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Distribution behavior of plutonium and americium in LiCl–KCl eutectic/liquid cadmium systems

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Abstract

The thermodynamics of plutonium and americium in LiCl–KCl eutectic/liquid cadmium systems was studied with interest in the oxidation state of americium in the salt phase. The standard potential of plutonium vs. the Ag/AgCl (1 wt% AgCl) electrode, $E^0_{\mathrm{Pu/Pu(III)}}$, in the LiCl–KCl eutectic was measured in the temperature range of 400–500°C and given by the equation with a standard deviation, $\sigma = 0.0009$ V: $E^0_{\mathrm{Pu/Pu(III)}}$ (V) $= -2.204 + 0.000845\ T$ (K). The Ag/AgCl electrode had been carefully calibrated using the Li–Al electrode. The potential of the cadmium containing plutonium and americium, E_{Cd}, was measured at 500°C as a function of the distribution coefficient (*D*: mole fraction in salt divided by mole fraction in cadmium), and represented by the following equations. over the range of $E_{\mathrm{Cd}} > -1.45$ V: $E_{\mathrm{Cd}} = -1.360\ (\pm 0.004) + 0.0511 \log D_{\mathrm{Am}} = -1.348\ (\pm 0.002) + 0.0511 \log D_{\mathrm{Pu}}$. It is indicated that americium as well as plutonium is present in the trivalent oxidation state in the salt under this condition. Based on the potential data, the activity coefficient of plutonium in liquid cadmium and the separation factor of americium relative to plutonium were determined to be $(1.74 \pm 0.28) \times 10^{-4}$ and 1.77 ± 0.46, respectively. Under the reducing conditions (i.e. $E_{\mathrm{Cd}} < -1.45$ V), the relationship between E_{Cd} and $\log D_{\mathrm{Am}}$, indicates that divalent americium is possibly present in the salt phase. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Electrode materials; Intermetallics; Metals; Electrochemical reactions; Thermodynamic properties

1. Introduction

Pyrometallurgical nuclear fuel recycling processes have been developed for the recovery of actinides from spent metallic [1–5] and nitride [6,7] nuclear fuels and high level radioactive liquid wastes [8–10]. In the processes, actinides are dissolved in a molten LiCl−KCl eutectic salt and are recovered into liquid cadmium by electrodeposition or chemical reduction, while the fission products are separated from the actinides. Noble fission products, which are less active than uranium, are not dissolved into the salt and active fission products such as alkali and alkaline-earth metals remain in the salt throughout the process. A certain amount of rare earth fission products possibly accompany actinides due to their chemical similarity. Since the separation behavior of actinides and rare earths is essential for the design of the pyrometallurgical processes, much effort has been made to measure the distribution between the LiCl–KCl eutectic and liquid cadmium [11–16].

This paper describes the study of the distribution behavior of plutonium and americium in LiCl–KCl eutectic salt/liquid cadmium systems. Distribution coefficients were measured as a function of the potential of the cadmium phase, which was varied by adding a reductant (lithium metal) or oxidant ($\mathrm{CdCl_2}$). The previous distribution studies [13,14] suggested that americium was present in the LiCl–KCl eutectic as a trivalent species, whereas some literature [17–19] claimed that americium was primarily divalent under reducing conditions in other molten salt systems. To verify the oxidation state of americium, the americium distribution was investigated over a wider range of the potential of the cadmium phase. In addition, the potential of plutonium metal electrodeposited on a tantalum wire was measured to obtain the thermodynamic properties such as the standard potential of the Pu/Pu(III) couple and the activity coefficient of plutonium in liquid cadmium. Ag/AgCl electrodes are often employed as the reference electrode in the LiCl–KCl eutectic system. Since each Ag/AgCl electrode has its own

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junction potential that depends on the electrode design such as electrolyte junction and AgCl concentration, the Ag/AgCl reference electrode potentials should be corrected to minimize the error in the potential values of the working electrodes. The thermoelectromotive force should be also taken into consideration. In the present study, the Li–Al electrode was used for the correction, which appears to be helpful for comparing the potential values separately measured.

2. Experimental

2.1. Materials

Polarographic grade LiCl–KCl eutectic (59:41 mol%), LiCl–KCl eutectic containing 1 wt% AgCl, and $CdCl_2$ with a purity of 99.99% were obtained from Anderson Physics Laboratory. Cadmium metal of 99.999% purity was supplied from Soekawa Chemicals Co. and the oxide on the surface was carefully removed before use. Lithium–cadmium alloy (15 atom% Li) was prepared by melting cadmium and lithium (purity 99.9%) metal in the LiCl–KCl eutectic salt at 500°C.

Plutonium chloride was prepared by oxidizing plutonium metal of 99.8% purity with $CdCl_2$ in a LiCl–KCl eutectic/cadmium system at 500°C:

$$2\,\mathrm{Pu(Cd)} + 3\mathrm{CdCl_2(LiCl{-}KCl)} \rightarrow 2\mathrm{PuCl_3(LiCl{-}KCl)} + 3\mathrm{Cd(Cd)}$$

where (Cd) and (LiCl–KCl) denote the respective phases. The product of the LiCl–KCl–$PuCl_3$, salt was blue and contained 31 wt% $PuCl_3$.

