represents the electrochemical window on gallium metal in CaCl₂ media. The peaks Ia and IIC are attributed respectively to the oxidation of gallium metal into gallium chloride (mono or trichloride) and to the reduction of Ca²⁺ into calcium metal in liquid gallium. By comparing the curve (a) and (b), the peaks I'a and I'c can be attributed respectively to the oxidation of plutonium metal (dissolved in liquid gallium) into plutonium trichloride and to the reduction of Pu(III) into Pu(Ga). The peak II'c is attributed to the formation of intermetallic Pu-Ga solid compounds on the electrode because this peak is independent of plutonium trichloride concentration.

On figure 6, where the salt is equimolar NaCl/KCl, two anodic peaks are evidenced with pure gallium (curve (a)), Ia and IIa and are attributed respectively to the oxidation of gallium metal into an adsorbed gallium mono-chloride and into gallium trichloride [22]. The peak IIIc is the reduction of sodium chloride into sodium in liquid gallium. By comparing the reduction potential of sodium chloride and calcium chloride into liquid gallium (to reduction potentials of the salt), we can note that the anodic depolarisation is more important with calcium chloride than for sodium chloride. This phenomenon is due to the different solvent/solute interactions in the two gallium alloys described by their activity coefficients values ($\log γ_{\text{Ca(Ga)}} = -4.95$, $\log γ_{\text{Na(Ga)}} = 0.175$) [11].

On figure 6, in presence of plutonium (curve (b)), the peak I'a represents 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 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.

Cyclic voltammetry in CaCl₂ and equimolar NaCl/KCl media evidence redox systems, that seem to be irreversible so we can not deduce some characteristic potentials on these voltammograms.

In order to obtained characteristic potential, for instance $E_{\text{pθ}}$, chronoamperograms have been obtained and are reported on I=f(E) curves at various time on figure 7 in CaCl₂.
at 1073K and on figure 8 in the equimolar NaCl-KCl at 1073K. The redox systems Ia and IIa on figure 7 and 8 are attributed to the oxidation of plutonium into plutonium trichloride and to the oxidation of gallium metal into gallium trichloride. The equilibrium potential at zero current can be deduced from these measurements, so the potential of the following galvanic cell can be obtained by using standard potential of plutonium in chloride media determined previously ($E^{\circ}_{PuCl_3/Pu} = -2.51$ V in CaCl$_2$ and $E^{\circ}_{PuCl_3/Pu} = -2.54$ V in NaCl-KCl):

$$Pu\text{(in Ga)}/PuCl_3\text{(in molten chloride)}/Pu\text{(s)} \quad [1]$$

The activity coefficient of plutonium in liquid gallium can be calculated with the following relation:

$$\Delta E = -\frac{2.3RT}{3F} \log(y_{Pu(Ga)} \cdot x_{Pu(Ga)}) \quad [2]$$

with $\Delta E$ the difference potential of galvanic cell (Eq.(1), $y_{Pu(Ga)}$ the activity coefficient of plutonium and $x_{Pu(Ga)}$ the molar fraction of plutonium in liquid gallium. The results are reported on Table 2. The activity coefficients of plutonium obtained with two molten chlorides are of the same order and that confirms that the coefficient activity of plutonium in gallium is independent of selected molten chlorides.

Figure 5: Cyclic voltammetry on liquid gallium in CaCl$_2$ at 1073K, curve (a): $x_{Pu(Ga)}=0, x_{PuCl_3}=0$, curve (b): $x_{Pu(Ga)}=0.0129, x_{PuCl_3}=0.0011$
Figure 6: Cyclic voltammetry on liquid gallium in NaCl/KCl at 1073K, curve (a): XPu(Ga)=0, XPuCl3=0, curve (b): XPu(Ga)=0.0137, XPuCl3=6.65x10^{-4}

Figure 7: Intensity-potential curve in CaCl2 at 1073K obtained from chronoamperograms, XPu(Ga)=0.0129, XPuCl3=0.0011
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 aluminum, bismuth and cadmium.

The equilibrium potentials of a redox couple $\text{Me}(\text{III})/\text{Me}$ (Pu(III)/Pu or Ce(III)/Ce) in a molten chlorides with a metallic solvent (MS) can be written as follows:

$$E_{\text{Me}} = E_{\text{Me}(\text{III})/\text{Me}}^{\text{stab}} + \frac{2.3RT}{3F} \log \left( \frac{y_{\text{Me}(\text{III}),x_{\text{Me}(\text{III})}}}{y_{\text{Me}(\text{MS}),x_{\text{Me}(\text{MS})}}} \right)$$

[3]
with $E^*_{\text{Me(III)/Me}}$ the standard potential (deduced from the standard free energy of formation), $\gamma_{\text{Me(III)}}$ the activity coefficient of metal chloride in the melt, $x_{\text{Me(III)$_{\text{melt}}$}}$ the molar fraction of metal chloride in the melt, $\gamma_{\text{Me(MS)}}$ the activity coefficient of metal in the metallic solvent and $x_{\text{Me(MS)}}$ the molar fraction of metal in the metallic solvent.

