ELSEVIER

Journal of Alloys and Compounds 234 (1996) 83–92

Journal of
ALLOYS
AND COMPOUNDS

Thermodynamic quantities of actinides and rare earth elements in liquid bismuth and cadmium

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Received 28 May 1995

Abstract

The activity coefficients of uranium, lanthanum, cerium, praseodymium, gadolinium and yttrium in liquid bismuth were measured electrochemically as $10^{-4.65}$, $10^{-13.44}$, $10^{-13.00}$, $10^{-12.81}$, $10^{-11.04}$ and $10^{-10.17}$ respectively at 773 K. The activity coefficients of neodymium and neptunium were estimated as $10^{-12.85}$ and $10^{-7.43}$ respectively from the standard potentials in LiCl–KCl eutectic molten salt and the distribution coefficients in the LiCl–KCl/bismuth system. The partial molar enthalpy of mixing and the partial molar excess entropy of solutes in both liquid bismuth and cadmium were evaluated from the change in the activity coefficients with temperature.

Keywords: Activity coefficient; Actinides; Rare earth elements; Bismuth; Cadmium

1. Introduction

Pyrometallurgical partitioning of long-lived radioactive nuclides contained in high level radioactive waste (HLW) from the reprocessing of spent fuels generated from light water reactors is being developed [1]. The major parts of the long-lived nuclides are minor actinides (MAs). According to the proposed concept of pyrometallurgical partitioning, a reductive extraction process using a molten chloride/liquid metal system can be employed for the extraction of MAs from the molten chloride and for the separation of MAs from rare earth elements (REs) after denitration and chlorination of the HLW.

To determine the separation efficiency between MAs and REs, the distribution coefficients of actinides and REs in the LiCl–KCl eutectic molten salt/liquid Cd and LiCl–KCl/liquid Bi systems were reported in the literature [2–8]. The separation factors calculated from the distribution coefficients are summarized in Table 1. Higher separation factors of trivalent REs, such as La, Ce, Pr, Nd, Gd and Y, with respect to (w.r.t.) actinides were obtained when Bi was employed as solvent than with Cd. On the other hand, the separation factors of divalent REs, such as Sm and Eu, were considerably larger in the LiCl–KCl/Cd system than in LiCl–KCl/Bi. The activity coefficient of each actinide and RE in LiCl–KCl should be almost equal in these experiments, because actinides and REs were dilutely added to LiCl–KCl. Therefore the difference between the separation factors in the LiCl–KCl/Bi and LiCl–KCl/Cd systems was assumed to originate mainly from the difference in the activity coefficients of actinides and REs in Bi from those in Cd. Moreover, the partial molar enthalpy of mixing and the partial molar excess entropy were evaluated from the relationship between the logarithm of the activity coefficient and the inverse temperature, which were useful for the estimations of the variation in the separation factor with increasing temperature.

The aims of this study are not only the electrochemical measurement of the activity coefficients in the liquid metals but also the evaluation of the partial thermodynamical quantities in Bi and Cd in order to investigate the distribution behaviour of actinides and REs in the LiCl–KCl/Bi and LiCl–KCl/Cd systems in detail.

SSDI 0925-8388(95)01960-X

Table 1
Separation factors of actinides and REs w.r.t. Ce in molten LiCl–KCl eutectic chloride/liquid metal systems (773 K)

Element	Separation factor				
	LiCl–KCl/Cd				LiCl–KCl/Bi
U		0.020	0.019	0.020	0.0012
Np			0.041	0.038	0.013
Pu		0.038		0.040	0.013[a]
Am		0.059		0.023	
Cm					
La	2.7	2.7	2.4	2.7	3.0
Ce	1	1	1	1	1
Pr	0.76	0.88		0.86	1.1
Nd	0.90	0.90	0.95	0.91	1.1
Pm					
Sm[b]				11800	248
Eu[b]				50600	1655
Gd		3.1		3.6	12
Dy		10.2			
Y	91	122		108	700
Ref.	[2]	[7]	[3]	[8]	[8]

[a] Estimated from activity coefficient in Bi and standard potential in LiCl–KCl; [b] where $\log D(\mathrm{Ce}) = 0$.

2. Experimental details

Concerning the measurement of the activity coefficients of actinides and REs in Cd, the experimental procedures and results have been fully described elsewhere [5]. Therefore the procedures for the measurement of the activity coefficients in Bi are only summarized in this paper.

2.1. Reagents

Polarographic grade LiCl–KCl eutectic salt (59–41 mol%) with a purity of 99.99% and unhydrated trichlorides of REs with a purity of 99.9% were obtained from Anderson Physics Laboratories. Rods of RE metals with a purity of 99.9% and a block of Bi metal with a purity of 99.9999% were purchased from Rare Earth Products Inc. For the measurement of the activity coefficients of U, trivalent U was prepared in LiCl–KCl in the following way. Uranium was transported electrochemically from a pure U metal electrode to a liquid Bi electrode using a U/LiCl–KCl/Bi cell and then U dissolved in Bi was oxidized by the addition of $BiCl_3$ and extracted to LiCl–KCl.

2.2. Apparatus

The experiments were carried out in the apparatus shown in Fig. 1 located in an argon atmosphere glove-box. The oxygen and water contents in the glove-box were maintained at less than 0.5 and 0.1 ppm respectively during all operations. The nitrogen content was estimated to be around 100 ppm.

