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Equilibrium Distributions of Actinides and Lanthanides in Molten Salt and Liquid Metal Binary Phase Systems*

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In support of the development of a pyrochemical group partitioning process of actinides and lanthanides, the equilibrium distributions of these elements were measured in some binary phase systems of molten salt and liquid metal. LiF-BeF_2 mixture was selected as the salt phase, and Bi, Sn, Cd and Zn were examined as the metal phase. In general, actinides were more easily reduced and extracted from the salt phase into the metal phase than lanthanides. The group partitioning is thus feasible. In different partitioning systems, systematic difference in the separation factor between actinides and lanthanides was observed. The difference is attributable to the difference in alloying energies in the metal phase.

KEYWORDS: group partitioning, pyrochemistry, actinides, lanthanides, molten salt, liquid metals, thermodynamics

1. Introduction

Molten salt and liquid metal binary phase systems are expected to be much useful for future nuclear chemical processing because of their radiation resistance, compactness and rapid reaction kinetics. Extensive studies of these systems are thus seen, for example, for the development of molten salt breeder reactors[1)] and of metallic fuel fast breeder reactors[2)]. Also, the application of some similar systems has been proposed for the recovery of such useful elements as platinum group ones from spent fuel.[3,4)]

The experiment of Ferris et al. at ORNL is known for the reductive extraction of actinides and fission products in a LiF-BeF_2/Bi system.[5,6)] They measured the equilibrium distributions of several elements to show the technical feasibility of this pyrochemical method. We also measured the equilibrium distributions[7-13)] and extraction kinetics[14)] in the same and similar systems. The equilibrium distributions were determined as a function of salt phase composition, metal phase composition and temperature, and the mechanism of the reductive extraction was discussed in some details.

In these studies, it has been shown that actinides are more easily reduced and extracted from the salt phase into the metal phase than lanthanides. Thus the reductive extraction may be applied to the group partitioning of actinides and lanthanides. For the quantitative assessment of technical feasibility, we have been measuring the equilibrium distribtuions of acinides and lanthanides.[15)] In the present report, the separation factors in different metal phase systems are discussed. By selecting a LiF-BeF_2 mixture as a reference salt phase, Bi, Sn, Cd and Zn are examined as the metal phase.

2. Experimental

The experimental apparatus and procedures employed in the present study were much the same as in the previous ones.[7-14)] In a typical experiment, 2 mol of LiF-BeF_2 mixture (66.7 mole% LiF), 2 mol of either Bi, Sn, Cd or Zn, and small amounts (less than 100mg each) of radioactive solute metals were loaded in a graphite crucible. After drying at 450K in vacuum, the system was heated to a given temperature under an inert gas atmosphere.

The distribution of solute elements was controlled by the incremental addition of a reductant Li to the system. The Li was added in the form of its alloy with each solvent metal in order to assure the addition to the metal phase. After the equilibrium distributions were attained with gas sparging, samples were taken out from each phase with a stainless steel sampling tube under a reduced pressure. The concentrations of radioactive solutes were measured by a direct γ-spectrometry, and those of the reductant Li in the metal phase were determined by atomic absorption spectrophotometry.

3. Results and Discussion

According to our previous studies,[7-13)] the equilibrium distribution of a solute element M is given by

$$Li_{m-n}MF_m + n\,Li + x\,A = MA_x + m\,LiF \qquad (1)$$

*IMR, Report No. 1962

where $Li_{m-n}MF_m$ and MA_x represent complex compounds in the salt phase and intermetallic compounds in the metal phase, respectively. The formation of these compounds has been inferred from the dependence of equilibrium distributions on the salt and metal phase compositions.

