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Thermodynamics of reductive extraction of actinides and lanthanides from molten chloride salt into liquid metal

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Abstract

For the development of a pyrochemical group-partitioning process of actinides and lanthanides, the equilibrium distributions of these elements were measured in some typical binary phase systems of molten salt and liquid metal. A LiCl-KCl mixture was selected as the salt phase, and Zn and Bi were examined as the metal phase. Generally speaking, actinides were more reducible and extractable from the salt phase into the metal phase than lanthanides, and the group partitioning of these elements was feasible in these systems. However, the separation factors which were the ratios in the distribution coefficient between actinides and lanthanides were found to be different in different systems due to different alloying energies. The thermodynamic quantities of actinides and lanthanides were evaluated from the equilibrium distributions and discussed in some detail. © 1998 Elsevier Science S.A.

Keywords: Reductive extraction; Actinides; Lanthanides; Liquid metal; Molten salt; Thermodynamic properties

1. Introduction

Pyrochemical processing of nuclear materials using molten salt and liquid metal as solvents is expected to be very useful for advanced nuclear chemical processing. For example, such a processing is indispensable for the recycling of nuclear fuels of molten salt breeder reactors [1] and of metallic fuel fast breeder reactors [2], and extensive studies have been performed in the development programs. Also, because of its high radiation resistance, compactness and less waste generation, it gets much attention for its use in place of aqueous processing. In fact, some applications have been proposed for the recovery of nuclear materials and useful elements from spent fuels [3,4].

The experiments by Ferris et al. at ORNL are well known as a typical study on pyrochemical processing. They investigated the reductive extraction of actinides and fission products in a LiF-BeF$_2$/Bi system [5,6] and, in their experiments, they measured the equilibrium distributions of several elements to show the technical feasibility of its application. The present authors also measured the equilibrium distributions [7–11] and extraction kinetics [12] in such systems as the LiF-BeF$_2$/Bi. In these studies, the equilibrium distributions of actinides and lanthanides were determined as a function of salt phase composition, metal phase composition and temperature, and the mechanism of the reductive extraction was studied in some detail. As a result, it has been shown that actinides are more reducible and extractable into the metal phase than lanthanides, but that different solvent metals give quite different separation factors between actinides and lanthanides [11].

The present study is an extension of our previous studies to systems using molten LiCl-KCl and, following a preliminary measurement [13], the reductive extraction behaviors of actinides and lanthanides have been studied in the LiCl-KCl/Zn and LiCl-KCl/Bi systems. Thermodynamic quantities of the solute elements have been determined from the experimental results and are discussed.

2. Experimental

The eutectic mixture of LiCl and KCl (mole ratio of lithium to potassium=51/49) was obtained from Anderson Physics Laboratory Engineered Materials Inc. and all other reagents of reagent grade were obtained from Nacalai Tesque, Co. The radioactive tracers of ^{239}Np and ^{233}Pa

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were produced by thermal neutron irradiation of U and Th metals (10 mg each), and those of lanthanides were produced by irradiation of the metals (less than 100 mg each). In some runs, ^{239}Pu, ^{241}Am and ^{242}Cm coprecipitated with LaF_3 (5 mg) were also used.

Experiments were performed in an argon glove box of <1 ppm H_2O, and the experimental apparatus and procedures employed in the present study were much the same as in the previous ones [7–13]. In a typical experiment for the LiCl-KCl/Zn system, 2 mol of LiCl-KCl mixture, 2 mol of Zn, and radioactive solutes were loaded in an alumina crucible. After drying at 450 K in vacuum, the system was heated to a given temperature under an inert gas atmosphere. The distribution of the solute elements was controlled by adding a Li-Zn alloy as a reductant. After every addition of the reductant, the system was gas-sparged for a few hours to attain the equilibrium, and then small portions of both phases were sucked into a stainless steel tube as samples. All the samples were weighed and their radioactivities were determined by γ-spectrometry. The radioactivity of ^{239}Pu, ^{241}Am and ^{242}Cm was measured by α-spectrometry. The Li concentration in the metal phase sample was determined by atomic absorption spectrophotometry.