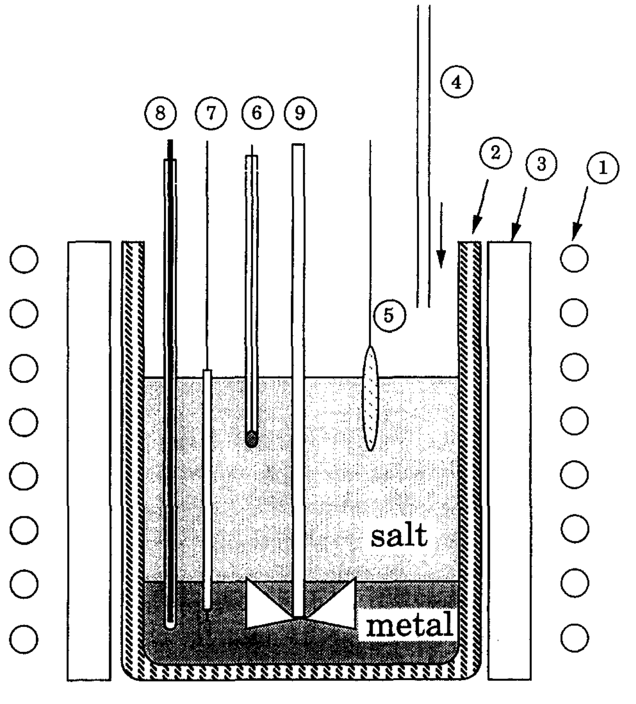

Fig. 1. Apparatus. 1, heater; 2, alumina crucible; 3, copper heat sink; 4, Pyrex sampling tube; 5, pure metal electrode; 6, Ag/AgCl reference electrode; 7, tantalum lead; 8, thermocouple; 9, tantalum wing.

2.3. Procedures

The e.m.f.s of Y, La, Ce, Pr, Gd and U in liquid Bi were measured in the temperature range from 673 to 873 K. About 80 g of LiCl–KCl, about 3 g of the trivalent chlorides of U or RE and about 100 g of Bi metal were loaded in an alumina crucible which was placed at the bottom of the apparatus and then they were heated to melt. An agitator was lowered into the upper part of the liquid Bi region after the melting of the salt and the Bi and then it was continuously rotated in the melt at about 60 rev min^{-1}. After the attainment of a fixed temperature a pure metal electrode and an Ag/AgCl reference electrode were inserted in the molten salt and a Ta lead was inserted in the liquid Bi. The Ta lead was covered with an alumina tube except for the end in Bi to prevent contact with the molten salt. The potentials between the reference electrode and the pure metal electrode and between the reference electrode and the Bi electrode were measured in the following way.

(i) Fixed amounts of U or RE were transported from the pure metal electrode to the Bi electrode by potentiostatic electrotransport with a current of 100 mA.

(ii) The pure metal electrode was exchanged for another one whose surface was mechanically polished before insertion in the molten salt.

(iii) The potentials between the reference electrode and the pure metal electrode and between the reference electrode and the Bi electrode were recorded when the voltage swing changed by not more than 0.2 mV.

(iv) The electrodes were removed from the melt.

Operations (ii)–(iv) were repeated after the temperature had been changed.

(v) Samples of the salt and the metal were taken after the measurements of the voltage.

These operations were repeated several times with increasing concentration of U or RE in Bi. Preliminary analysis of the concentration of U or RE transported to Bi indicated that the current efficiency was almost 100%.

The potentials between the reference electrode and the pure metal (M) electrode and between the reference electrode and the Bi electrode are given respectively by the Nernst equations

$$E_{\mathrm{M}} = E^{\circ}_{\mathrm{MCl_3}} + \frac{RT}{3F}\ln\left(\frac{a_{\mathrm{MCl_3}}}{a_{\mathrm{M}}}\right) - E_{\mathrm{AgCl}} \qquad (1)$$

$$E_{\mathrm{M\ in\ Bi}} = E^{\circ}_{\mathrm{MCl_3}} + \frac{RT}{3F}\ln\left(\frac{a_{\mathrm{MCl_3}}}{a_{\mathrm{M\ in\ Bi}}}\right) - E_{\mathrm{AgCl}} \qquad (2)$$

where E_{M} is the potential of the pure metal electrode, $E_{\mathrm{M\ in\ Bi}}$ is the potential of the Bi electrode, $E^{\circ}_{\mathrm{MCl_3}}$ is the standard potential of the trivalent chloride, E_{AgCl} is the potential of the reference electrode, a_i is the activity of i, R is the gas constant and F is the Faraday constant. The potential of the $\mathrm{Cl_2/Cl^-}$ electrode was selected as the standard state of these potentials. The e.m.f. between the pure metal electrode and the Bi electrode is simply given as the following equation by subtracting Eq. (2) from Eq. (1), where a_{M} is unity in the

$$E_{\mathrm{M}} - E_{\mathrm{M\ in\ Bi}} = \frac{RT}{3F}\ln a_{\mathrm{M\ in\ Bi}} = \frac{2.303RT}{3F}\log a_{\mathrm{M\ in\ Bi}} \qquad (3)$$

From the relationship among the activity, the activity coefficient (γ_i) and the mole fraction (X_i) Eq. (3) can be transformed to

$$\log \gamma_{\mathrm{M\ in\ Bi}} = \frac{3F}{2.303RT}(E_{\mathrm{M}} - E_{\mathrm{M\ in\ Bi}}) - \log X_{\mathrm{M\ in\ Bi}} \qquad (4)$$

Therefore the activity coefficient of M in Bi can be calculated from the measurement of the e.m.f. and the mole fraction.

