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Journal of Nuclear Materials 341 (2005) 124–130
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Plutonium chemical properties in NaCl–KCl and $CaCl_2$ at 1073 K

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Received 12 July 2004; accepted 3 January 2005

Abstract

The electrochemical properties of plutonium have been studied in molten equimolar NaCl/KCl and $CaCl_2$ at 1073 K by cyclic voltammetry. The respective standard potentials of Pu(III)/Pu redox couple, −2.54 V and −2.51 V (versus Cl^-/Cl_2 reference electrode), led to the calculation of the activity coefficients of Pu(III) in each electrolyte. In $CaCl_2$ the complexation of Pu(III) ions is lower and the voltage gap between Pu(III)/Pu redox system and the solvent limit is higher. Use of these results to construct potential–pO^{2-} diagrams for plutonium at 1073 K gives a rational overview of plutonium properties in these media.

1. 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. Many studies have been carried out on 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 1073 K by cyclic voltammetry. Then, a study of standard potential of Pu(III)/Pu in $CaCl_2$ has been performed at 1073 K. The combination of published thermochemical data and our experimental measurements of Pu(III)/Pu standard potentials leads us to set up a potential–pO^{2-} diagram of plutonium in equimolar NaCl–KCl and $CaCl_2$ at 1073 K. These diagrams give an instantaneous and comprehensive view of the properties of plutonium in such media.

2. Experimental

The chlorides $CaCl_2$, NaCl and KCl were previously heated at 200 °C under vacuum during five days to

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0022-3115/$ - see front matter
doi:10.1016/j.jnucmat.2005.01.010

remove water. The salts (NaCl, KCl and $CaCl_2$ ACS Reagents) were melted in a magnesia crucible placed in a stainless steel container inside a furnace. The mixture was fused under dry argon at atmospheric pressure. The plutonium trichloride was obtained by an anodic electrolysis of plutonium metal in the molten salt. The reference electrode was made of a silver wire (1 mm diameter) dipped into a porous alumina tube containing a solution of silver chloride 0.75 mol kg^{-1} in the corresponding chloride [11]. All the potential values in this paper are related to Cl_2 (0.1 MPa)/Cl^- redox system. 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 a AUTOLAB PGSTAT30 potentiostat coupled with a PC computer.

3. Results and discussion

3.1. Electrochemical window of chloride solvent salt

The electrochemical windows in NaCl–KCl and $CaCl_2$ were studied using metallic tungsten working electrodes. Cyclic voltammogram obtained in equimolar NaCl–KCl at 1073 K on tungsten electrode is reported (Fig. 1). On tungsten electrode, an oxidation peak IIa is observed close to −0.5 V. It was attributed to an oxidation/passivation process of tungsten electrode due to tungsten oxide compound formation. The oxidation limit is characterized by the current increases (electrochemical process Ia). It corresponds to chlorine evolution. On tungsten working electrode, the reduction potential of Na^+ into Na is equal to −3.28 V (peak IIIc). This potential is in good agreement with the decomposition potential of NaCl in NaCl–KCl at 1073 K obtained from the NaCl Gibbs energy of the dissociation reaction:

$$NaCl \leftrightarrow Na + 0.5Cl_2(g)$$

$$E_{NaCl/Na} = -\frac{\Delta G^*}{F} + \frac{2.3RT}{F}\log(a_{NaCl}) = -3.276\ V, \qquad (1)$$

ΔG^* of the above reaction is calculated from the pure compounds thermochemical data ($\Delta G^* = 312366$ J [12]), a_{NaCl} is the activity of NaCl in the equimolar NaCl–KCl molten salt ($a_{NaCl} = 0.65$ [11]) and $F = 96500$ C, $R = 8.32$ J mol^{-1} K^{-1} and $T = 1073$ K. $E_{NaCl/Na}$ is the calculated NaCl/Na system redox potential related to Cl_2 (0.1 MPa)/Cl^- redox system.