By taking reaction (1), the extractibility D_M/D_{Li}^n of each element is represented by

$$\log (D_M/D_{Li}^n) = -(2.3RT)^{-1}[\Delta G_f^\circ(MBi_x) + m\Delta G_f^\circ(LiF) - \Delta G_f^\circ(Li_{m-n}MF_m)] + x \log X_A - (m-n) \log X_{LiF} - \log \gamma_{MAx} - m \log \gamma_{LiF} + \log \gamma_{Lim-nMFm} + n \log \gamma_{Li} + x \log \gamma_A \quad (2)$$

where the distribution coefficients D_M and D_{Li} are defined as $D_M = X_{M(metal)}/X_{M(salt)}$ and $D_{Li} = X_{Li(metal)}/X_{Li(salt)}$. The terms in the right hand side in Eq (2) are constant at a given temperature and composition. The extractability of the solute element M has been evaluated from the measured D_M and D_{Li} values, as summarized in Tables 1-4.

Table 1. log (D_M/D_{Li}^n) in LiF-BeF_2/Bi.*

Element(n)	873K	973K	1073K	Ref.
La(3)	7.33		5.62	8)
	6.924	6.362		6)
Ce(3)	7.67		5.98	8)
Nd(3)	7.66±0.30		5.75±0.21	
	7.806			6)
Sm(2)	4.65±0.17		3.51±0.01	
	4.740			6)
Eu(2)	4.47±0.21		3.33±0.24	
	3.861			6)
Gd(3)	6.40±0.26		4.73±0.11	
	6.217			6)
Tb(3)	6.49±0.34		4.91±0.34	
Dy(3)	6.50±0.01			
	5.663			6)
Er(3)	5.85±0.26		4.29±0.10	
Tm(3)	6.68±0.25		4.69±0.17	
Yb(2)	4.08±0.34		3.02±0.06	
Lu(3)	4.15±0.26		2.93±0.35	
Th(4)	10.2			7)
	9.731	8.702		6)
Pa(4)	13.09		10.19	8)
	13.304			6)
U(3)	12.204			6)
Np(3)	10.52		8.51	6)
Pu(3)	11.265			6)
Am(3)	11.44			6)
Cm(3)	10.472			6)
Cf(3)	11.472			6)

* Uncertainties are of the relative ones which are obtained from the comparison of the D_M values with D_{La}.

Table 2. log (D_M/D_{Li}^n) in LiF-BeF_2/Sn.*

Element(n)	873K	1073K
La(3)	9.94±0.56	7.82±1.06
Ce(3)	10.3±0.15	8.29±0.12
Nd(3)	10.8	8.31±0.10
Sm(2)	7.55±0.45	5.20±0.12
Eu(2)	5.24±0.55	3.78±0.10
Gd(3)	10.0±0.15	7.20±0.11
Dy(3)	10.4±0.30	7.06±0.18
Er(3)	9.78±0.36	6.26±0.12
Tm(3)	9.95±0.45	6.12±0.16
Yb(2)	6.43±0.20	3.98±0.11
Pa(4)	16.0±0.83	14.8±0.17
Np(3)	12.4±0.68	9.88±1.09

* See Table 1 footnote.