3. Results and discussion

3.1. Measurement of activity coefficient

The relationships between the e.m.f. and the logarithms of the mole fraction in Bi at 723 and 773 K are shown in Figs. 2(a) and 2(b) respectively. The saturated solubilities of Y, La, Ce, Pr and U in Bi reported by Schweitzer and Weeks [9,10] and that of Gd by Kober et al. [11] are also shown in Fig. 2 by the arrows. The e.m.f. value for each element decreases linearly and then becomes almost constant with increasing logarithm of the mole fraction. According to Eq. (4), the linear decrease in the e.m.f. corresponds to a fixed activity coefficient. On the other hand, Eq. (3) shows that the logarithm of the activity should be fixed when the e.m.f. is fixed, corresponding to a decreasing activity coefficient with increasing mole fraction. These facts indicate that intermetallic compounds between Bi and the solute, such as U and REs, were formed when the e.m.f. was kept constant with increasing mole fraction. The concentrations where the e.m.f.s for U and REs started to remain constant in Fig. 2 were in fairly good agreement with their reported saturated solubilities, with the exception of Gd. The saturated solubilities of Gd in Bi were estimated to be 0.20 and 0.41 at.% at 723 and 773 K respectively in Fig. 2. These satuarated solubilities are much lower than those reported by Kober et al. [11], namely 1.4 and 2.1 at.% respectively. A more precise measurement of the solubility of Gd in Bi appears to be necessary.

Fig. 3 shows the relationships between the logarithms of the activity coefficient calculated from Eq. (4) and the logarithms of the mole fraction at 773 K. The previous results on the saturated solubilities are also shown in Fig. 3 by the arrows. The activity coefficients are almost fixed in unsaturated Bi,

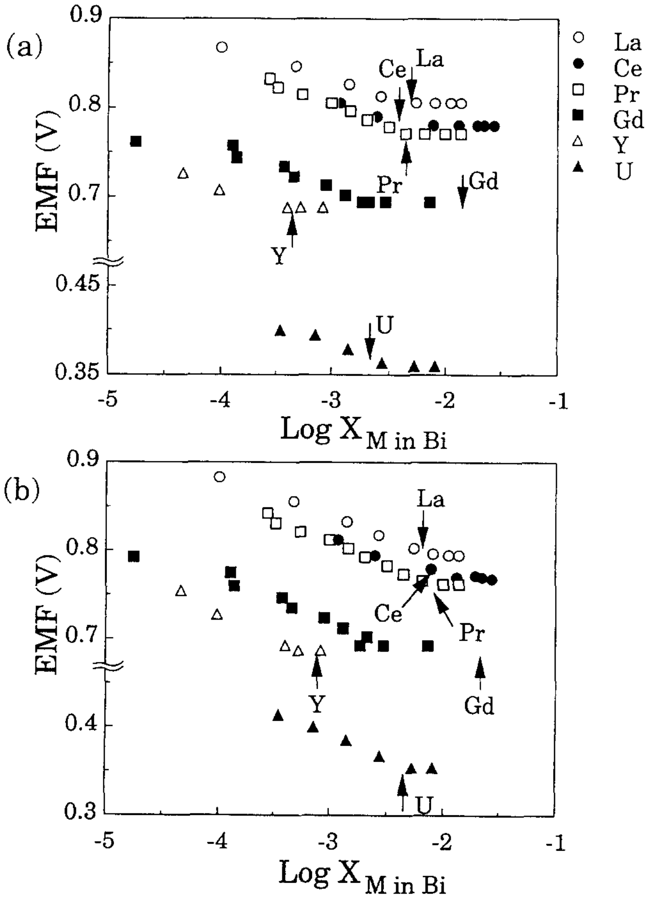

Fig. 2. Relationship between e.m.f. and logarithms of mole fraction of U and REs at (a) 723 K and (b) 773 K. Arrows indicate solubility limits of U and REs reported previously [9–11].

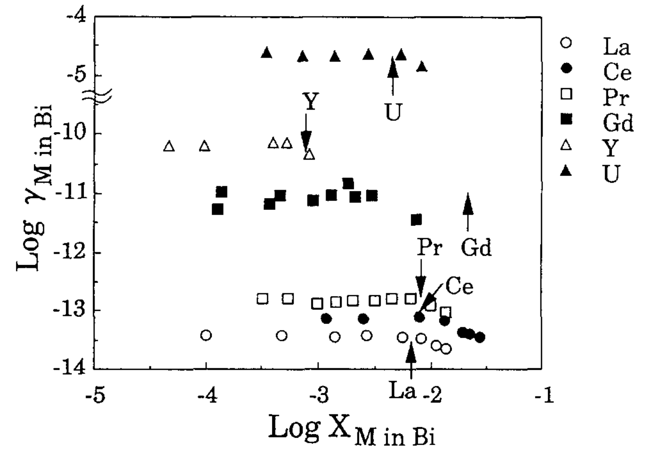

Fig. 3. Relationship between logarithms of activity coefficient and logarithms of mole fraction of U and REs at 773 K. Arrows indicate solubility limits of U and REs reported previously [9–11].

suggesting that Henry's law can be applied until Bi is saturated with U or RE. The average values of the activity coefficients of U, La, Ce, Pr, Gd and Y in unsaturated Bi at 773 K were obtained as $10^{-4.65}$, $10^{-13.44}$, $10^{-13.00}$, $10^{-12.81}$, $10^{-11.04}$ and $10^{-10.17}$ respectively and are summarized in Table 2. The activity coefficients obtained in the present study are in good agreement with values reported by Lebedev et al. [19] and Kober et al. [11–15]. The activity coefficients in saturated Bi decreased with increasing mole fraction, corresponding to the coexistence of intermetallic compounds.