Fig. 2 exhibits a cyclic voltammogram obtained in $CaCl_2$ molten salt at 1073 K on tungsten working electrode. In the anodic side, the limit IIa corresponds to the oxidation of chlorine ion in chlorine gas. An oxidation process Ia is observed just before IIa and is attributed to tungsten working electrode oxidation. The potential of tungsten oxidation in NaCl–KCl and $CaCl_2$ are quite similar and equal to −0.5 V/Cl_2 (0.1 MPa), Cl^- (Fig. 1, peak IIa and Fig. 2, peak Ia). However, tungsten oxidation in $CaCl_2$ does not lead to electrode passivation as it was observed in NaCl–KCl. That is probably due to a difference of the solubility of the oxide compounds in the two media, the solubility being much higher in $CaCl_2$ melt. In the cathodic region of Fig. 2, two peaks I′c and II″c are observed. They can be attributed to the successive reductions of Ca^{2+} into an intermediate adsorbed specie (Ca^+ or Ca_2^{2+}) and into metallic calcium. Several authors have mentioned the existence of this phenomenon [13–15]. Recently, Chen and Fray have attributed the intermediate reduction wave to the reduction of Ca^{2+} into CaC_2 on a carbon electrode [16]. In molten $CaCl_2$ at 1073 K, the electrochemical window is equal to 3.1 V. This value is of the same order that Chen reports [16], but is smaller than the one obtained from the standard free potential of formation of $CaCl_2$ equal to 3.27 V.

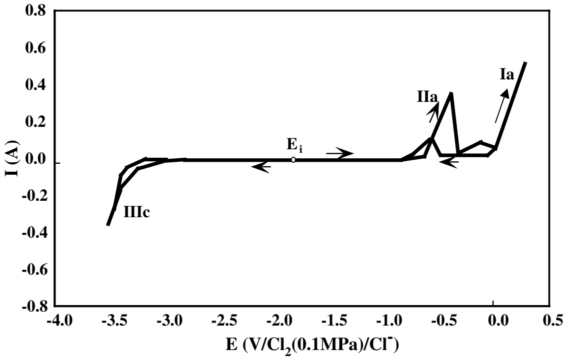

Fig. 1. Cyclic voltammogram recorded on tungsten working electrode in the equimolar NaCl–KCl molten salt at 1073 K (scan rate: 0.1 V/s, electrode surface: 0.287 cm^2).

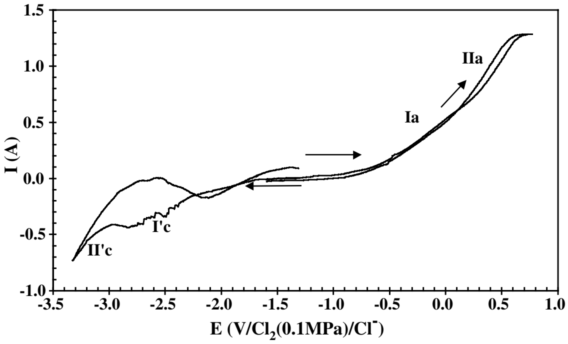

Fig. 2. Cyclic voltammogram recorded on tungsten working electrode in $CaCl_2$ at 1073 K (scan rate: 0.1 V/s, electrode surface: 1 cm^2).

3.2. Electrochemistry of plutonium(III) in NaCl–KCl and CaCl$_2$

Cyclic voltammograms were recorded on tungsten electrode in equimolar NaCl–KCl and CaCl$_2$ molten salts at 1073 K in which was introduced by coulometry under applied potential Pu(III) with a mole fraction $x_{\mathrm{Pu(III)}}$ equal to 1.05×10^{-3} and 1.1×10^{-3} (Figs. 3 and 4). In NaCl–KCl, Fig. 3 shows one cathodic peak Ic followed by the electroactivity limit IIc at potential values respectively equal to −2.8 V and −2.9 V. Many studies have demonstrated a one step reduction of Pu(III) into plutonium metal. 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 the one measured in the melt without Pu(III) (Fig. 1, peak IIIc). This potential increase can be due to the presence of plutonium metal on the electrode before Na$^+$ reduction leading to the formation of Pu–Na alloys in which the sodium activity is lower than 1. This difference can also be due to the presence of a complex anion in the melt, e.g. PuCl$_6^{3-}$, that changes the acidity of the melt and probably NaCl activity at the interface. In NaCl–KCl, the reduction potential of Pu(III) is close to the reduction of Na$^+$. That confirms the observation of McCurry and Moy [17] who observed that addition of sodium chloride (6 mol%) in a KCl melt decreases the voltage