The plutonium–platinum alloy, $PuPt_3$, was prepared from PuO_2 that contained about 2 wt% americium, daughter of Pu-241, by the chemical reactions:

(a) $2PuO_2 + 4C + N_2 \rightarrow 2PuN + 4CO$
(b) $2PuN + 6Pt \rightarrow 2PuPt_3 + N_2$.

(a) The mixture of PuO_2 and carbon powder was allowed to react in a N_2–8%H_2 mixed gas stream at 1550°C to give PuN [20]. Some americium possibly evaporated during this process. (b) The PuN was mixed with platinum powder and heated at 800°C for 6 h. The product was identified as $PuPt_3$ by the X-ray diffraction method. The gamma counting analysis with a germanium detector indicated that the $PuPt_3$ contained americium.

2.2. Standard potential of the Pu/Pu(III) couple

About 80 g of the LiCl–KCl eutectic melt was placed in a high-purity alumina crucible (99.5% Al_2O_3, Nikkato Co.). In the salt, a 1 mm tantalum wire cathode, a counter electrode of 1 mm tantalum wire, an Ag/AgCl reference electrode with a Pyrex sheath and a type-K thermocouple were placed. The Ag/AgCl electrodes consisted of a silver wire immersed in the LiCl–KCl eutectic salt mixture with 1 wt% AgCl, which was contained in a closed-end Pyrex or Vycor tube. Since each Ag/AgCl electrode has its own junction potential, the potential was checked against a Li–Al electrode prior to the electromotive force measurements. The Li–Al electrode was made of a Li–Al alloy (42 atom% Li) attached to a 1 mm tantalum wire. The Li–Al alloy electrode has a constant potential over a wide composition range and exhibits a very stable and reproducible potential [21]. As the Li–Al alloy reacts with $PuCl_3$, the Li–Al electrode cannot be directly used in the measurements.

Plutonium metal was electrodeposited on the tantalum cathode and the potential vs. the Ag/AgCl reference electrode was measured for various $PuCl_3$ concentrations in the temperature range of 400–500°C. The galvanic cell can be described as

$$(-)\ \mathrm{Pu}|\mathrm{PuCl_3,\ LiCl{-}KC1}\|\mathrm{AgCl,\ LiCl{-}KCl}|\mathrm{Ag}\ (+).$$

The concentration of $PuCl_3$ was incrementally changed by adding the prepared LiCl–KCl–$PuCl_3$ salt. The cell potential and current during the electrodepositions were controlled using a potentio/galvanostat (Hokuto Denko Co. HABF-501), and potential data were acquired by an electrometer (Hokuto Denko Co. HE-104).

The cell was located in a stainless steel thermowell externally heated with an electric furnace. All the measurements were carried out in an argon gas atmosphere glove box (H_2O, $O_2 < 2$ ppm).

Salt samples were taken by inserting a Pyrex glass tube into the melt and were dissolved in dilute nitric acid. The concentrations of plutonium in the solutions were determined using an inductively coupled plasma atomic emission spectrometer (ICP–AES). The accuracy of the ICP–AES technique was estimated to be ±5%.

2.3. Distribution of plutonium and americium between LiCl–KCl eutectic and liquid cadmium

After measuring the potential of the Pu/Pu(III) couple, anodic dissolution of the $PuPt_3$ that contained a small quantity of americium was carried out using a liquid cadmium cathode in order to increase the americium concentration in the salt. Americium is slightly more electronegative than plutonium. During the anodic dissolution, the increase in gamma activity of the salt was observed. The LiCl–KCl eutectic salt containing plutonium and americium was then harvested.

The harvested salt, cadmium metal and the Li–Cd alloy (1.1 wt% Li), as shown in Table 1, were put into an alumina crucible, and then the temperature was controlled at 500±1°C. Because a large excess of lithium metal was contained in the Li–Cd alloy, almost all of the plutonium and americium in the salt was initially extracted into the cadmium phase. The experimental apparatus is schemati-

Table 1
Starting materials put in the alumina crucible for the plutonium–americium distribution test

Material	Weight (g)
LiCl–KCl–$PuCl_3$ (1.5 wt% $PuCl_3$)[a]	65.641
Cd metal	36.075
Cd–Li alloy (1.1 wt% Li)	9.014

[a] The salt contained a small quantity of americium.

cally shown in Fig. 1. An Ag/AgCl reference electrode with a Vycor sheath, a tantalum wire lead for the cadmium phase, a thermocouple and an agitator were immersed into the melt. The potential of the cadmium phase vs. the Ag/AgCl electrode was measured and samples of the salt and cadmium phases were taken for analysis. To increase the plutonium and americium concentrations in the salt, $CdCl_2$ was added little by little. The reaction is described by

$$\mathrm{M(Cd)} + n/2\mathrm{CdCl_2(LiCl{-}KCl)} \rightarrow \mathrm{MCl}_n\mathrm{(LiCl{-}KCl)} + n/2\mathrm{Cd\,(Cd)}$$

where M denotes a metallic element and n is the oxidation state of M in the salt phase. After each $CdCl_2$ addition, the cadmium potential and temperature were allowed to stabilize before measuring the potential and taking samples. The procedure was repeated until the plutonium in the cadmium phase was exhausted.