As seen in Table 2, the activity coefficients of actinides and REs in Bi are extremely small, especially those of light REs, such as La, Ce, Pr and Nd. The activity coefficients of heavy REs, such as Y and Gd, are somewhat larger than those of light REs. The ratios between the activity coefficients of heavy REs and light REs in Bi are larger than those in Cd. In contrast, the ratios between the activity coefficients of actinides and light REs in Bi are smaller than those in Cd. The Gibbs energy of formation of UCl_3, $CeCl_3$ and YCl_3 per unit chlorine in LiCl–KCl have been reported to be −239, −295 and −297 kJ mol^{-1} respectively [5]. The separation of Ce from Y and that of U from Ce in the LiCl–KCl/Bi system were therefore assumed to be easier than their separations in the LiCl–KCl/Cd system.

3.2. Calculation of distribution coefficient

The exchange reaction between two elements M_1 and M_2 with valences n_1 and n_2 respectively in the LiCl–KC/Bi system can be expressed as

$$\underset{\text{(in LiCl-KCl)}}{M_1Cl_{n_1}} + \frac{n_1}{n_2}\underset{\text{(in Bi)}}{M_2} \leftrightarrow \underset{\text{(in Bi)}}{M_1} + \frac{n_1}{n_2}\underset{\text{(in LiCl-KCl)}}{M_2Cl_{n_2}} \qquad (5)$$

The Gibbs energies of formation of the compounds in Eq. (5) are given respectively by

$$\Delta G^*_{M_1Cl_{n_1}} = n_1FE^*_{M_1Cl_{n_1}} = \Delta G^\circ_{M_1Cl_{n_1}} + RT\ln\gamma^*_{M_1} \qquad (6)$$

$$\Delta G^\#_{M_2} = RT\ln\gamma^\#_{M_2} \qquad (7)$$

$$\Delta G^\#_{M_1} = RT\ln\gamma^\#_{M_1} \qquad (8)$$

$$\Delta G^*_{M_2Cl_{n_2}} = n_2FE^*_{M_2Cl_{n_2}} = \Delta G^\circ_{M_2Cl_{n_2}} + RT\ln\gamma^*_{M_2} \qquad (9)$$

where ΔG^*_i is the Gibbs energy of formation of i in LiCl–KCl, ΔG°_i is the standard Gibbs energy of formation of i, $\Delta G^\#_i$ is the Gibbs energy of mixing of i in Bi, E^*_i is the standard potential of i in LiCl–KCl, γ^*_i is the activity coefficient of i in LiCl–KCl and $\gamma^\#_i$ is the activity coefficient of i in Bi. Therefore the change in the Gibbs energy of the reaction shown in Eq. (5) is given by

$$\Delta G = n_1F(E^*_{M_2Cl_{n_2}} - E^*_{M_1Cl_{n_1}}) - RT[\ln(\gamma^\#_{M_2})^{n_1/n_2} - \ln\gamma^\#_{M_1}] \qquad (10)$$

On the other hand, the equilibrium constant K of Eq. (5) is given by

Table 2
Activity coefficients of actinides and REs in liquid Bi and Cd (773 K)

Element	Log γ in Bi			Log γ in Cd		
	This work	Other	Ref.	This work	Other	Ref.
Y	−10.17	−10.76	[12]		−6.09	[5]
La	−13.44	−13.39	[13]		−8.42	[5]
Ce	−13.00	−12.71	[14]		−7.93	[5]
Pr	−12.81	−12.53	[15]		−7.70	[5]
Nd	−12.85[a]	−12.42	[16]		−7.94	[5]
Sm		−13.48	[17]	−8.4[b]		
Eu		−11.57	[18]	−6.7[b]		
Gd	−11.14	−11.52	[11]		−6.20	[5]
U	−4.65	−4.57	[19]		1.95	[5]
Np	−7.4[a]				−2.07	[21]
Pu		−9.35	[20]		−3.84	[22]
Am					−3.91[c]	[5]

[a]Calculated from distribution coefficient in LiCl–KCl/Bi and standard potential in LiCl–KCl; [b]calculated from distribution coefficient and pseudostandard potentials in LiCl–KCl; [c]measured at 723 K.

$$\Delta G = -RT\ln K = -RT\ln\left(\frac{(X^*_{\mathrm{M_2Cl}_{n_2}})^{n_1/n_2}X^\#_{\mathrm{M}_1}}{X^*_{\mathrm{M_1Cl}_{n_1}}(X^\#_{\mathrm{M}_2})^{n_1/n_2}}\right) \quad (11)$$

where X^*_i is the mole fraction of i in LiCl–KCl and $X^\#_i$ is the mole fraction of i in Bi. Here the distribution coefficients D of M_1 and M_2 between LiCl–KCl and Bi are defined respectively as

$$D_{\mathrm{M}_1} = \frac{X^*_{\mathrm{M}_1}}{X^\#_{M_1}} \quad (12)$$

$$D_{\mathrm{M}_2} = \frac{X^*_{\mathrm{M}_2}}{X^\#_{\mathrm{M}_2}} \quad (13)$$

From Eqs. (10)–(13), the relationship between the distribution coefficients of M_1 and M_2 can be obtained as

$$\ln D_{\mathrm{M}_1} - \frac{n_1}{n_2}\ln D_{\mathrm{M}_2} = \frac{n_1F}{RT}(E^*_{\mathrm{M_2Cl}_{n_2}} - E^*_{\mathrm{M_1Cl}_{n_1}}) + \ln\left(\frac{\gamma^\#_{\mathrm{M}_1}}{(\gamma^\#_{\mathrm{M}_2})^{n_1/n_2}}\right) \quad (14)$$

