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Characteristics of the electrolytic amalgamation of trivalent f-elements and its application

Hajimu Yamana*, Hirotake Moriyama

Research Reactor Institute, Kyoto University, Noda, Kumatori-cho, Sennan-gun, Osaka 590-04, Japan

Abstract

Based on reported radiopolarography data, the thermodynamic systematics of the aqueous electrolytic amalgamation of trivalent f-elements was studied. The free energy changes of alloy formation in an aqueous amalgamation system were compared with those in the pyrochemical reductive extraction system of Zn and Cd. It is shown that the free energy changes of mercury alloy formation by trivalent f-elements exhibits a unique dependency on the metallic radii. Using basic parameters of the electrolytic amalgamation of f-elements, the feasibility of the separation of Am and Cm from lanthanides by electrolytic amalgamation was studied. © 1998 Elsevier Science S.A.

Keywords: Electrolytic amalgamation; Trivalent f-elements

1. Introduction

From the viewpoint of the importance of actinide recycling, various chemical investigations are being performed on the mutual separation of trivalent f-elements, americium, curium and lanthanides. Among the various separation techniques for f-elements, we have focused on the uniqueness of pyrochemical reductive extraction, and have reported the distribution behavior of f-elements between molten salt and liquid metal at high temperature [1–3]. In contrast to pyrochemical reductive extraction, electrolytic reductive extraction of f-elements from aqueous solution at room temperature is possible by using mercury as the cathode [4], and this has been widely investigated by radiopolarography of the precursors of actinide chemistry [5,6]. Although the principal mechanisms of aqueous electrolytic amalgamation and pyrochemical reductive extraction are the same, they have never been discussed together. In addition, the application of aqueous electrolytic amalgamation for the separation of f-elements has not been reported.

In this paper, based on reported radiopolarography data for trivalent actinides and lanthanides, we report a study of the basic thermodynamic systematics of the aqueous amalgamation of trivalent f-elements. A comparison with the pyrochemical reductive extraction system using Zn and Cd was made to determine the differences in the interactions of f-elements with different Group IIb metals. In addition, the feasibility of applying electrolytic amalgamation to the separation of trivalent f-elements is discussed.

2. Electrolytic amalgamation and pyrochemical reductive extraction

The mechanism of aqueous electrolytic amalgamation (AEA) is given by the equation

$$M^{y+} + x\mathrm{Hg} + ye^- \rightarrow \mathrm{MHg}_x \qquad (1)$$

where $y = 2$ or 3, M^{y+} is an f-element cation and MHg_x is an intermetallic compound of M with Hg (amalgam). Pyrochemical reductive extraction (PRE), which is performed at high temperature (>700 K), extracts the f-elements from the molten salt by reducing them to the metallic state by the use of a suitable reductant, e.g. Li. The mechanism is expressed by the equation

$$\mathrm{MCl}_x + x\mathrm{A} + y\mathrm{Li} \rightarrow \mathrm{MA}_x + y\mathrm{LiCl} \qquad (2)$$

where $x = 2$ or 3 and A is bulk metal. The thermodynamic relations in these extraction mechanisms are shown schematically in Fig. 1, in which the similarity of AEA and PRE is evident. In both systems, the absorption of the

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*Corresponding author. Tel.: +81 724 51 2442; fax: +81 724 51 2634; e-mail: yamana@hl.rri.kyoto-u.ac.jp

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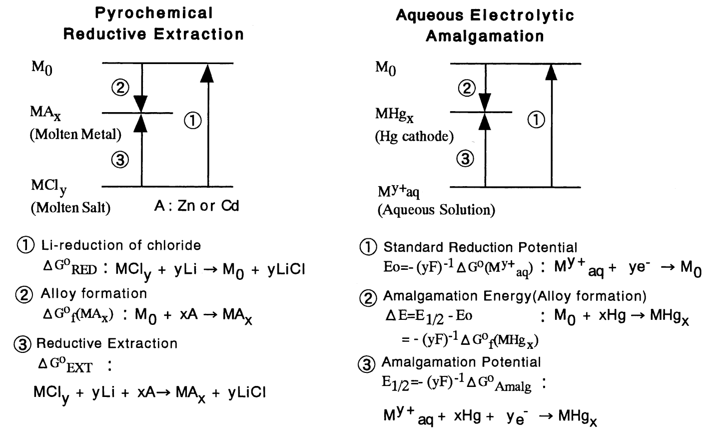


Fig. 1. Similarity of the thermodynamics of pyrochemical reductive extraction and aqueous electrolytic amalgamation.

f-element to the metallic phase occurs at low reductive potential (positive-sided cathodic potential in AEA and low reductant concentration in PRE) with the aid of a large energetic stabilization of alloy formation of the f-elements with bulk metals, which is represented by $\Delta G_f°(MA_x)$ in the figure.