3. Results and discussion

3.1. Mechanism of equilibrium distributions

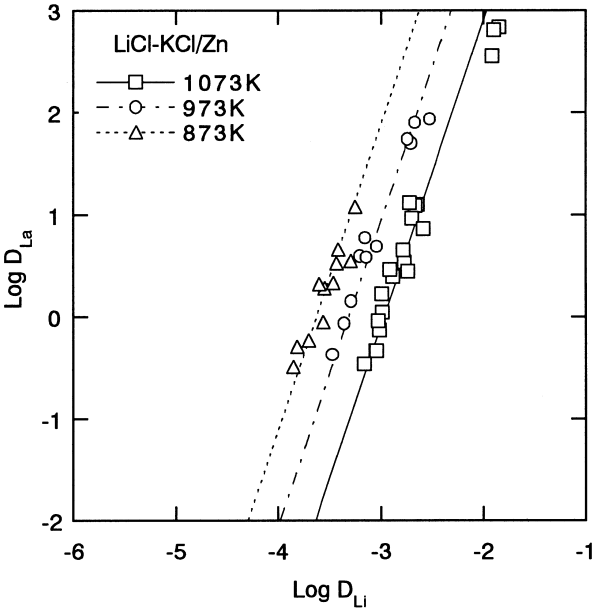

Fig. 1. Distribution coefficient of La as a function of that of Li in LiCl-KCl/Zn system.

According to our previous studies [7–11], the equilibrium distribution of a solute element M in the LiCl-KCl/A (A: Zn or Bi) system is given by

$$\mathrm{Li}_{m-n}\mathrm{MCl}_m + n\mathrm{Li} + x\mathrm{A} = \mathrm{MA}_x + m\mathrm{LiCl} \qquad (1)$$

where $\mathrm{Li}_{m-n}\mathrm{MCl}_m$ and MA_x represent complex compounds in the salt phase and intermetallic compounds in the metal phase, respectively.

By taking reaction (1), the D_M/D^n_{Li} value which is

Table 1
Extractability values in $\log(D_M/D^n_{Li})$ of lanthanides and actinides in the LiCl-KCl/Zn and LiCl-KCl/Bi systems

Element	*n*	*m*	$\log(D_M/D^n_{Li})$ in LiCl-KCl/Zn at:		$\log(D_M/D^n_{Li})$ in LiCl-KCl/Bi at:	
			873 K	1073 K	873 K	1073 K
La	3	3	10.879±0.065	8.903±0.061	6.605±0.063	5.328±0.111
Ce	3	3	11.197±0.119	9.226±0.072	6.713±0.099	5.668±0.111
Pr	3	3	11.578±0.030	9.558±0.056	6.911±0.067	5.664±0.114
Nd	3	3	10.935±0.165	8.920±0.243	6.648±0.250	5.608±0.111
Pm						
Sm	2	2	6.665±0.112	5.208±0.080	3.492±0.322	3.136±0.080
Eu	2	2	5.110±0.100	3.555±0.109	2.617±0.099	1.873±0.128
Gd	3	3	10.638±0.351	8.667±0.118	6.478±0.111	5.206±0.125
Tb	3	3	11.195±0.103	9.352±0.044	6.389±0.123	5.071±0.125
Dy	3	3		9.693±0.085		
Ho	3	3	11.010±0.175	9.298±0.091		
Er	3	3	10.829±0.197	9.386±0.111		
Tm	3	3	10.558±0.074	8.776±0.053	5.708±0.102	5.011±0.114
Yb	2	2	6.474±0.196	4.929±0.088	2.568±0.093	1.815±0.095
Lu	3	3	10.356±0.080	8.899±0.040		
Pa	4	6	17.827±0.293	13.262±0.351		
U	3	3				
Np	3	3	11.222±0.174	9.089±0.138	8.282±0.080	6.468±0.167
Pu	3	3	11.674±0.184		9.666±0.597	7.564±0.200
Am	3[a]	3[a]	12.353±0.205	10.309±0.159	9.485±0.202	8.056±0.139
Cm	3	3	11.984±0.208	10.040±0.170	9.113±0.150	7.690±0.109