The difference of potential (electrochemical selectivity) between plutonium and cerium can be expressed as:

$$
E_{P_{u-C_{e}}} = E^*_{P_{u-C_{e}}} + \frac{b}{3} \log \left( \frac{x_{\text{Pu(III)$_{\text{melt}}$}}x_{\text{Ce(III)$_{\text{melt}}$}}}{x_{\text{Pu(III)$_{\text{melt}}$}}x_{\text{Ce(III)$_{\text{melt}}$}}} \right) + \frac{b}{3} \log \left( \frac{\gamma_{\text{Pu(MS)}}}{\gamma_{\text{Ce(MS)}}} \right)
$$

with $\Delta E^*_{P_{u-C_{e}}}$ the difference of potential of the standard potential, b the constant $2.3RT/F$.

We can observe that for final composition elements (depending on process), the electrochemical selectivity depends on the ratio of cerium and plutonium chloride activity coefficient in the melt and the cerium and plutonium activity coefficient in the metallic solvent. Cerium and plutonium chloride activity coefficients in molten salt yield information about the complexation by melt [24]. A previous study has shown by electrochemical methods that the complexation constants of Nd(III) and Am(III) in LiCl-KCl-LiF at 743K are in the same order [25]. So, we can consider that for plutonium chloride and cerium chloride (with an oxidation state equal to 3), the activity coefficients $\gamma_{\text{Pu(III)}}$ and $\gamma_{\text{Ce(III)}}$ evolve in the same order. On Figure 9 are reported the activity coefficients of plutonium and cerium in various metal and it is shown that the dependence of activity coefficient value of plutonium and cerium in metal is important.

Consequently, the electrochemical selectivity between plutonium and cerium in a molten chloride depends on the following relation:

$$
\Delta E_{(P_{u-C_{e})MS}} = \frac{2.3RT}{3F} \log \left( \frac{\gamma_{\text{Ce(MS)}}}{\gamma_{\text{Pu(MS)}}} \right)
$$

with $\gamma_{\text{Pu(MS)}}$ and $\gamma_{\text{Ce(MS)}}$ the activity coefficient plutonium and cerium in metal solvent. These values for gallium, cadmium, bismuth and aluminium are reported on Figure 10 and values of $\Delta E_{(P_{u-C_{e)})M}$ as function of temperature by using published values and our results are given in Figure 9. If the term $\Delta E_{(P_{u-C_{e})M}}$ is important (in absolute value), the electrochemical selectivity decreases. For a high temperature, the use of liquid gallium is better than aluminium, bismuth and cadmium. At a low temperature (around 873K) we can see that the electrochemical selectivity between plutonium and cerium in cadmium decreases and in aluminum increases, for bismuth 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.
Figure 9: Temperature dependence of activity coefficients of plutonium in bismuth, cadmium, aluminium [11], gallium (this work) and activity coefficients of cerium in gallium, bismuth, aluminium [11], cadmium [23].

Figure 10: Electrochemical selectivity between plutonium and cerium in gallium, cadmium, aluminium and bismuth as a function of temperature.
CONCLUSIONS

The electrochemical properties of plutonium have been studied in equimolar NaCl-KCl and pure CaCl₂ molten salts at 1073 K. The standard potential of Pu(III)/Pu in NaCl-KCl solvent salt, -2.54 V (versus Cl⁻/Cl₂) is in agreement with previous works. In more acidic melt, like CaCl₂, the standard potential is close to the reference. In NaCl-KCl media, the presence of plutonium seems to involve a decrease of the solvent limit (sodium reduction) so that the gap between Pu³⁺/Pu and Na⁺/Na couples is small.

Electrochemical investigations on plutonium in liquid gallium molten chlorides have been carried out. Gallium can be used as solvent metal for pyrochemical process involving plutonium (and cerium in our example) at 1073 K. Cyclic voltammetry demonstrated that a selective extraction of plutonium dissolved in gallium by anodic oxidation is easy. The deposition of plutonium on 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. For these elements the interest of solvent metal is to trap the elements as liquid phase.

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