3. Potential data for f-elements by radiopolarography

Radiopolarography, which is an analytic technique for radioactive elements, provides basic data on electrolytic amalgamation behavior [4]. The half-wave potentials ($E_{1/2}$) observed by radiopolarography give directly the cathodic potential at which the reduction of the ions to the metallic state begins. For lanthanides [5,7], the values summarized by Nugent [5] are adopted. Although the $E_{1/2}$ for Pr, Nd, Pm, Dy, Er and Tm were not reported, they were estimated by interpolating the linear relation between the metallic radii of the trivalent f-elements and their amalgamation energies [5]. An element's amalgamation energy (ΔE) is defined as the difference between the observed $E_{1/2}$ and the standard reduction potential ($E°$), and thus represents the energetic stabilization of the metallic state by the formation of a mercury alloy. For Am and Cm, the $E_{1/2}$ of the reduction waves, which were observed as true diffusion controlled waves in a careful study of Shiokawa [8], were adopted. All the $E_{1/2}$ value of actinides and lanthanides adopted in this paper are listed in Table 1.

4. Thermodynamic systematics of electrolytic amalgamation

The relations of thermodynamic parameters in the AEA system, i.e. amalgamation potential ($E_{1/2} = (-yF)^{-1}\Delta G°_{\mathrm{Amalg}}$), amalgamation energy ($\Delta E = (-yF)^{-1}\Delta G°_f(\mathrm{MHg}_x)$) and standard reduction potential ($E° = (-yF)^{-1}\Delta G°(\mathrm{M}^{y+}_{\mathrm{aq}})$), and those in the PRE system, i.e. free energy change of reductive extraction (ΔG_{EXT}), alloy formation free energy change ($\Delta G°_f(\mathrm{MA}_x)$) and free energy change of Li reduction (ΔG_{RED}), are shown in Fig.

Table 1
Summary of radiopolarography data for trivalent f-elements

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ac	Am	Cm
Metallic radius (Å)	1.88[b]	1.83[b]	1.83[a]	1.82[a]	1.81[a]	1.80[b]	2.04[b]	1.80[b]	1.78[b]	1.77[a]	1.77[b]	1.76[a]	1.75[a]	1.94[b]	1.74[b]	1.878[a]	1.73[b]	1.74[b]
$E_{1/2}$ (V) (NHE)	1.75[b]	1.83[b]	**1.88**	**1.83**	**1.79**	1.71[b]	1.70[b]	1.78[b]	1.73[b]	**1.79**	1.77[b]	**1.74**	**1.73**	1.81[b]	1.68[b]	1.91[d]	1.72[e]	1.77[e]
$E°$ (0–III) (V) (NHE)	2.36[b]	2.32[b]	2.35[c]	2.32[c]	2.29[c]	2.28[b]	1.98[b]	2.26[b]	2.27[b]	2.29[c]	2.34[b]	2.31[c]	2.31[c]	2.23[b]	2.28[b]	2.18[b]	2.07[f]	2.06[f]
$E°$ (0–II) (V) (NHE)						2.65[b]	2.79[b]							2.77[b]				
Δ3 (V)	0.61[b]	0.49[b]	**0.47**	**0.49**	**0.50**			0.48[b]	0.54[b]	**0.56**	0.57[b]	**0.57**	**0.58**		0.60[b]	0.27	0.35	0.29
Δ2 (V)						0.94[b]	1.09[b]							0.96[b]				

Δ3: Amalgamation energy of trivalent cations.

Δ2: Amalgamation energy of divalent cations.

Data in bold type were estimated in this study.

[a] Ref. [10].

[b] Ref. [5].

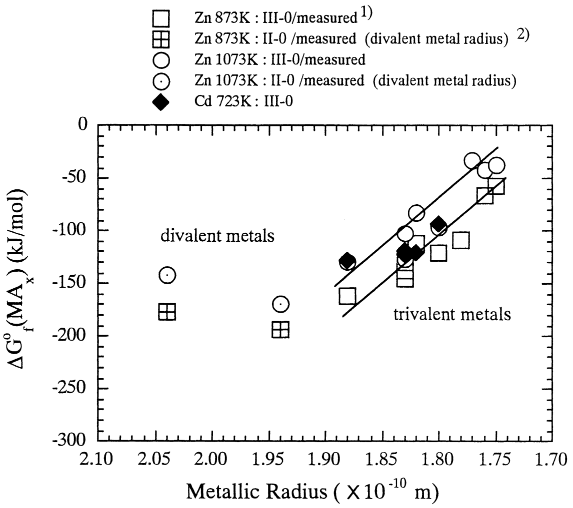
[c] Ref. [11].