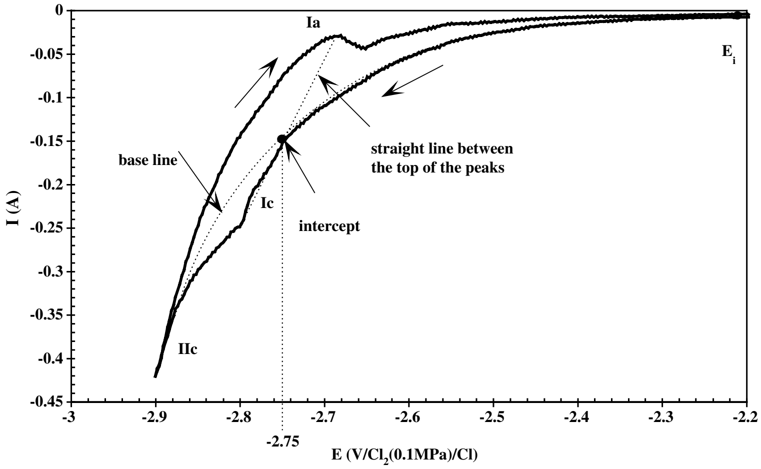

Fig. 3. Cyclic voltammogram recorded on tungsten working electrode in equimolar NaCl–KCl at 1073 K containing Pu(III) ions (scan rate 0.1 V/s, electrode surface: 0.31 cm^2, $x_{\mathrm{Pu(III)}} = 1.05 \times 10^{-3}$).

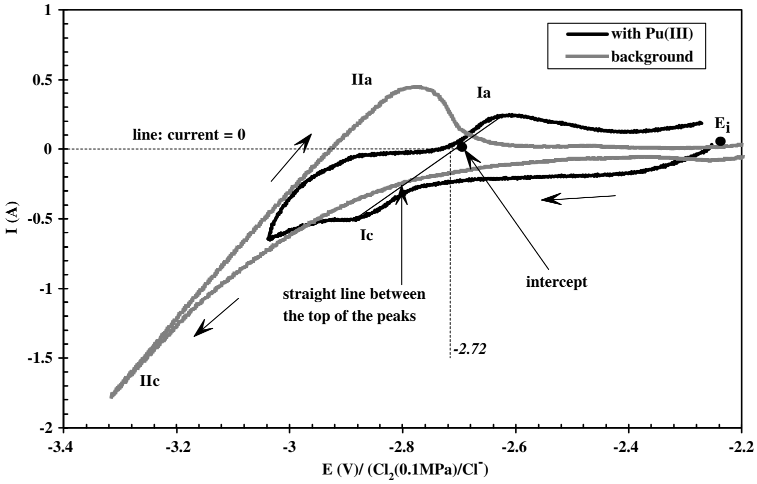

Fig. 4. Cyclic voltammogram obtained on tungsten working electrode in CaCl$_2$ containing Pu(III) ions at 1073 K (scan rate 0.1 V/s, electrode surface: 0.31 cm^2, $x_{\mathrm{Pu(III)}} = 1.1 \times 10^{-3}$).

separation between plutonium and sodium reduction processes. Consequently, it is difficult to distinguish the plutonium trichloride reduction and the sodium reduction.

Fig. 4 shows a typical cyclic voltammogram of Pu(III) obtained in $CaCl_2$ at 1073 K on tungsten electrode. Comparing 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 is big enough to separate the two phenomena.

The values of the Pu(III)/Pu redox potential have been estimated from the results of cyclic voltammetric studies in equimolar NaCl–KCl and $CaCl_2$ at 1073 K. The equilibrium potential is measured at open circuit potential (the current is equal to 0). It can be determined by cyclic voltammetry at the intercept between the base line (generally corresponding to a current equal to 0) and the straight line connecting the tops of the anodic and cathodic peaks. This method was used for the two solvents (Figs. 3 and 4). In the case of NaCl–KCl solvent, the capacitive current intensity is the same order as the Pu(III) cathodic intensity. Then, a base line was derived from the shape of the voltammogram such as indicated Fig. 3. The uncertainties in E values obtained by the apparatus used is about 1 mV. Therefore, the uncertainty in E_{eq} values measured by cyclic voltammetry is estimated at 10 mV.