The salt and cadmium samples were dissolved in nitric acid contained in separate 20 ml vials. The surfaces of the vials were completely decontaminated, which was checked with a α-ray survey meter. The activities of americium for the vial samples were measured by 59.5 keV gamma counting using a germanium detector, followed by determining the plutonium concentrations in the solutions by ICP–AES analysis.

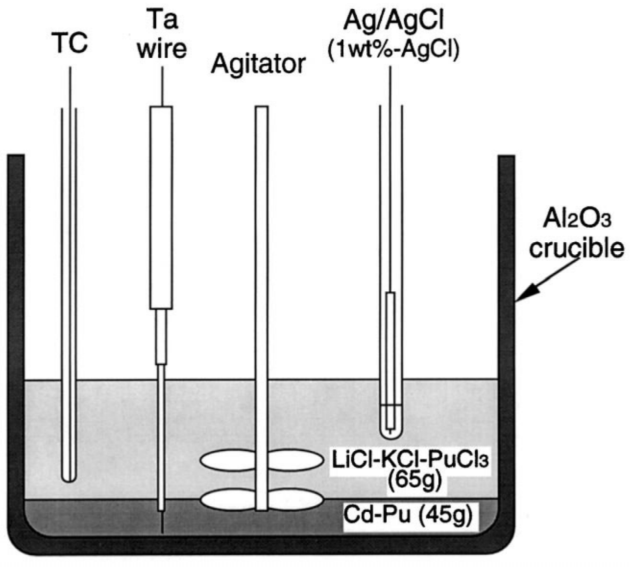

Fig. 1. Schematic view of experimental apparatus.

3. Results and discussion

3.1. Calibration of Ag/AgCl reference electrodes

The potential of the Ag/AgCl reference electrode with a Pyrex sheath, which was used for the standard potential test, was measured relative to the Li–Al electrode in the temperature range of 400–500°C. The results are given in Table 2(a). The potential, $E_{\mathrm{Ag(Pyrex)\ vs.\ LiAl}}$, can be represented as a function of temperature by a least-squares equation with a standard deviation $\sigma = 0.0003$ V:

$$E_{\mathrm{Ag(Pyrex)\ vs.\ LiAl}} = 2.552 - 0.000541\,T \quad (1)$$

where T is temperature in K.

The Ag/AgCl electrode with a Vycor sheath was used for the distribution test. The potential relative to the Li–Al electrode, $E_{\mathrm{Ag(Vycor)\ vs.\ LiAl}}$ is presented in Table 2(b) and may be expressed by

$$E_{\mathrm{Ag(Vycor)\ vs.\ LiAl}} = 2.538 - 0.000536\,T \quad (2)$$

with a standard deviation of 0.0008 V. The potential difference at 500°C between the two Ag/AgCl electrodes was found to be 11 mV.

3.2. Standard potential of the Pu/Pu(III) couple

Plutonium metal was electrodeposited on the tantalum cathode and the potential vs. the Ag/AgCl reference electrode was measured. Fig. 2 shows the typical potential decay curves after the electrodepositions. The potential value at which the change in the deposit potential with time was the slowest was recorded as the equilibrium potential and is given in Table 3. Fairly stable potentials were observed except at extremely low $PuCl_3$ concentrations in the salt. The potential was plotted versus temperature as shown in Fig. 3, and the potential values at 400, 450 and 500°C were obtained from the least-squares lines. The relationship between the potential and logarithm of the mole fraction of $PuCl_3$ in the salt, X_{PuCl_3} is represented in Fig. 4.

Table 2
Potentials of the Ag/AgCl electrodes (1 wt% AgCl) vs. the Li–Al electrode: (a) the Ag/AgCl electrode with a Pyrex sheath used for the standard potential test (b) the Ag/AgCl electrode with a Vycor sheath used for the distribution test

(a)		(b)	
Temperature (°C)	$E_{\mathrm{Ag\ vs.\ LiAl}}$ (V)	Temperature (°C)	$E_{\mathrm{Ag\ vs.\ LiAl}}$ (V)
500	2.134	505	2.121
451	2.161	500	2.1235
400	2.188	499	2.123
450	2.161	451	2.1495
500	2.134	450.5	2.1505
		501	2.124

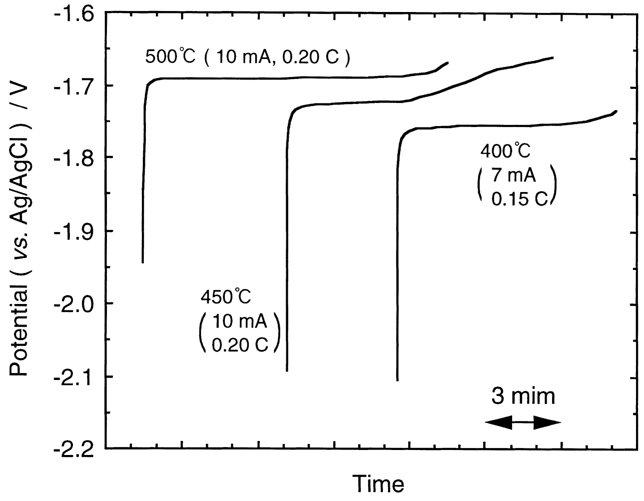

Fig. 2. Potential decay curves for a tantalum cathode after constant current electrolyses in LiCl–KCl–PuCl$_3$ salt ($X_{PuCl_3} = 0.0024$). Each of the curves instantly started when the current was cut off.