When M_1 and M_2 are replaced by M and Ce respectively, Eq. (14) is modified to

$$\log D_{\mathrm{M}} - \frac{n}{3}\log D_{\mathrm{Ce}} = \frac{nF}{2.303RT}(E^*_{\mathrm{CeCl_3}} - E^*_{\mathrm{MCl}_n}) + \log\left(\frac{\gamma^\#_{\mathrm{M}}}{(\gamma^\#_{\mathrm{Ce}})^{n/3}}\right) \quad (15)$$

which was used for the calculation of the distribution coefficients. The left side of Eq. (15) corresponds to the separation factor (SF) of M w.r.t. Ce:

$$\mathrm{SF} = \frac{D_{\mathrm{M}}}{D^{n/3}_{\mathrm{Ce}}} \quad (16)$$

The first term on the right side of Eq. (15) corresponds to the difference in the Gibbs energy of formation between MCl_n and $\mathrm{CeCl_3}$ in LiCl–KCl. The second term on the right side of Eq. (15) indicates the difference in the Gibbs energy of mixing between M and Ce in Bi.

The logarithms of the distribution coefficient of M calculated from Eq. (15) are shown in Fig. 4 in comparison with those measured directly by Kurata et al. [8]. The standard potentials in LiCl–KCl used for the calculation were previously evaluated by Sakamura et al. [5]. The full lines calculated for U, La and

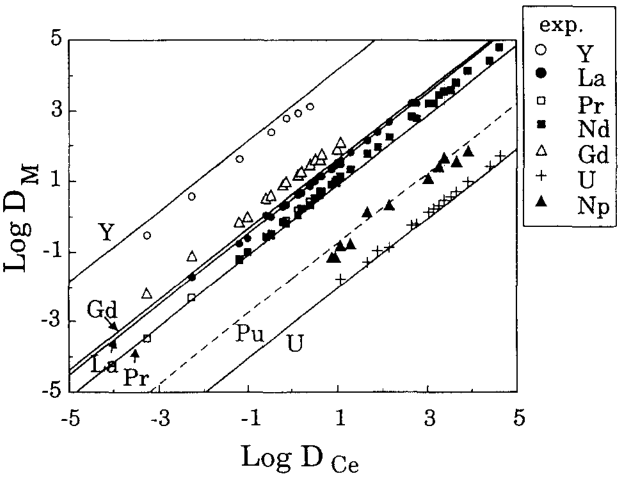

Fig. 4. Comparison of distribution coefficients of U, Np and REs obtained experimentally in LiCl–KCl/Bi system with those calculated from activity coefficients in Bi and standard potentials in LiCl–KCl (773 K). Full lines indicate calculated distribution coefficients of U and REs and dotted line indicates calculated distribution coefficient of Pu.

Pr are in good agreement with the experimental data points. The lines for Y and Gd are slightly different from the experimental data points. The differences between the calculated distribution coefficients and the experimental ones for Y and Gd are 0.148 and −0.093 respectively, which can be converted to differences in the potential of 6.7 and −4.0 mV respectively. The dotted line in the figure indicates the distribution coefficient for Pu calculated from the standard potential of Pu in LiCl–KCl [5] and the activity coefficient of Pu in Bi [20]. The separation factor of Pu w.r.t. Ce in the LiCl–KCl/Bi system can be estimated to be about 0.013 from the calculated distribution coefficient, which is similar to that of Np, about 0.011, reported previously [8]. On the other hand, the activity coefficients of Np and Nd in Bi, which are not measured directly in this study, can be estimated from the distribution coefficients in the LiCl–KCl/Bi system and the standard potentials coefficients in the LiCl–KCl/Bi system and the standard potentials in LiCl–KCl. The calculated activity coefficients of Np and Nd are $10^{-7.40}$ and $10^{-12.85}$ at 773 K respectively, as given in Table 2. Unfortunately, the activity coefficient of Np in Bi has not been reported in the literature so far. The activity coefficient of Nd estimated in this study was in good agreement with the value obtained by Kober et al. [16].

The distribution coefficients for U, Np, La, Pr, Nd, Gd and Y measured directly at 773 K in the LiCl–KCl/Cd system [8] are shown in Fig. 5 in comparison with the present results calculated from Eq. (15), where the activity coefficients in Bi are replaced by those in Cd. The activity coefficients of actinides and REs in liquid Cd used for the calculation were obtained previously by Krumpelt et al. [21], Johnson et al. [22] and Sakamura et al. [5]. Each calculated line is in good agreement with the experimental data points. The largest difference between the experimental distribution coefficient and the calculated one is observed to be 0.229 for Np, corresponding to 10.3 mV as the difference in potential. The recommended activity coefficients in Cd are summarized in Table 2.

The relationship between the distribution coefficients for actinides and that of Nd is shown in Fig. 6. Eq. (15) is modified to the relationship between actinides and Nd, because the experimental distribution coefficient shown in Fig. 6 was obtained as a function of the distribution coefficient of Nd [5]. Since Am was treated as a divalent element, the slope of the distribution coefficient for Am is smaller than the others. The differences between the experimental and calculated distribution coefficients for U, Np and Pu are 0.165, −0.292 and −0.002 respectively, corresponding to differences in the potential of 7.4, −13.1 and 0.1 mV respectively.