[a] Assumed. Divalent species may also be present in the LiCl-KCl/Bi system.

defined as the extractability value of each element [9] is represented by

$$\begin{aligned}\log(\mathrm{D_M}/\mathrm{D^n_{Li}}) = & -(2.3RT)^{-1}[\Delta G_f°(\mathrm{MA}_x) + m\Delta G_f°(\mathrm{LiCl}) \\ & - \Delta G_f°(\mathrm{Li}_{m-n}\mathrm{MCl}_m)] \\ & + x\log \mathrm{X_A} - (m-n)\log \mathrm{X_{LiCl}} - \log\gamma_{\mathrm{MA_x}} \\ & - m\log\gamma_{\mathrm{LiCl}} \\ & + \log\gamma_{\mathrm{Li}_{m-n}\mathrm{MCl}_m} + n\log\gamma_{\mathrm{Li}} + x\log\gamma_{\mathrm{A}} \qquad (2)\end{aligned}$$

where the distribution coefficients $\mathrm{D_M}$ and $\mathrm{D_{Li}}$ are defined as $\mathrm{D_M} = \mathrm{X_{M(metal)}}/\mathrm{X_{M(salt)}}$ and $\mathrm{D_{Li}} = \mathrm{X_{Li(metal)}}/\mathrm{X_{Li(salt)}}$. The terms in the right hand side in Eq. (2) are constant at a given temperature and composition, and then the logarithm of $\mathrm{D_M}$ is proportional to that of $\mathrm{D_{Li}}$ with a slope of n.

$$\log \mathrm{D_M} = n\log \mathrm{D_{Li}} + \log K'_{\mathrm{M}} \qquad (3)$$

where K'_{M} is a constant under the above defined conditions.

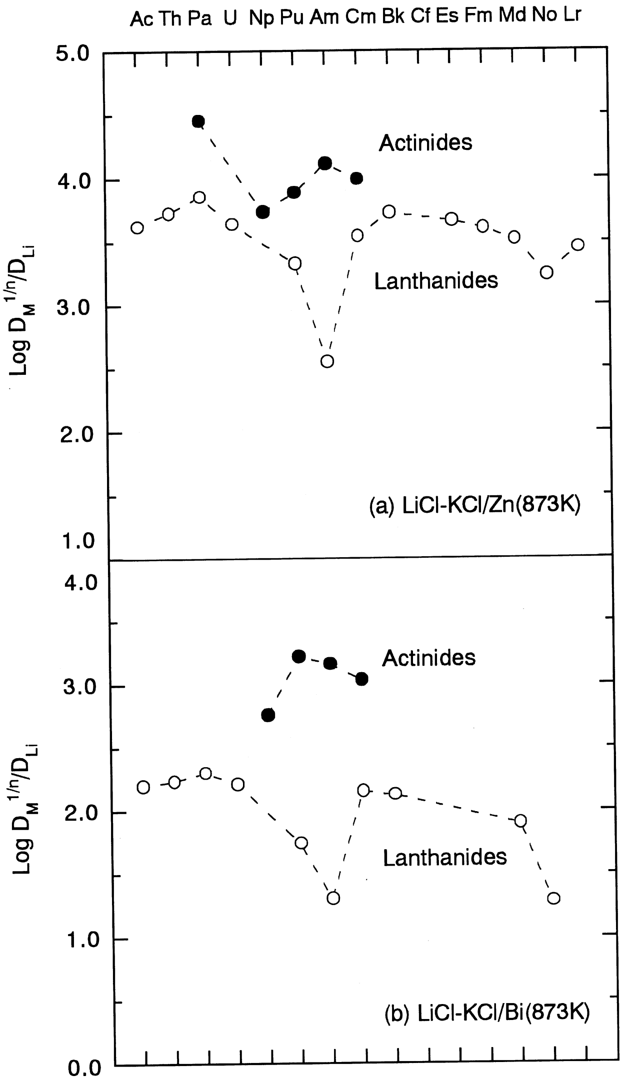

Fig. 2. Atomic number dependence of measured extractability in (a) LiCl-KCl/Zn system and (b) LiCl-KCl/Bi system.