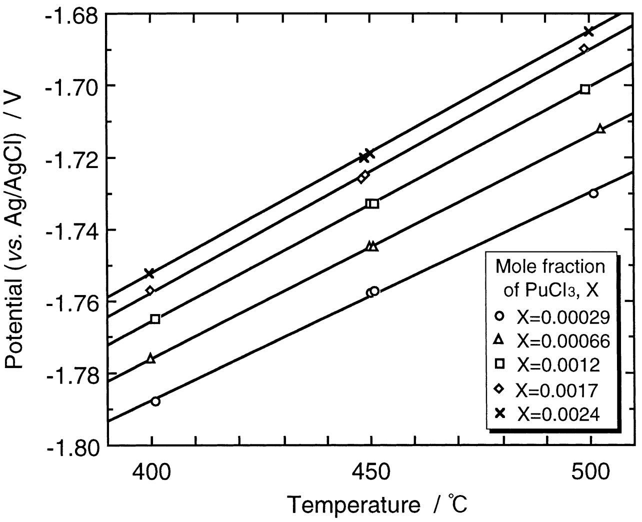

Fig. 3. Plutonium potential for various PuCl$_3$ concentrations in LiCl–KCl eutectic salt as a function of temperature.

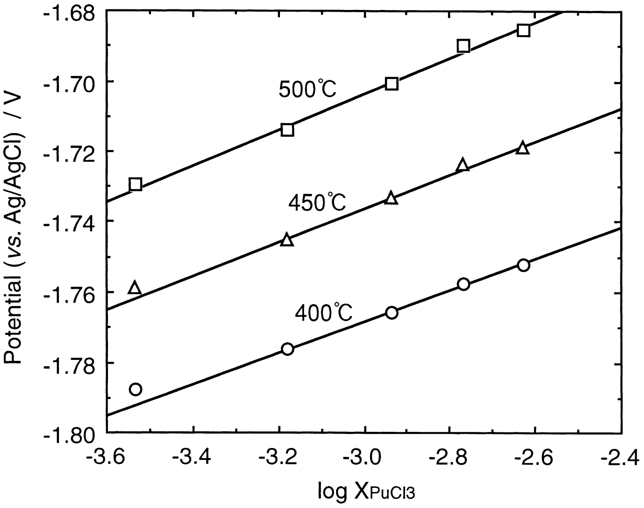

Fig. 4. Plutonium potential as a function of mole fraction of PuCl$_3$ in LiCl–KCl eutectic salt at 400, 450 and 500°C.

If it is defined that activity of PuCl$_3$ in a salt approaches X_{PuCl_3} as X_{PuCl_3} approaches zero, the observed potential of the plutonium metal electrode, E_{Pu} is given by the Nernst equation when X_{PuCl_3} is sufficiently low:

$$E_{Pu} = E^0_{Pu/Pu(III)} + (2.303RT/3F) \log X_{PuCl_3} - E_{Ag/AgCl} \tag{3}$$

where R is the gas constant, T is the absolute temperature, F is the Faraday constant, $E^0_{Pu/Pu(III)}$ is the standard potential of the Pu/Pu(III) couple and $E_{Ag/AgCl}$ is the Ag/AgCl reference electrode potential. As expected from Eq. (3), linear relationships between the potential values and log X_{PuCl_3} are observed in Fig. 4. The Nernst slopes of the least-squares lines drawn from the four higher concentration data indicate that the value of the number of electrons involved in the electrode reaction is three as shown in Table 4. It is confirmed that plutonium is present

Table 3
Potentials of plutonium metal deposited on the tantalum electrode vs. the Ag/AgCl electrode (1 wt% AgCl)

Mole fraction of PuCl$_3$	Temperature (°C)	$E_{Pu\ vs.\ Ag}$ (V)
0.00029	501	−1.730
	450	−1.758
	401	−1.788
	451	−1.757
0.00066	451	−1.745
	503	−1.712
	400	−1.776
	450	−1.745
0.00117	451	−1.733
	499	−1.701
	401	−1.765
	450	−1.733
0.00170	448	−1.726
	499	−1.690
	400	−1.757
	449	−1.725
0.00235	448.5	−1.720
	500	−1.685
	399.5	−1.752
	450	−1.719

Table 4
The Nernst slopes of the least-squares lines for E_{Pu} vs. log X_{PuCl_3} presented in Fig. 4 and calculated oxidation state of plutonium in the salt, n

Temperature (°C)	Slope	n
400	0.0444	3.0
450	0.0490	2.9
500	0.0537	2.9

in only the trivalent oxidation state in the salt phase under the condition investigated in this study, which is consistent with the cyclic voltammetry results [22].