3.3. Calculation of activity coefficients of Sm and Eu in Cd

Although the activity coefficients of Sm and Eu in Bi were reported by Lebedev et al. [17] and Dybinin et al. [18] respectively, those in Cd have not been reported so far. On the other hand, the distribution coefficients of Sm and Eu in the LICl–KCl/Bi and LiCl–KCl/Cd systems have been obtained previously [8]. In order to estimate the activity coefficients of Sm and Eu in Cd, the pseudostandard potential of a divalent element in LiCl–CKl was assumed in this study. From Eq. (15) the pseudostandard potential of a divalent chloride can be calculated as

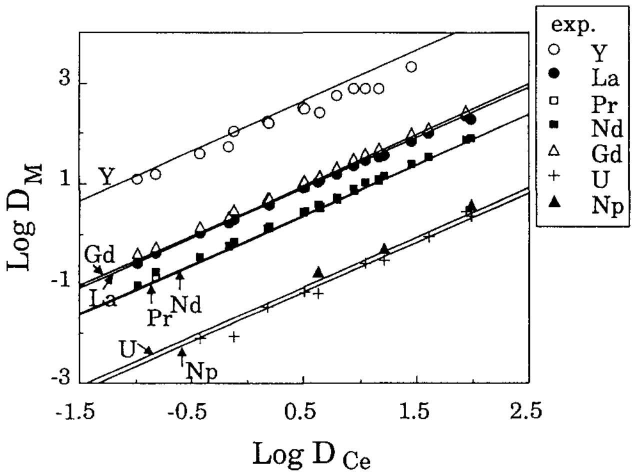

Fig. 5. Comparison of distribution coefficients of U, Np and REs obtained experimentally in LiCl–KCl/Cd system [8] with those calculated from activity coefficients in Cd and standard potentials in LiCl–KCl (773 K). Lines indicate calculated distribution coefficients.

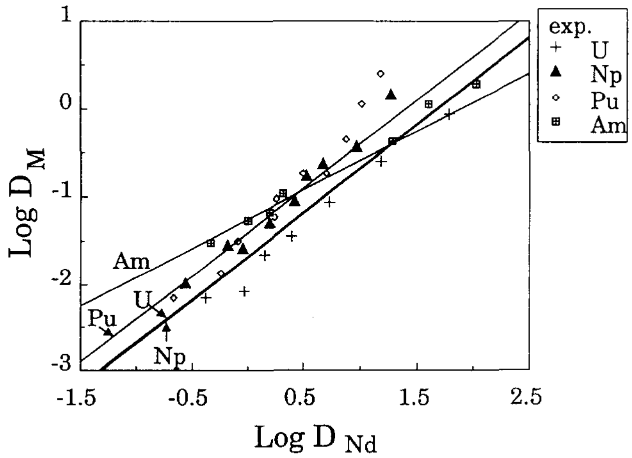

Fig. 6. Comparison of distribution coefficients of actinides obtained experimentally in LiCl–KCl/Cd system with those calculated from activity coefficients in Cd and standard potentials in LiCl–KCl (723 K). Lines indicate calculated distribution coefficients.

$$E^*_{\mathrm{M'Cl_2}} = -\left\{\frac{2.303RT}{2F}\left[\log D_{\mathrm{M'}} - \frac{2}{3}\log D_{\mathrm{Ce}} - \log\left(\frac{\gamma^{\#}_{\mathrm{M'}}}{(\gamma^{\#}_{\mathrm{Ce}})^{2/3}}\right)\right] - E^*_{\mathrm{CeCl_3}}\right\} \tag{17}$$

where M′ denotes a divalent element such as Sm or Eu. The pseudostandard potentials of divalent Sm and Eu in LiCl–KCl were calculated as −3.611 and −3.527 V respectively from their activity coefficients in Bi and their distribution coefficients in the LiCl–KCl/Bi system. These pseudostandard potentials are considerably lower than the standard potential of Li which would be used as reductant in the reductive extraction process. The activity coefficients of Sm and Eu in Cd can be determined as $10^{-8.44}$ and $10^{-6.69}$ respectively from the pseudostandard potentials calculated from Eq. (17), the distribution coefficients in the LiCl–KCl/Cd system and the activity coefficient of Ce in Cd:

$$\gamma^{\#}_{\mathrm{M'}} = (\gamma^{\#}_{\mathrm{Ce}})^{2/3} \times 10^{\log D_{\mathrm{M'}} - \frac{2}{3}\log D_{\mathrm{Ce}} - \frac{2F}{2.303RT}(E^*_{\mathrm{CeCl_3}} - E^*_{\mathrm{M'Cl_2}})} \tag{18}$$

The order of the degree of the activity coefficient of actinides and REs was U > Np > Pu > Y > Gd > Eu > La ≈ Ce ≈ Pr ≈ Nd > Sm in liquid Bi and U > Np > Pu > Eu > Sm ≈ Y ≈ Gd > La ≈ Ce ≈ Pr ≈ Nd in liquid Cd. The positions of Sm and Eu were different from each other. Sm and Eu were quite stable in Bi.

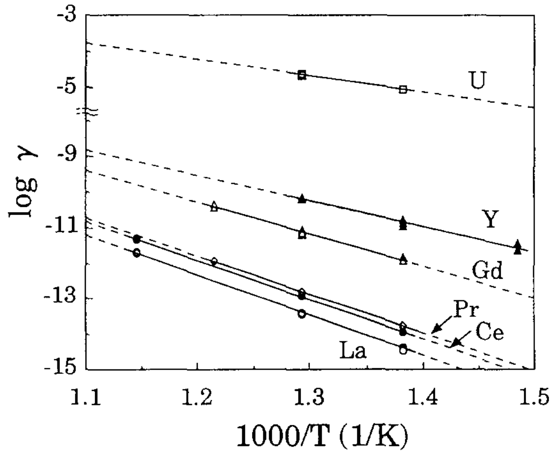

Fig. 7. Relationship between logarithms of activity coefficient of U, La, Ce, Pr, Gd and Y in Bi and inverse temperature.