E_{eq} led us to calculate the standard potential $E^0_{Pu(III)/Pu}$ using the following relation:

$$E_{eq} = E^0_{Pu(III)/Pu} + 2.3\frac{RT}{3F}\log x_{Pu(III)}, \quad (2)$$

$x_{Pu(III)}$ being the mole fraction of Pu(III) in the melt. The obtained results have been summarized in Table 1 and compared to those previously determined. Even if the E_{eq} determination in the case of NaCl–KCl was difficult, our potential determination of Pu(III)/Pu in NaCl–KCl is of the same order as that of Skiba reports [10]. In order to compare the standard potential in the NaCl–KCl and $CaCl_2$ melt, we have calculated the activity coefficients of Pu(III).

Table 1
Values of $E^0_{Pu(III)/Pu}$, standard potential of Pu(III)/Pu in various molten chloride mixtures at 1073 K (V/Cl_2 (0.1 MPa)/Cl^-, mole fraction scale)

Molten chlorides	Skiba et al.	Benz et al.	This work
NaCl–KCl	−2.585 [10]		−2.54 ± 0.01
NaCl	−2.513 [19]	−2.393 [8]	
KCl	−2.605 [19]	−2.381 [9]	
$CaCl_2$			−2.51 ± 0.01

3.3. Activity coefficients of Pu(III)

Calculation of actinide chlorides activity coefficients in the molten salt can yield information about the complexation of the cations in melts [20]. The activity coefficients, γ_{PuCl_3}, are calculated comparing the standard free energy (determined using electrochemical methods) with the reference free energy (deduced from thermal measurements). The chosen reference state is the supercooled liquid actinide chloride. Activity coefficients are calculated using the following equation [18]:

$$\log(\gamma_{PuCl_3}) = \frac{3FE^0_{Pu(III)/Pu} - \Delta G^*_{PuCl_3}}{2.3RT}. \quad (3)$$

The standard free energy of formation $\Delta G^*_{PuCl_3}$ ($=-7.25\times10^5$ J) of the supercooled liquid is determined using the published values of Fusselman et al. [21]. Table 2 gives the logarithm of the activity coefficient of $PuCl_3$ in different molten chlorides calculated using the potential values given in Table 1.

Activity coefficients determined by Benz [8,9] cannot be discussed because the EMF measurements were made at a high concentration ($0.5 < x_{Pu(III)} < 1$) in $PuCl_3$–NaCl and $PuCl_3$–KCl, and cannot be considered as dilute solutions.

The activity coefficient is characteristic of the complexation of plutonium ions in the salt at a given temperature [20]. By comparing the activity coefficients obtained in the different molten chlorides, we observe that the complexation of plutonium(III) is less important when a Lewis acid is used. The classification of the molten salts versus to plutonium(III) complexation is

$$Ca^{2+} < Na^+ < K^+$$

The complexation power of the melt depends on the nature of the salts. Using monovalent cations (Na^+ or K^+) increases the complexation phenomena. But if the temperature varies, the complexation power of a molten salt can be quantified only by its oxoacidity measurement [22,23].

The largest activity coefficient of plutonium (III) is obtained in $CaCl_2$ at 1073 K which is the most oxoacidic of the considered molten salts and corresponds to a low complexation by chloride ions. Low complexation is

Table 2
Logarithm of the activity coefficient of plutonium ($\gamma_{Pu(III)}$) in different molten chlorides using the standard potential values given in Table 1

Molten chlorides	Skiba et al.	Benz et al.	This work
NaCl–KCl	−1.14		−0.507
NaCl	−0.126	1.56	
KCl	−1.42	1.73	
$CaCl_2$			−0.084

also characterized by a measured standard potential that is close to the calculated one.

3.4. Potential–pO^{2-} diagram of plutonium

Potential–acidity stability ranges of plutonium compounds in equimolar NaCl–KCl and $CaCl_2$ at 1073 K can be described in equilibrium potential–pO^{2-} diagrams [24] with pO^{2-} being the co-logarithm (p$O^{2-} = -\log a(O^{-2})$) of activity of oxide anions in the molten salt. The nature and the solubility products of plutonium oxides are determined by using thermochemical data and activity coefficient previously determined. The oxide compounds considered for diagram calculations are PuO_2, Pu_2O_3 and PuOCl. The cubic phase Pu_2O_3 has a composition that varies between $PuO_{1.5}$ and $PuO_{1.6}$ [25]. We have only considered $PuO_{1.5}$ because the thermodynamic data related to $PuO_{1.6}$ are at our knowledge unknown.