In Fig. 4, least-squares lines were drawn by using the theoretical slopes of $2.303RT/3F$, and the standard potentials at 400, 450 and 500°C were extrapolated as presented in Table 5. The standard potential vs. the Ag/AgCl electrode, $E^0_{\mathrm{Pu/Pu(III)\ vs.\ Ag}}$, may be expressed by a least-squares equation in the temperature range of 400–500°C with a standard deviation of 0.0009 V:

$$E^0_{\mathrm{Pu/Pu(III)\ vs.\ Ag}} = -2.204 + 0.000845T \qquad (4)$$

where T is in K. The standard potential vs. the Li–Al electrode, $E^0_{\mathrm{Pu/Pu(III)\ vs.\ LiAl}}$ can be obtained from Eqs. (1) and (4):

$$E^0_{\mathrm{Pu/Pu(III)\ vs.\ LiAl}} = 0.348 + 0.000304\,T. \qquad (5)$$

The standard deviation is 0.0010 V. Since the tantalum lead was used for both the plutonium metal electrode and the Li–Al electrode, the thermoelectromotive force was canceled in Eq (5). The standard potential vs. the Li/Li(I) couple in the LiCl–KCl eutectic is also given in the last column of Table 5, which was computed from the Li–Al electrode potential vs. the Li/Li(I) couple, $E_{\mathrm{LiAl\ vs,\ Li}}$, reported elsewhere [23]:

$$E_{\mathrm{LiAl\ vs.\ Li}} = 0.476 - 0.000264\,T. \qquad (6)$$

The standard potential of the Pu/Pu(III) couple was previously reported by Campbell and Leary [24] and Roy et al. [25]. The Ag/AgCl reference electrode used by Campbell and Leary had an asbestos fiber seal and the AgCl concentration, X_{AgCl} was 0.000568 mole fraction. Roy et al. used the Ag/AgCl electrode with a Vycor sheath ($X_{\mathrm{AgCl}} = 0.00487$). In the present study, the sheath was made of Pyrex glass ($X_{\mathrm{AgCl}} = 0.00390$). A plot of $\{E_{\mathrm{Pu}} + (2.303RT/F)\log X_{\mathrm{AgCl}}\}$ vs. $\log X_{\mathrm{PuCl_3}}$ from this study is compared with the literature values as shown in Fig. 5. Campbell and Leary reported the empirical formula for E_{Pu} in the temperature range of 412–456°C. It is seen that the potential values agree with each other within the uncertainties of the Ag/AgCl electrode potentials due to the membrane potential. Eqs. (1) and (2) suggest that the potential difference between the Pyrex and Vycor membrane Ag/AgCl electrodes was approximately 10 mV, which could satisfactorily explain the difference between the potential values obtained by Roy et al. and us.

Table 5
Standard potential, E^0, for the Pu/Pu(III) couple in LiCl–KCl eutectic salt

Temp. (°C)	$E^0(V)$		
	vs. Ag/AgCl[a]	vs. Li–Al	vs. Li(0)/Li(I)
400	−1.635	0.553	0.851
450	−1.593	0.569	0.853
500	−1.550	0.584	0.855

[a] The concentration of AgCl was 1 wt%.

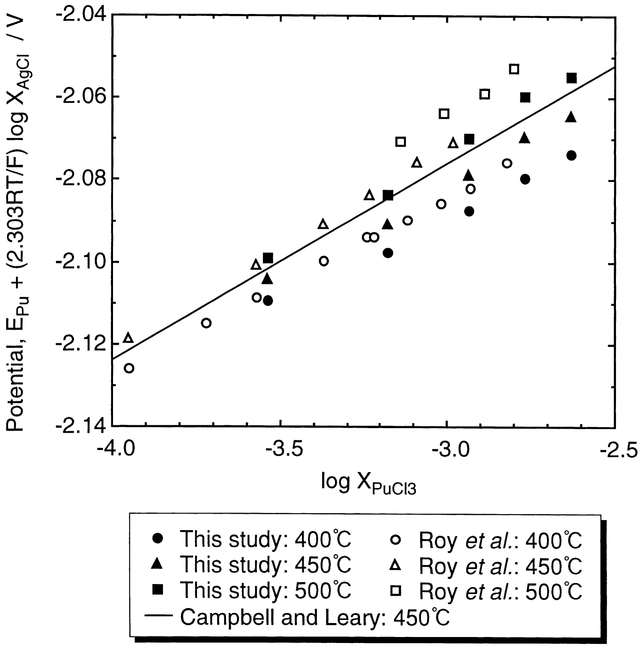

Fig. 5. The normalized potential values for the Pu/Pu(III) couple from this study compared with those from Roy et al. and Campbell and Leary.

Combining the standard potential data of many elements separately obtained may cause some errors due to the variety of experimental equipment and reference electrodes that are used. In this study, more reliable and helpful potential data in the LiCl–KCl eutectic system were obtained by the correction of the Ag/AgCl reference electrode potential using the Li–Al electrode.