[d] Ref. [12].

[e] Ref. [8].

[f] Ref. [6].

1. In this paper, the systematic trend of these parameters over the f-series was studied by comparing these different systems. The free energy changes in the AEA system are all calculated based on the thermodynamic relation of Fig. 1 using the known electrolytic potentials summarized in Table 1. The ΔG_{RED} and $\Delta G^{\circ}_{\mathrm{f}}(\mathrm{MA}_x)$ of the PRE Zn system are calculated in the same manner from the experimental equilibrium of distributions of f-elements in the binary phase system of molten chloride and liquid Zn [1,3]. Those of the Cd PRE system were obtained from observed activity coefficients of lanthanides in Cd metal [9].



1) Reduction from trivalent to metal occurs
2) Reduction from divalent to metal occurs

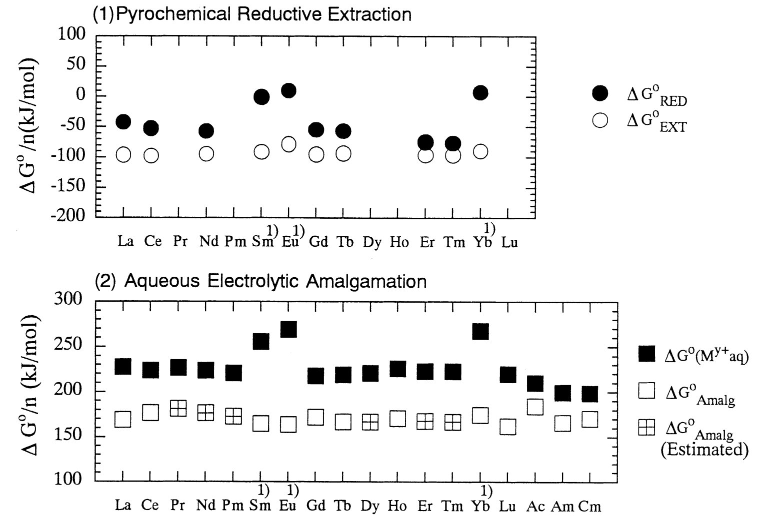
Fig. 3. Dependence of the free energy change of alloy formation on the metallic radii of f-elements.

4.1. Characteristics of the thermodynamic parameters

$\Delta G^{\circ}_{\mathrm{Amalg}}$, $\Delta G^{\circ}(M^{y+}_{\mathrm{aq}})$, $\Delta G^{\circ}_{\mathrm{RED}}$ and $\Delta G^{\circ}_{\mathrm{EXT}}$ are plotted along the 4f- and part of the 5f-series in Fig. 2. The following points are emphasized. In the AEA system: (a) Sm, Eu and Yb, which are probably divalent in the alloy, exhibit a very large amalgamation energy, hence their amalgamations are as endothermic as other trivalent f-elements; (b) the amalgamation energy increases slightly along the 4f-series; (c) actinides show a relatively smaller amalgamation energy than the 4f-series. In the PRE system of Zn: (a) the alloy formation energy of Sm, Eu and Yb is also large; (b) the alloy formation energy gradually decreases along the 4f-series. These similarities and differences between the Hg (AEA) and Zn (PRE) systems may possibly be attributed to the difference of the intermetallic interaction of f-elements with the different IIb metals. From the viewpoint of the application of AEA as a practical separation technique, the difference in the amalgamation energies is a significant factor. In this sense, the difference of the systematics of divalent metals in the AEA system is significant because it is likely to determine their separation from other trivalent elements.

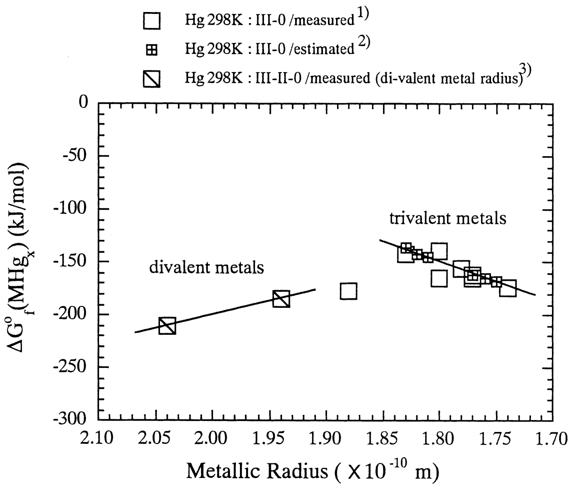
4.2. Characteristics of alloy formation

The free energy change of alloy formation ($\Delta G^{\circ}_{\mathrm{f}}(\mathrm{MA}_x)$) in the PRE and AEA systems is plotted in Figs. 3 and 4 as



1) Elements reduced via di-positive state.
2) The difference of two gives the alloy formation energy($\Delta G^{\circ}_{\mathrm{f}}$(MAx)) .