3.4. Partial molar enthalpy of mixing and partial molar excess entropy

Fig. 7 shows the relationship between the inverse temperature and the logarithms of the activity coefficient of U, La, Ce, Pr, Gd and Y in Bi. The logarithms of the activity coefficient are seen to change linearly with increasing inverse temperature. The slope for U is much larger than those for REs, while the slopes for heavy REs are larger than those for light REs. The variations in the slope suggested that the differences between the activity coefficients of U and REs and the differences between the activity coefficients of heavy REs and light REs decreased with increasing temperature.

The variations in the separation factor as a function of temperature can be calculated from Eq. (16) when the variations in the standard potential in LiCl–KCl and the activity coefficients in Bi are known. The calculated separation factors are summarized in Table 3. The separation factors for the various elements calculated in the LiCl–KCl/Cd and LiCl–KCl/Bi

Table 3
Relationship between separation factors w.r.t. Ce and temperature

System	Element	Separation factor			
		Calculated			Experimental
		673 K	773 K	873 K	773 K
LiCl–KCl/Bi	La	3.09	3.02	2.80	3.03
	Ce	1	1	1	1
	Pr	0.67	0.72	0.66	1.01
	Gd	4.67	4.04	3.43	11.68
	Y	4741	1391	435	689
	U	0.00015	0.00082	0.00247	0.00119
LiCl–KCl/Cd	La	4.44	2.69	1.83	2.70
	Ce	1	1	1	1
	Pr	0.78	0.79	0.82	0.88
	Nd	0.83	0.75	0.30	0.96
	Gd	4.88	3.00	2.76	3.71
	Y	513	142	31	101
	U	0.0130	0.0279	0.0344	0.0180
	Np	0.0111	0.0219	0.1393	0.0372
	Pu	0.0357	0.0464	0.1052	0.040

systems approach each other with increasing temperature. According to a previous study [2], the separation factors of Y w.r.t. Ce in the LiCl–KCl/Cd system were 104, 91 and 50 at 723, 773 and 873 K respectively, which is consistent with the tendency of the variations in the separation factors calculated in this study.

The partial molar excess Gibbs energy of the solute M in the liquid metal is calculated from the activity coefficient as

$$\Delta \bar{G}^{\mathrm{ex}}_{\mathrm{M}} = RT \ln \gamma^{\#} \tag{19}$$

If the logarithm of the activity coefficient is assumed to be approximated by

$$\ln \gamma^{\#}_{\mathrm{M}} = 2.303 \log \gamma^{\#}_{\mathrm{M}} = 2.303 \left(A - \frac{B}{T} \right) \tag{20}$$

where A and B are constants, then the partial molar enthalpy of mixing and the partial molar excess entropy are given respectively by

$$\Delta \bar{H}^{\mathrm{mix}}_{\mathrm{M}} = -2.303\, BR \tag{21}$$

$$\Delta \bar{S}^{\mathrm{ex}}_{\mathrm{M}} = -2.303\, AR \tag{22}$$

Table 4
Partial molar enthalpy of mixing and partial molar excess entropy of solutes

Solvent	Solute	$\Delta \bar{H}^{mix}$ (kJ mol^{-1})	$\Delta \bar{S}^{ex}$ (J K^{-1} mol^{-1})	Ref.
Bi	Y	−137.2	17.5	This work
	Y	−166.8	−9.6	[12]
	La	−219.8	−27.3	This work
	La	−209.8	−14.9	[13]
	Ce	−209.8	−23.4	This work
	Ce	−218.3	−38.9	[14]
	Pr	−207.8	−23.6	This work
	Pr	−228.6	−55.7	[15]
	Nd	−212.0	−36.4	[16]
	Sm	−225.4	−33.5	[17]
	Eu	−166.3	−28.7	[18]
	Gd	−172.3	−10.2	This work
	Gd	−188.7	−23.6	[11]
	U	−88.6	−25.4	This work
	U	−83.1	−19.9	[19]
	Pu	−164.4	−33.7	[20]
Cd	Y	−73.0	21.6	[5]
	La	−169.8	−58.0	[5]
	La	−188.9	−83.2	[23]
	Ce	−178.7	−79.3	[5]
	Ce	−193.0	−99.0	[23]
	Pr	−178.2	−82.9	[5]
	Pr	−189.9	−99.2	[23]
	Nd	−150.4	−41.0	[5]
	Gd	−134.8	−56.9	[5]
	U	−22.5	−66.7	[5]
	U	−28.6	−75.1	[24]
	U	−32.9	−77.2	[25]
	Np	−99.5	−95.4	[21]
	Np	−95.5	−88.1	[26]
	Pu	−121.3	−86.8	[22]
	Pu	−112.1	−71.0	[27]

The partial molar enthalpy of mixing and the partial molar excess entropy calculated from Eqs. (21) and (22) are summarized in Table 4. The results indicate that the order of the partial molar enthalpy of mixing is similar in both Bi and Cd: $\Delta \bar{H}^{\mathrm{mix}}_{\mathrm{U}} > \Delta \bar{H}^{\mathrm{mix}}_{\mathrm{Y}} > \Delta \bar{H}^{\mathrm{mix}}_{\mathrm{Np}} > \Delta \bar{H}^{\mathrm{mix}}_{\mathrm{Pu}} > \Delta \bar{H}^{\mathrm{mix}}_{\mathrm{G}} > \Delta \bar{H}^{\mathrm{mix}}_{\mathrm{Ls}} \approx \Delta \bar{H}^{\mathrm{mix}}_{\mathrm{Ce}} \approx \Delta \bar{H}^{\mathrm{mix}}_{\mathrm{Pr}} \approx \Delta \bar{H}^{\mathrm{mix}}_{\mathrm{Nd}}$. The partial molar enthalpy of mixing for each actinide or RE in Bi is much smaller than that in Cd, although the values in Table 4 are fairly scattered. This suggests that the cohesive energy between Bi and the solute is larger than that between Cd and the solute. The partial molar excess entropy in Bi is larger than that in Cd, with the exception of Y.