3.3. Distribution of plutonium and americium between LiCl–KCl eutectic and liquid cadmium

The distribution experiment was carried out at 500°C and the results are presented in Table 6. As for americium, the relative concentrations that are sufficient to calculate the distribution coefficients are given. The initial cadmium phase contained lithium metal as well as almost all of the plutonium and americium. The plutonium concentration was about 0.5 atom%, which was smaller than the reported plutonium solubility in cadmium of 1.8 atom% at 500°C [26]. With the addition of $CdCl_2$, the lithium metal oxidation in the cadmium phase occurred followed by extraction of plutonium and americium into the salt phase as shown in Fig. 6. When the amounts of plutonium and americium in both phases were computed, the amounts of the cadmium and salt in the crucible were roughly estimated from the weights initially loaded and removed for the analysis. The lithium concentration in the cadmium phase was estimated from the cadmium potential vs. the Ag/AgCl electrode, E_{Cd}, using the following equation:

Table 6
Results for the americium–plutonium distribution experiment between the LiCl–KCl eutectic and liquid cadmium at 500°C

Sample number	Weight $CdCl_2$ cum. (g)	Cd phase potential[a] (V)	Am concentration (cpm mol^{-1})		Pu concentration (mole fraction)		Distribution coefficient, D_M		Separation factor $SF_{Am/Pu}$
			Salt phase	Cd phase	Salt phase	Cd phase	log D_{Am}	log D_{Pu}	
1	0	1.7037	8.42E+3	3.82E+7	ND[b]	4.79E−3	−3.66		
2	0.114	1.6847	1.10E+3	4.01E+7	ND	5.02E−3	−4.56		
3	0.311	1.6389	2.54E+3	4.58E+7	ND	5.51E−3	−4.26		
4	0.411	1.5974	4.39E+3	4.62E+7	ND	5.62E−3	−4.02		
5	0.463	1.5654	4.99E+4	4.54E+7	ND	5.48E−3	−2.96		
6	0.497	1.5102	1.13E+5	4.44E+7	ND	5.69E−3	−2.60		
7	0.512	1.4892	2.37E+5	4.56E+7	1.75E−5	5.61E−3	−2.28	−2.51	1.66
8	0.542	1.4498	1.05E+6	4.29E+7	5.95E−5	5.54E−3	−1.61	−1.97	2.27
9	0.641	1.4075	4.74E+6	3.50E+7	3.52E−4	4.81E−3	−0.87	−1.14	1.85
10	0.841	1.3725	1.07E+7	1.97E+7	9.74E−4	3.10E−3	−0.26	−0.50	1.73
11	0.991	1.3518	1.43E+7	1.07E+7	1.48E−3	1.81E−3	0.13	−0.09	1.64
12	1.108	1.3244	1.72E+7	3.96E+6	1.91E−3	7.50E−4	0.64	0.41	1.71
13	1.157	1.2936	1.80E+7	1.07E+6	2.05E−3	1.82E−4	1.22	1.05	1.49

[a] vs. Ag/AgCl (1 wt% AgCl).
[b] ND : not detected.

$$E_{Cd} = E_{Li} - (2.303RT/F)\log(X_{Li\ in\ Cd}\,\gamma_{Li\ in\ Cd}) \qquad (7)$$

where E_{Li} is the potential of the Li/Li(I) couple vs. the Ag/AgCl electrode, $X_{Li\ in\ Cd}$ and $\gamma_{Li\ in\ Cd}$ are the mole fraction and activity coefficient of lithium in the cadmium, respectively. E_{Li} at 500°C was obtained from Eqs. (2) and (6) to be −2.395 V, and $\gamma_{Li\ in\ Cd}$ was 0.002 under these conditions [27]. Consequently, $X_{Li\ in\ Cd}$ may be given by

$$\log X_{Li\ in\ Cd} = -(E_{Cd} + 1.981)/0.1534. \qquad (8)$$

The potential of the cadmium phase is generally expressed by the Nernst equation:

$$E_{Cd} = E^0_{M/M(n)} + (2.303RT/nF) \times \log(X_{M\ in\ salt}\gamma_{M\ in\ salt})/(X_{M\ in\ Cd}\gamma_{M\ in\ Cd}) \qquad (9)$$

where $E^0_{M/M(n)}$ is the standard potential of the M/M(n) couple relative to the Ag/AgCl electrode. The distribution coefficient for M between the molten salt and liquid cadmium, D_M, is defined as

$$D_M = (X_{M\ in\ salt})/(X_{M\ in\ Cd}). \qquad (10)$$

When the concentrations of M in both phases are sufficiently low, the solute would obey Henry's law and γ is expected to be nearly constant. Moreover, $\gamma_{M\ in\ salt}$ is assumed to be unity in Eq. (3). Eq. (9) would then reduce to

$$E_{Cd} = Const + (2.303RT/nF)\log D_M \qquad (11)$$

where

$$Const = E^0_{M/M(n)} - (2.303RT/nF)\log \gamma_{M\ in\ Cd}$$

Hence, a plot of E_{Cd} vs. log D_M would give a line having the slope of $2.303RT/nF$.