Table 3. log (D_M/D_{Li}^n) in LiF-BeF_2/Zn.*

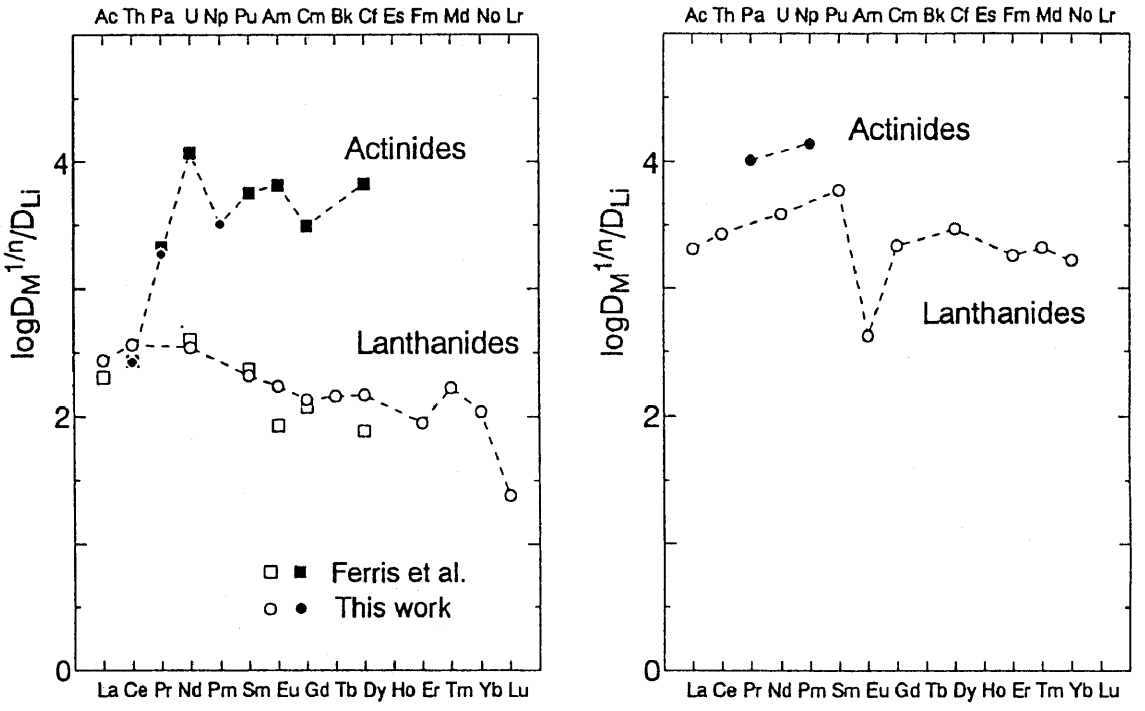
Element(n)	873K	1073K
La(3)	9.75±0.47	7.60±0.62
Ce(3)	10.0±0.17	8.00±0.18
Nd(3)	10.4±0.23	8.23±0.22
Sm(2)	6.38±0.12	5.65±0.27
Eu(2)	3.98±0.43	3.63±0.41
Gd(3)	10.0±0.25	8.03±0.04
Dy(3)	10.3±0.43	8.86±0.06
Er(3)	10.0±0.61	7.78±0.04
Tm(3)	10.2±0.64	8.78±0.61
Yb(2)	5.56±0.29	3.63±0.43
Pa(4)	15.2±1.09	12.9±0.10
Np(3)	10.5±0.59	9.36±0.11

* See Table 1 footnote.

Table 4. log (D_M/D_{Li}^n) in LiF-BeF_2/Cd.*

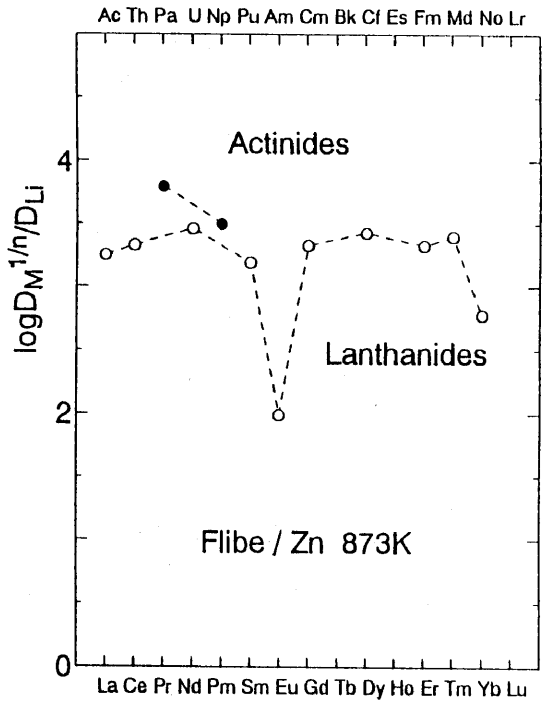
Element(n)	773K	873K
La(3)	9.45±0.49	8.58±0.12
Ce(3)	9.93±0.14	8.88±0.01
Nd(3)	9.78±0.08	8.70±0.06
Sm(2)	5.37±0.25	4.96±0.08
Eu(2)	<5.05	4.94±0.06
Gd(3)	8.59±0.18	8.05±0.04
Dy(3)	<8.15	7.41±0.06
Er(3)	7.75±0.12	7.44±0.09
Tm(3)	<8.03	<7.09
Yb(2)	4.75±0.16	4.86±0.04
Pa(4)	12.4±0.09	12.1±0.28
Np(3)	8.27±0.13	8.23±0.10