3.5. Relationship among activity coefficient, ionic radii and electronegativity

The activity coefficient or the partial molar excess Gibbs energy of actinides and REs in Bi and Cd exhibits an extreme negative deviation from Raoult's law, with the exception of U in Cd. This suggests that the bonding between the liquid metals and the solute is strong. Figs. 8(a) and 8(b) show the relationship

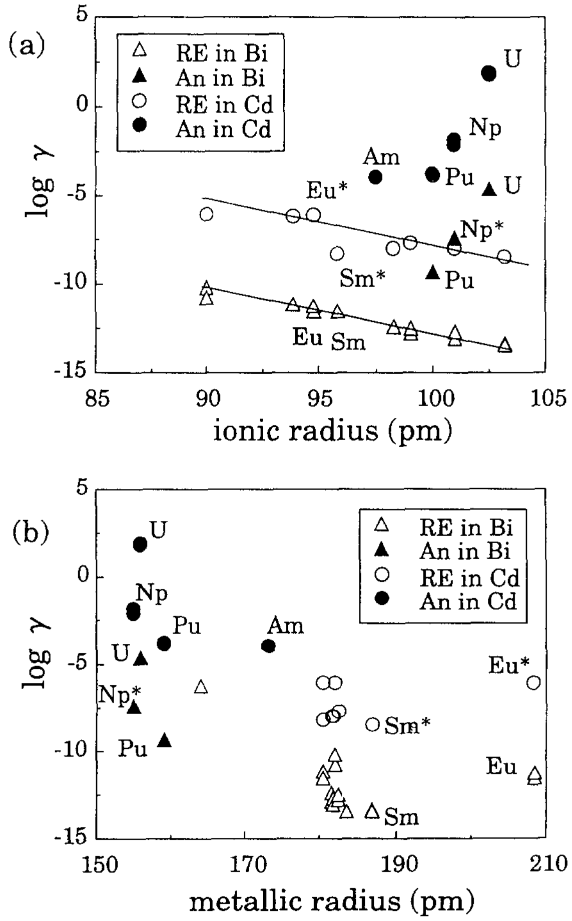

Fig. 8. (a) Relationship between logarithms of activity coefficient and trivalent ionic radius of solute. Activity coefficients of Sm and Eu in Cd and that of Np in Bi are estimated values. (b) Relationship between logarithms of activity coefficient and metallic radius of solute.

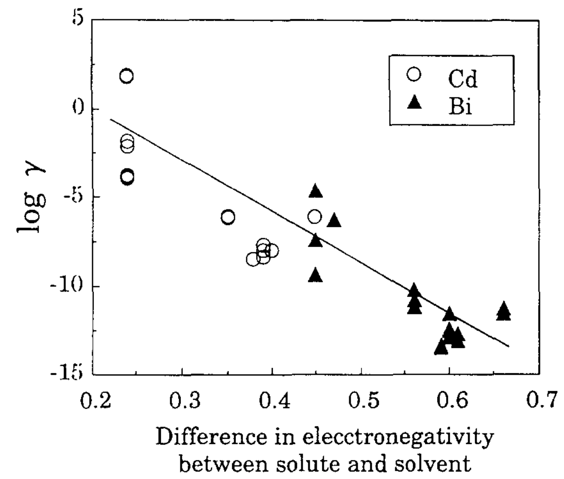

Fig. 9. Relationship between logarithms of activity coefficient of solute and difference in Allred–Rochow electronegativity [28] between liquid Bi or Cd and solute.

between the logarithms of the activity coefficient and the trivalent ionic radius and the relationship between the logarithms of the activity coefficient and the metallic radius respectively. The linear correlation between the logarithms of the activity coefficient and the ionic radius is clearly seen in Fig. 8(a), including the estimated values of Sm and Eu. Fig. 9 shows the relationship between the logarithms of the activity coefficient and the difference in the Allred–Rochow electronegativity [28] between the liquid metals and the solute. A linear correlation is also seen.

4. Conclusions

The activity coefficients of U and some REs were measured electrochemically. The activity coefficients of Np and Nd were evaluated from the distribution coefficients in the LiCl–KCl/Bi system and the standard potentials in LiCl–KCl. The separation factor of Pu in the LiCl–KCl/Bi system was calculated from the activity coefficient in Bi and the standard potential in LiCl–KCl. Moreover, the activity coefficients of Sm and Eu in liquid Cd were estimated from the distribution coefficients in the LiCl–KCl/Cd system and the pseudostandard potentials which were obtained from the distribution coefficients in the LiCl–KCl/Bi system and the activity coefficients in Bi. The variations in the separation factor as a function of temperature were estimated. The estimated separation factors of actinides and REs gradually decreased with increasing temperature.

Acknowledgments

The authors wish to express their thanks to Professor H. Moriyama and Dr. S. Nishikawa of Kyoto University Reactor Institute and Dr. Inoue of Central Research Institute of Electric Power Industry for their help with the experiment. They are grateful to Dr. Bychkov for helpful discussion on molten salts and liquid metals.

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