In order to estimate values of $pK_{s(PuOCl)}$ and $pK_{s(Pu_2O_3)}$ (Table 3) for NaCl–KCl and $CaCl_2$, we have calculated the constants K^* related to the following equilibrium between pure compounds.

In NaCl–KCl molten salt:

$$PuOCl_{(s)} + 2NaCl_{(l)} \overset{K_1^*}{\rightarrow} PuCl_{3(l)} + Na_2O_{(s)} \tag{4}$$

$$Pu_2O_{3(s)} + 6NaCl_{(l)} \overset{K_2^*}{\rightarrow} 2PuCl_{3(l)} + 3Na_2O_{(s)} \tag{5}$$

In $CaCl_2$ melt:

$$PuOCl_{(s)} + CaCl_{2(l)} \overset{K_3^*}{\rightarrow} PuCl_{3(l)} + CaO_{(s)} \tag{6}$$

$$Pu_2O_{3(s)} + 3CaCl_{2(l)} \overset{K_4^*}{\rightarrow} 2PuCl_{3(l)} + 3CaO_{(s)} \tag{7}$$

As shown by Combes [11], the following relations lead to the solubility product determination for each media:

- In NaCl–KCl media:

$$pK_{s(PuOCl)} = pK_1^* - 2\log a_{NaCl} + \log \gamma_{Pu(III)_{NaCl-KCl}} + \log \gamma_{Na_2O}, \tag{8}$$

$$pK_{s(Pu_2O_3)} = pK_2^* - 6\log a_{NaCl} + 2\log \gamma_{Pu(III)_{NaCl-KCl}} + 3\log \gamma_{Na_2O}. \tag{9}$$

- In $CaCl_2$ media:

$$pK_{s(PuOCl)} = pK_3^* - \log a_{CaCl_2} + \log \gamma_{Pu(III)_{CaCl_2}} + \log \gamma_{CaO}, \tag{10}$$

$$pK_{s(Pu_2O_3)} = pK_4^* - 3\log a_{CaCl_2} + 2\log \gamma_{Pu(III)_{CaCl_2}} + 3\log \gamma_{CaO}. \tag{11}$$

wherein K_1^*, K_2^*, K_3^* and K_4^* are deduced from Gibbs enthalpy calculation of the equilibrium given above (calculated using the thermodynamical data of the literature [12]) and the relation:

$$\Delta G^* = 2.3RT\log K^*. \tag{12}$$

The activity coefficient of Pu(III), $\gamma_{Pu(III)}$ was previously determined (Table 2). The activity coefficient of Na_2O in NaCl–KCl is derived from experimental data and chemical potentials ($\log \gamma(Na_2O) = -6.12$) [11]. NaCl activity, a_{NaCl}, in NaCl–KCl media is equal to 0.65 [11]. The activity coefficient of CaO is derived from the measured solubility (S_{CaO}) of CaO in $CaCl_2$ at 1073 K ($\gamma_{CaO} = 1/S_{CaO}$) [26]. The calculated values of pK_s are given in Table 3.

The potentials of the redox systems $E^0_{PuOCl/Pu}$ and $E^0_{Pu_2O_3/Pu}$ are deduced from both solubility products and standard potentials $E^0_{Pu(III)/Pu}$ for each media using relations given in Table 4. The explanation of the potential determination of $E^0_{PuO_2/Pu}$ has been previously described [27]. Combining $E^0_{PuO_2/Pu}$ and the solubility product $pK_{s(Pu_2O_3)}$, we can give an expression for the potential $E^0_{PuO_2/Pu_2O_3}$.

Plutonium oxy-chloride PuOCl is not stable at our experimental conditions. Its precipitation occurs for high plutonium activity in the melt. Potentiometric titration of plutonium trichloride by oxide ion using a pO^{2-} indicator electrode in $CaCl_2$–NaCl molten salt at 823 K [27] and in LiCl–KCl eutectic at 723 K [28] have shown the precipitation of the only one plutonium oxide, Pu_2O_3. No insoluble plutonium oxychloride has been found in these melts by potentiometric titration for low $PuCl_3$ amounts. Fig. 5 presents the solubility limits

Table 3
Solubility products of plutonium oxides calculated by thermochemical and experimental data: NaCl–KCl$^{(*)}$, $CaCl_2^{(**)}$

Equilibrium	Expression for solubility products	Stability constant pK_s (mole fraction scale)
$PuOCl_{(s)} \rightarrow Pu^{3+} + O^{2-} + Cl^-$	$K_{s(PuOCl)} = x_{Pu^{3+}} * x_{O^{2-}}$	$12.4^{(*)}$ $8^{(**)}$
$Pu_2O_{3(s)} \rightarrow 2Pu^{3+} + 3O^{2-}$	$K_{s(Pu_2O_3)} = (x_{Pu^{3+}})^2(x_{O^{2-}})^3$	$36^{(*)}$ $21.7^{(**)}$

Symbols (*) and (**) respectively used to designate NaCl–KCl and $CaCl_2$ solvents.