3.2. Observed distribution behaviors of solutes

As a typical example, the observed distribution coefficients of La are plotted as a function of those of Li in Fig. 1. Curves represent the least squares fitting of the data to Eq. (3) in which the slope of 3 is assumed. The agreements are satisfactorily good and this means that La is present as trivalent species in the salt phase, as already observed in the preliminary measurement [13]. The scatters of the data were much improved in the present study, and the extractability values in log $(\mathrm{D_M}/\mathrm{D^n_{Li}})$ were determined for La. Similarly, the distribution data of all other elements were analyzed by using Eq. (3) and the extractability values were obtained as summarized in Table 1.

Fig. 2 shows the atomic number dependence of the obtained extractability values in the LiCl-KCl/Zn and LiCl-KCl/Bi systems at 873 K. It can be seen that actinides Pa, Np, Pu, Am and Cm are more extractable than lanthanides in both systems. This is important since such differences may be applied to the group partitioning of actinides and lanthanides. However, the separation factors which are the ratios in the distribution coefficient between actinides and lanthanides are different in different systems, and the separation factors in the Bi system are higher than those in the Zn system. The observed trend is the same as that in our previous study [11] in which the separation factors have been studied in the systems of $\mathrm{LiF\text{-}BeF_2/Bi}$, $\mathrm{LiF\text{-}BeF_2/Sn}$, $\mathrm{LiF\text{-}BeF_2/Cd}$ and $\mathrm{LiF\text{-}BeF_2/Zn}$. No apparent difference in the separation factors is observed due to different salt phases, and the importance of the alloying energies in the metal phase on the separation factors is confirmed.

4. Thermodynamic considerations

The thermodynamic quantities in the metal phase are evaluated from the obtained extractability data. Eq. (2) is used to calculate the standard Gibbs free energy of formation of intermetallic compounds, $\Delta G_f°(\mathrm{MA}_x)$, and the $\Delta H_f°(\mathrm{MA}_x)$ and $\Delta S_f°(\mathrm{MA}_x)$ values can be calculated from the temperature dependence of the $\Delta G_f°(\mathrm{MA}_x)$ by using the equation: $\Delta G_f°(\mathrm{MA}_x) = \Delta H_f°(\mathrm{MA}_x) - T\Delta S_f°(\mathrm{MA}_x)$. In the present system, each solute is present in low concentration (less than 1 mol.%) and, by assuming that $\mathrm{Li}_{m-n}\mathrm{MCl}_m$ and MA_x do not interact with the solvent, the values γ_{MA_x} and $\gamma_{\mathrm{Li}_{m-n}\mathrm{MCl}_m}$ are approximately estimated to be unity. The γ_{LiCl} is taken from the literature [14] and the γ_{Li} in Zn [15] and Bi [6] is given by $\log \gamma_{\mathrm{Li(Zn)}} = 0.78 - 2346/T$ and $\log \gamma_{\mathrm{Li(Bi)}} = 0.1958 - 3780/T$, respectively. The other thermodynamic data of $\Delta G_f°(\mathrm{MCl}_n)$ are taken from the literature [16–18] and, referring to the case of Th [7], the $\Delta G_f°(\mathrm{Li_2MCl_6})$ value of Pa is estimated by

$\Delta G_f^\circ(\mathrm{Li_2MCl_6}) = \Delta G_f^\circ(\mathrm{MCl_4}) + 2\Delta G_f^\circ(\mathrm{LiCl}) - 10$ (kcal/mol). Table 2 summarizes the evaluated enthalpy and entropy of formation of intermetallic compounds MZn_x and MBi_x together with the literature values of lanthanides [19] and actinides [20].