Fig. 7 shows the distribution coefficients for plutonium and americium as a function of the cadmium phase potential. When E_{Cd} was less positive than −1.5 V, the plutonium concentrations in the salt phase were too low to be detected by the ICP–AES. The solid lines were drawn using the least-squares method with the theoretical slope of $nF/2.303RT$ ($n = 3$, $T = 773$K). It is indicated that americium as well as plutonium is present in the salt in the trivalent oxidation state over the range of $E_{Cd} > -1.45$ V. Therefore, E_{Cd} may be represented by

$$E_{Cd} = -1.360 + 0.0511\log D_{Am}(\sigma = 0.004) \qquad (12)$$

$$= -1.348 + 0.0511\log D_{Pu}(\sigma = 0.002). \qquad (13)$$

The activity coefficient of plutonium in liquid cadmium, $\gamma_{Pu\ in\ Cd}$, at 500°C was determined to be $1.74 \pm 0.28\ (\pm\sigma) \times 10^{-4}$ ($0.0056 > X_{Pu\ in\ Cd} > 0.0002$) from Eqs. (4), (11) and (13) when the potential difference between the Ag/AgCl reference electrodes calculated from Eqs. (1) and (2) was taken into account. Previously, Johnson et al. measured $\gamma_{Pu\ in\ Cd}$ as a function of $X_{Pu\ in\ Cd}$ [26]. According to their empirical formula, $\gamma_{Pu\ in\ Cd}$ varies from 1.40×10^{-4} to 1.64×10^{-4} over the concentration range investigated in the present study.

The separation factor of americium relative to plutonium, $SF_{Am/Pu}$, is defined as

$$SF_{Am/Pu} = (X_{Am\ in\ Salt}/X_{Am\ in\ Cd})/(X_{Pu\ in\ Salt}/X_{Pu\ in\ Cd}) = D_{Am}/D_{Pu} \qquad (14)$$

From Eqs. (12), (13) and (14), $SF_{Am/Pu}$ is computed to be $1.77 \pm 0.46\ (\pm\sigma)$. Fig. 8 shows a comparison of the log D_{Am} vs. log D_{Pu} plots derived from this study and Ackerman et al. [14]. The agreement between the two data sets is excellent. In their experiment, no significant variation in $SF_{Am/Pu}$ with temperature was observed in the temperature range of 481–517°C and $SF_{Am/Pu}$ was determined to be $1.54 \pm 0.15\ (\pm 2\sigma)$. Koyama et al. measured

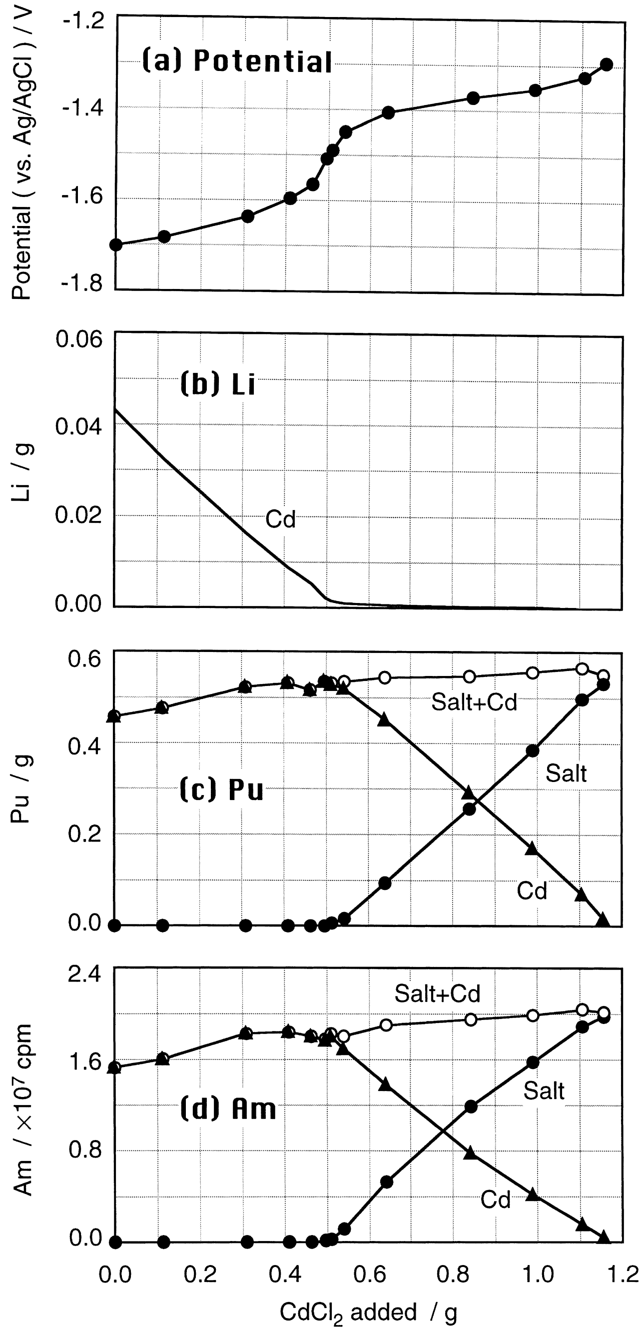

Fig. 6. Potential of the cadmium phase and amounts of lithium, plutonium and americium in the salt and cadmium phases as a function of cumulative $CdCl_2$ added to the system. The lithium concentration in the cadmium was estimated from the potential.

the separation factor of plutonium and americium relative to uranium at 500°C using the salt consisting of the LiCl–KCl eutectic and small amounts of NaCl, $CaCl_2$ and $BaCl_2$ [13]. Dividing $SF_{\mathrm{Am/U}}$ by $SF_{\mathrm{Pu/U}}$ gives $SF_{\mathrm{Am/Pu}}$ to be 1.64±0.49. Both references indicate that the americium species in the salt phase is trivalent over the range of $-1.41\ V < E_{\mathrm{Cd}} < -1.30\ V$ investigated in their studies.