Table 4
Equilibrium potentials and values of standard potentials of redox systems of plutonium in NaCl–KCl$^{(*)}$ and $CaCl_2^{(**)}$ at 1073 K (reference system: Cl^-/Cl_2 (0.1 MPa))

Redox systems	Expression of the equilibrium potential	Standard potential (mole fraction scale) (V)
$Pu(III) + 3e^- \rightarrow Pu_{(s)}$	$E^0_{Pu(III)/Pu} + \frac{2.3RT}{3F}\log x_{Pu(III)}$	$E^0_{Pu(III)/Pu} = -2.54^{(*)}$ $E^0_{Pu(III)/Pu} = -2.51^{(**)}$
$Pu_2O_{3(s)} + 6e^- \rightarrow 2Pu_{(s)} + 3O^{2-}$	$E^0_{Pu_2O_3/Pu} + \frac{2.3RT}{2F}pO^{2-}$	$E^0_{Pu_2O_3/Pu} = E^0_{Pu(III)/Pu} - \frac{2.3RT}{6F}pK_{s(Pu_2O_3)}$ $= -3.81^{(*)} = -3.35^{(**)}$
$PuOCl_{(s)} + 3e^- \rightarrow Pu_{(s)} + O^{2-} + Cl^-$	$E^0_{PuOCl/Pu} + \frac{2.3RT}{3F}pO^{2-}$	$E^0_{PuOCl/Pu} = E^0_{Pu(III)/Pu} - \frac{2.3RT}{3F}pK_{s(PuOCl)}$ $= -3.42^{(*)} = -3.08^{(**)}$
$PuO_{2(s)} + e^- \rightarrow Pu(III) + 2O^{2-}$	$E^0_{PuO_2/Pu(III)} - \frac{2.3RT}{F}\log x_{Pu(III)}$ $+\frac{2 * 2.3RT}{F}pO^{2-}$	$E^0_{PuO_2/Pu(III)} = -5.93^{(*)}$ $E^0_{PuO_2/Pu(III)} = -3.25^{(**)}$
$2PuO_{2(s)} + 2e^- \rightarrow Pu_2O_{3(s)} + O^{2-}$	$E^0_{PuO_2/Pu_2O_3} + \frac{2.3RT}{2F}pO^{2-}$	$E^0_{PuO_2/Pu_2O_3} = E^0_{PuO_2/Pu(III)} + \frac{2.3RT}{2F}pK_{s(Pu_2O_3)}$ $= -2.1^{(*)} = -0.93^{(**)}$

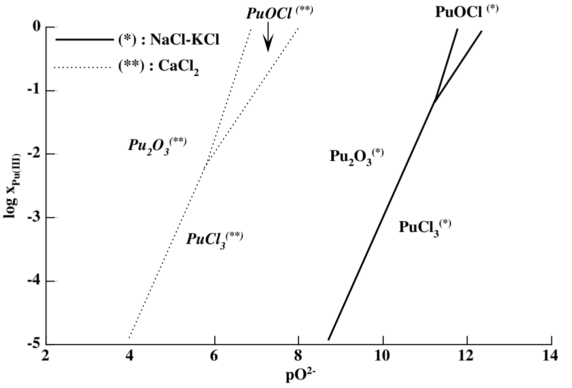

Fig. 5. Solubility of Pu(III) calculated as a function of pO^{2-} in equimolar NaCl–KCl$^{(*)}$ molten salt and $CaCl_2^{(**)}$ melt at 1073 K.

of Pu(III) as a function of melt acidity (pO^{2-}) and Pu(III) concentration calculated from experimental and thermochemical data. It shows very small PuOCl stability domains corresponding to high Pu(III) amounts whatever the molten salt considered and that confirms the experimental results. We observe a large acidity difference ($\Delta pO^{2-} > 4$) between the solubility of Pu(III) in the two media. Due to the high oxoacidity power of $CaCl_2$, solubility is higher in this melt. This character was already observed by the electrochemical study on the tungsten working electrode with the formation of an oxide tungsten compound in NaCl–KCl (leading to tungsten passivation) and tungsten dissolution in $CaCl_2$.