Fig. 3 shows the correlation of the $\Delta H_f^\circ(\mathrm{MA}_x)$ values with the normalized standard enthalpy change $\Delta H_f^\circ(\mathrm{MCl}_n)/n$ of the chloride compounds. The $\Delta H_f^\circ(\mathrm{MCl}_n)/n$ values directly reflect the ionic bonding strength between the metal cation and chloride anion in the salt phase and, by comparing both values, some information may be obtained on the nature of the intermetallic compounds MA_x in the metal phase. As shown in Fig. 3a, a good correlation has been observed between both values for trivalent lanthanides in the Zn system. This indicates that the intermetallic interaction between the lanthanides and zinc is of similar type of bonding as of the cation-anion bonding, i.e. ionic bonding in the salt phase. Similar correlations are expected to hold for divalent lanthanides such as Sm, Eu and Yb, for trivalent actinides such as U through Cm, and possibly for tetravalent actinides such as Th and Pa, and the same situation may be drawn for each group.

As shown in Fig. 3b for the Bi system, similar correlations of the $\Delta H_f^\circ(\mathrm{MA}_x)$ values are also observed to those for the Zn system. By comparing the correlations in both systems, however, it is found that the group of trivalent actinides is positioned at more negative values than that of lanthanides, and that the observed gap between both groups is larger in the Bi system than in the Zn system. This means the interactions of actinides with the solvent metals are stronger than those of lanthanides and the interactions of actinides with Bi are stronger than those with Zn. As for the difference between the Bi and Zn systems, the separation factors of actinides and lanthanides have already been observed to be larger in the LiF-$\mathrm{BeF_2}$/Bi system than in the LiF-$\mathrm{BeF_2}$/Zn system in our previous study [9] and, referring to the atomistic model of Miedema for the alloying energies [21], it has been attributed to the difference in additional energy contributions such as hybridization between d- and p-elements. The presently observed differences in the $\Delta H_f^\circ(\mathrm{MA}_x)$ values between actinides and lanthanides are also attributed to different hybridization energies. A larger gap comes from a higher hybridization energy, and a higher separation factor is attained by selecting a metal phase of a higher hybridization energy.

The observed correlations are important not only to discuss the nature of the intermetallic interactions but also to predict the unknown $\Delta H_f^\circ(\mathrm{MA}_x)$ values and then the extractability data. Once the $\Delta H_f^\circ(\mathrm{MA}_x)$ value of an element is given, the $\Delta S_f^\circ(\mathrm{MA}_x)$ value can also be

Table 2
Thermodymanic quantities of intermetallic compounds of lanthanides and actinides in liquid Zn and Bi