* See Table 1 footnote.

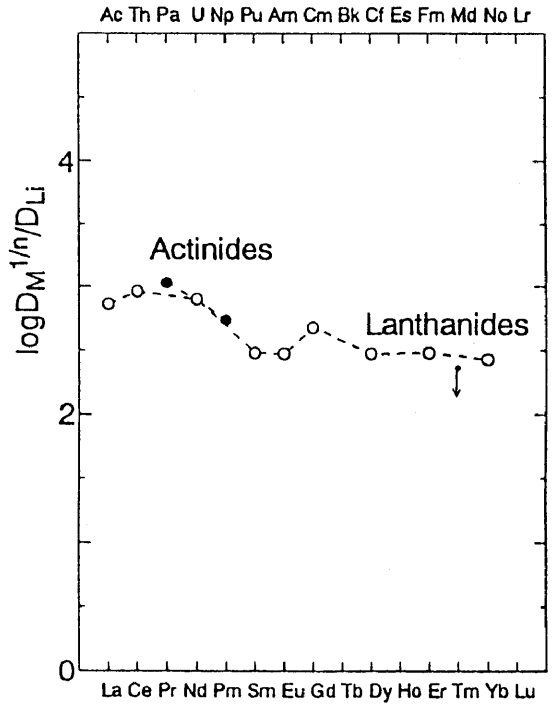


(a) LiF–BeF_2/Bi

(b) LiF–BeF_2/Sn



(c) LiF–BeF_2/Zn



(d) LiF–BeF_2/Cd

Fig. 1. Atomic number dependence of measured extractability in (a) LiF-BeF_2/Bi, (b) LiF-BeF_2/Sn, (c) LiF-BeF_2/Cd and (d) LiF-BeF_2/Zn systems at 873K. Circles are of the present study and squares are of the literature[6].

Fig. 1 shows the dependence of the evaluated extractability on atomic number. By comparing the extractability in different systems, the observations are summarized as:

(1) Actinides are more easily reduced and extracted from the salt phase into the metal phase than lanthanides. Thus, actinides and lanthanides behave as different groups.

(2) The separation factor between actinides and lanthanides depends on the selection of metal phase. The separation factor is the highest in the Bi system, it becomes smaller in the order of Sn, Zn and Cd systems.

The observations are important for the application of these systems to the group partitioning, and are to be discussed from basic chemical points of view. The observed tendency of the separation facor is discussed here on the basis of atomistic model of Miedema.[16] Such an analysis is important for searching the extraction systems of the highest performance.

Miedema has proposed the following equation for the enthalpy of formation of alloys.[16]

$$\Delta H/N_0 = f(c)[- P(\Delta\phi^*)^2 + Q(\Delta n_{ws}^{1/3})^2 - R] \qquad (3)$$

where $\Delta H/N_0$ is the enthalpy of formation per atoms, f(c) inculdes the factors such as concentration dependence, $\Delta\phi^*$ is the difference in electronegativity between atoms, Δn_{ws} is the difference in electron density, and P, Q and R are the constants. The electronegativity ϕ^* has been determined from the work functions of metal, and the electron density n_{ws} from the compressibilities and molar volumes of metal. The concentration dependence factor f(c) has been given by simple equations and the parameters P, Q and R have been determined empirically.