All this study allowed us to draw the potential–pO^{2-} equilibrium diagram in NaCl–KCl and $CaCl_2$ at 1073 K (Figs. 6 and 7) using the relations between potential and

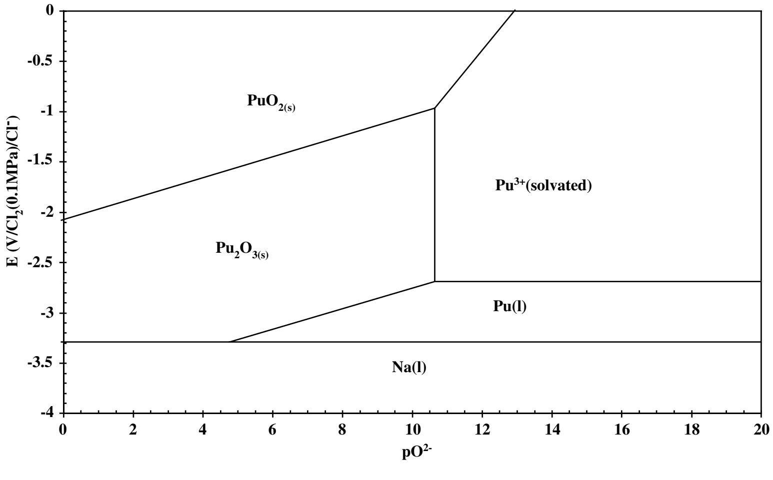

Fig. 6. Potential–pO^{2-} diagram calculated for plutonium compounds in the equimolar NaCl–KCl at 1073 K ($x_{Pu(III)} = 0.01$).

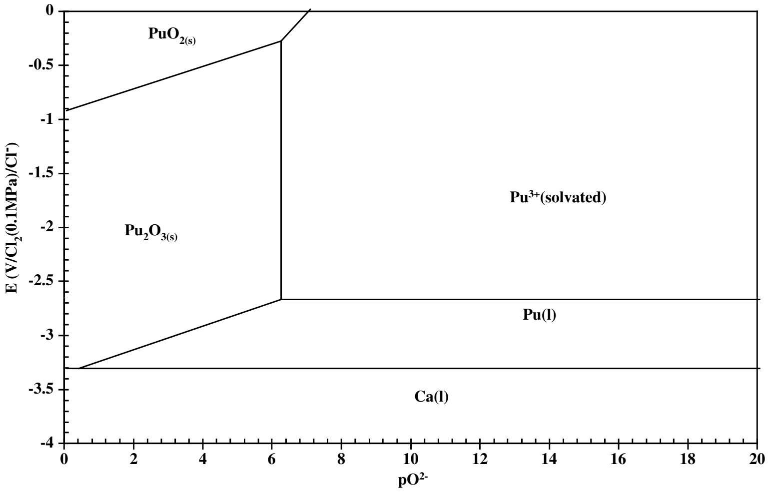

Fig. 7. Potential–pO^{2-} diagram calculated for plutonium compounds in $CaCl_2$ at 1073 K ($x_{Pu(III)} = 0.01$).

pO^{2-} given in Table 4. The possibility of forming Pu–Na alloys was not considered to preparation of these diagrams. As expected the stability domain of Pu(III) is higher in $CaCl_2$ than in NaCl–KCl molten salts.

4. Conclusions

The electrochemical properties of plutonium were studied in equimolar NaCl–KCl and pure $CaCl_2$ molten salts at 1073 K. The standard potential of Pu(III)/Pu in NaCl–KCl solvent salt, −2.54 V (versus Cl^-/Cl_2), is in agreement with previous works. In more acidic melt, like $CaCl_2$, the standard potential is close to the reference one. In NaCl–KCl media, the presence of plutonium seems to involve a decrease of the solvent limit (sodium reduction) so that the gap between Pu^{3+}/Pu and Na^+/Na redox systems is small. The potential–oxacidity diagrams derived using these results and the published data concerning oxides give a rational approach of the plutonium properties in these media.

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