Element	$\Delta H_f^\circ(\mathrm{MZn}_x)$ (kcal mol^{-1})	$\Delta S_f^\circ(\mathrm{MZn}_x)$ (cal K^{-1} mol^{-1})	$\Delta H_f^\circ(\mathrm{MBi}_x)$ (kcal mol^{-1})	$\Delta S_f^\circ(\mathrm{MBi}_x)$ (cal K^{-1} mol^{-1})	Note
La	−47.90±1.91	−23.50±2.21	−52.61±2.73	−17.89±3.14	
	−52.54	−19.27			[19]
Ce	−44.16±2.97	−22.56±3.45	−44.01±3.19	−12.35±3.68	
	−56.11	−24.27			[19]
Pr	−45.35±1.36	−21.38±1.56	−48.47±2.82	−15.75±3.24	
	−54.19	−22.13			[19]
Nd	−42.06±6.28	−24.11±7.24	−40.84±5.85	−11.78±6.80	
Pm					
Sm	−60.47±2.95	−22.18±3.41	−50.02±7.09	−4.36±8.25	
Eu	−66.54±3.16	−31.86±3.65	−62.29±3.47	−18.03±4.00	
Gd	−33.61±7.93	−25.06±9.22	−38.32±3.57	−18.94±4.12	
Tb	−24.31±2.39	−15.16±2.78	−32.76±3.76	−16.27±4.34	
Dy					
Ho	−26.79±4.22	−17.69±4.90			
Er	−19.24±4.84	−11.85±5.62			
Tm	−25.35±1.94	−21.16±2.25	−21.80±3.28	−8.73±3.79	
Yb	−57.77±4.60	−23.61±5.34	−53.93±2.85	−16.71±3.29	
Lu	−21.23±1.91	−17.43±2.22			
Th	−43.550	−21.86	−37.035	−9.278	[20]
Pa	−28.11±9.79	−67.53±11.29			
			−48.825	−25.37	[20]
U	−3.907	−2.832	−18.64	−4.20	[20]
Np	−14.67±4.92	−25.56±5.69	−27.48±3.97	−23.15±4.56	
Pu			−48.44±13.47	−25.36±15.66	
	−43.452	−23.1	−38.250	−6.82	[20]
Am	−31.83±5.55	−18.86±6.42	−38.34±5.25	−8.89±6.09	
Cm	−28.79±5.75	−26.27±6.65	−37.28±3.97	−18.62±4.60	

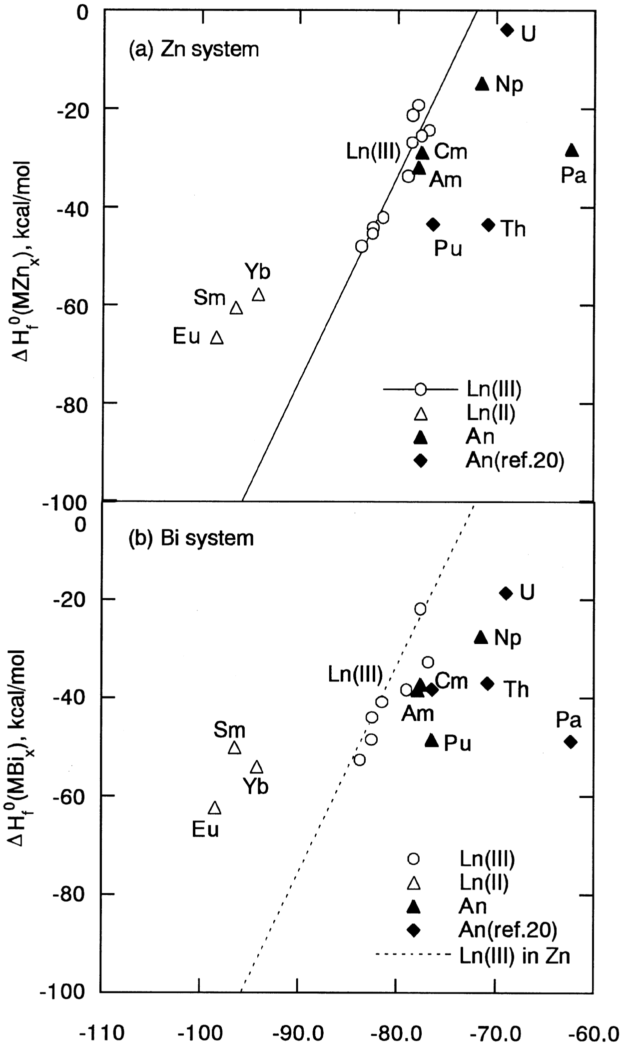

Fig. 3. Dependence of $\Delta H_f°(MA_x)$ values on $\Delta H_f°(MCl_n)/n$ values. Curves are drawn to aid the eyes in (a) Zn and (b) Bi systems.

predicted with the help of such a semi-empirical relationship as obtained before [9], and the $\Delta G_f°(MA_x)$ value and the extractability value will be predicted for the elements of which the experimental values are lacking. The predictions are useful for examining the technical feasibility of the pyrochemical processing.

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