Examining the parameters of Miedema, one may find that the correction factor R, which is attributed to the additional energy contributions such as of hybridization between d- and p-elements, is important for actinides and lanthanides. According to him, the R value is given to be 2.3, 2.1, 1.4 and 1.4 for Bi, Sn, Cd and Zn, respectively. The higher R value suggests the higher contribution of hybridization energies, which may give the higher separation factor between actinides and lanthanides. In fact, the order is found to be consistent with the observed tendency of the separation factors. Consequently, it can be said that the metal phase of the higher R value is preferred for the group partitioning of actinides and lanthanides. From this point of view, Sb(R = 2.3) and Pb(R = 2.1) are also promising as the metal phase.

4. Conclusions

By selecting a LiF-BeF_2 as a reference salt phase, Bi, Sn, Cd and Zn have been examined for the metal phase. Actinides and lanthanides behaved as different groups and the separation factor beween both groups markedly depended on the selection of the metal phase. With the help of the Miedema's model, the separation factor between actinides and lanthanides was attributed to such hybridization energies as of d- and p-elements. The metal phase of higher hybridization energy may be suggested for higher separation factor.

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1) A. M. Weinberg et al.: Nucl. Appl. Technol. **8** (1970) 105.
2) D. C. Wade and Y. I. Chang: Nucl. Sci. Eng. **100** (1988) 507.
3) G. A. Jensen, A. M. Platt, G .B. Mellinger and W. J. Bjorklund: Nucl. Technol. **65** (1984) 305.
4) K. Naito, T. Matsui and Y. Tanaka: J. Nucl. Sci. Technol. **23** (1986) 540.
5) L. M. Ferris, J. C. Mailen and F. J. Smith: J. Inorg. Nucl. Chem. **32** (1970) 2019.
6) L. M. Ferris, J. C. Mailen and F. J. Smith: J. Inorg. Nucl. Chem. **33** (1971) 1325.
7) H. Moriyama, K. Yajima, Y. Tominaga, K. Moritani and J. Oishi: Nucl. Technol. **62** (1983) 133.
8) H. Moriyama, K. Yajima, N. Nunogane, T. Ohmura, K. Moritani and J. Oishi: J. Nucl. Sci. Technol. **21** (1984) 949.
9) H. Moriyama, N. Nunogane and J. Oishi: J. Nucl. Sci. Technol. **24** (1987) 120.
10) J. Oishi, H. Moriyama, K. Moritani, S. Maeda, M. Miyazaki and Y. Asaoka: J. Nucl. Mater. **154** (1988) 163.
11) H. Moriyama, K. Kinoshita and Y. Ito: J. Nucl. Sci. Technol. **27** (1990) 827.
12) H. Moriyama, K. Kinoshita, Y. Asaoka, K. Moritani and Y. Ito: J. Nucl. Sci. Technol. **27** (1990) 937.
13) H. Moriyama, K. Kinoshita, T. Seshimo, Y. Asaoka, K. Moritani and Y. Ito: Proc. of 3rd Int. Conf. on Nuclear Fuel Reprocessing and Waste Management, Vol.2, Sendai (1991) p.639.
14) H. Moriyama, M. Miyazaki, Y. Asaoka, K. Moritani and J. Oishi: J. Nucl. Mater. **182** (1991) 113.
15) H. Moriyama, T. Seshimo, K. Moritani, Y. Ito and T. Mitsugashira, Actnides-93 International Conference, Santa Fe, New Mexico, Sept. 19-24, 1993.
16) F. R. de Boer, R. Boom, W. C. M. Mattens, A. R. Miedema and A. K. Niessen: Cohesion in Metals, Transition Metal Alloys, North-Holland, Amsterdam (1988).