Under a reducing condition (i.e. $E_{\mathrm{Cd}} < -1.45\ V$), the values of log D_{Am} deviate from the line for $n = 3$ and the line for $n = 2$ might represent the results as shown in Fig. 7. When the distribution coefficient was small (i.e. the americium concentration in the salt phase was extremely low), contamination of the salt samples with a trace of radioactive dust containing americium would cause experimental errors. However, it seems reasonable that americium is mainly present in the divalent oxidation state in the salt phase under the reducing conditions. This is consistent with the cyclic voltammetry results in a LiCl–KCl–$AmCl_n$ solution at 450°C, which pointed out that the

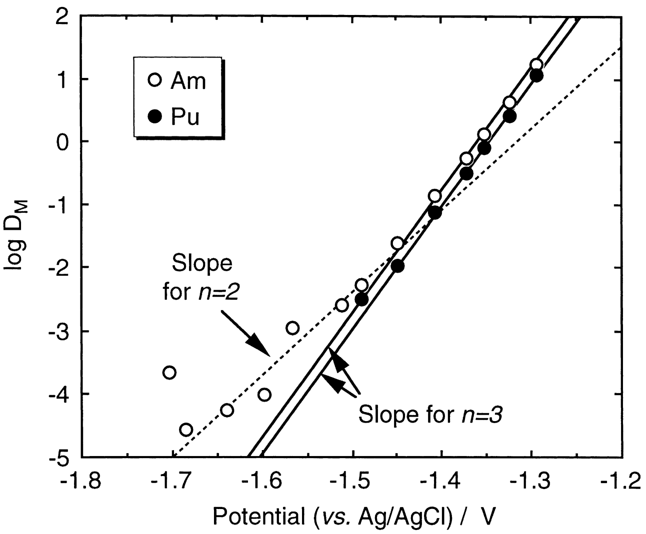

Fig. 7. The distribution coefficient, D_{M}, for plutonium and americium as a function of the potential of the cadmium phase.

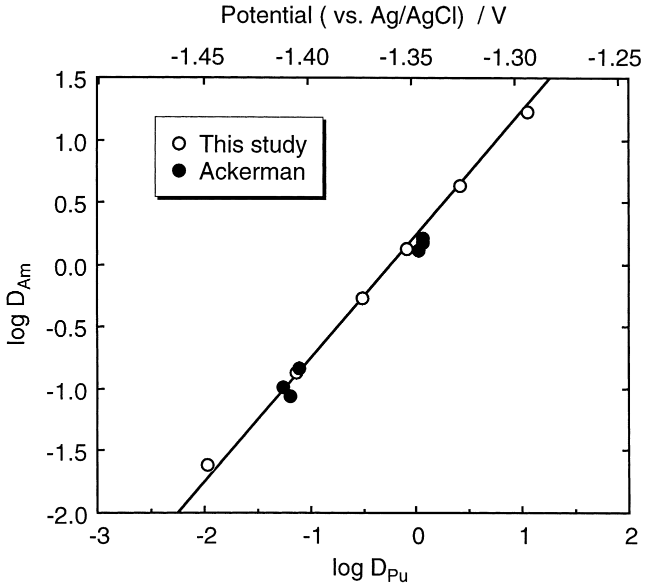

Fig. 8. Plots of log D_{Am} vs. log D_{Pu} and the potential of the cadmium phase derived from this study and Ackerman et al. [14]. The values from Ackerman et al. were measured in the temperature range of 481–517°C.

potential of the Arn(II)/Am(III) couple was about -1.45 V [23].

4. Conclusions

Actinide chemistry in LiCl–KCl eutectic/liquid metal systems has been studied for the pyrometallurgical reprocessing of nuclear spent fuels. In this study, the thermodynamics of plutonium and americium in LiCl–KCl eutectic/liquid cadmium systems was studied with interest in the oxidation state of americium in the salt. The standard potential of plutonium vs. the Ag/AgCl electrode calibrated with the Li–Al electrode was determined in the temperature range of 400–500°C. The potential of the cadmium containing plutonium and americium was measured at 500°C as a function of the distribution coefficient. It is indicated that americium as well as plutonium is present in the trivalent oxidation state over the range of $E_{Cd} > -1.45$ V. From the potential data, the activity coefficient of plutonium in liquid cadmium and the separation factor of americium relative to plutonium were determined. They are in excellent agreement with the literature values. Under reducing conditions (i.e. $E_{Cd} < -1.45$ V), the relationship between E_{Cd} and log D_{Am} indicates that divalent americium is possibly present in the salt phase. Hence, in case of recovering more than 99% of americium into liquid cadmium from the molten salt (i.e. log $D_{Am} < -2$), the presence of divalent americium should be taken into account, otherwise more americium would remain in the salt than is expected.

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