Fig. 2. Free energy change of reactions in pyrochemical reductive extraction and aqueous electrolytic amalgamation.



1) Reduction from trivalent to metal occurs
2) Estimated from the systematics on metallic radii
3) Reduction from trivalent via divalent to metal occurs

Fig. 4. Dependence of intermetallic interaction on the metallic radii of f-elements (Hg at 298 K).

a function of the metallic radii of f-elements. The $\Delta G°_f(MA_x)$ of trivalent metals in the Zn and Cd PRE systems becomes less negative as the contraction of the element proceeds (Fig. 3) while that of Hg in the AEA system becomes slightly more negative (Fig. 4). Both in the Zn and Hg systems, Eu and Yb, which are possibly divalent in their metallic state, appear to show different systematics from that of trivalent metals.

The contrasting systematics of trivalent metals in the AEA and PRE systems suggests two possible explanations. One is the different dependence of the enthalpy change of formation ($\Delta H°_f(MA_x)$) on the metallic radii, which represents the trend of metallic bonding between f-elements and IIb metals. The other is the dependence of the entropy change ($\Delta S°_f(MA_x)$) of formation on the metallic radii. If we assume the latter as the main reason, there has to be an opposite dependenc of $\Delta S°_f(MA_x)$ on the metallic radii in the AEA and (Zn) PRE systems. It appears that, as the contraction of the element proceeds, $\Delta S°_f(MA_x)$ becomes slightly less negative in the (Hg) AEA, and more negative in the (Zn) PRE, system. Because the temperature of the PRE system is much higher than that of the AEA system, the appearance of the entropy change is generally magnified in the PRE system, which may fit the observation. On the other hand, considering $\Delta H°_f(MA_x)$ as the main reason will require a discussion as to if such a large loss of $\Delta H°_f(MA_x)$ along the 4f series is reasonable. Precise measurements of $\Delta H°_f(MA_x)$ and $\Delta S°_f(MA_x)$ are highly desired.

The different systematics of divalent metals in Hg is interesting for the unique intermetallic interactions, but are also important from the viewpoint of their separation from other metals. Because of the highly negative alloy formation energies of Eu, its amalgamation occurs at a similar cathodic potential as the trivalent f-elements (Fig. 2), which is a drawback of AEA.

5. Feasibility of the separation of f-elements by electrolytic amalgamation

Using the parameters for the amalgamation of f-elements listed in Table 1, the feasibility of their group separation by potential-controlled electrolytic amalgamation was studied by theoretical calculations.

5.1. Calculation of current–potential curves at the Hg cathode

The polarographic current density is given by Eq. (4) [4], where E, i, i_d, α, D, δ and C_0 denote the cathode potential, reduction current density, limiting diffusion current, transfer coefficient, diffusion coefficient, diffusion layer thickness (0.1 mm), and bulk concentration of the solute, respectively

$$i = nF(D/\delta)C_0\{\exp[(\alpha nF/RT)(E - E_{1/2})] + 1\}^{-1} \tag{4}$$

In order to evaluate the feasibility of the application to an actual waste solution, a hypothetical reference mixed waste solution was assumed. The reference solution consists of the f-elements generated from the spent nuclear fuel of a Light Water Reactor. The concentrations of the elements are 2.2, 1.6, 1.2, 2.3, 1.1, 3.8, 2.9, 6.8, 1.3 and 1.1 mM dm^{-3} for Am, Cm, La, Ce, Pr, Nd, Pm, Sm, Eu and Gd, respectively. Lanthanides heavier than Tb are omitted in this evaluation because of their low abundance in spent fuel. The solution is hypothetically assumed to be chloride solution of pH ~2.5. This solution condition is achieved by denitrating the reprocessing waste solutions, and is preferable for a smaller evolution of hydrogen. The transfer coefficients of the lanthanides are not reported in the literature, hence as a most conservative assumption, they were assumed to be unity. The diffusion coefficients were taken from their infinite diffusion coefficients [4].

5.2. Calculated current–potential curves

The current–potential curves for the reference waste solution are shown in Fig. 5. Because of the high irreversibility ($\alpha = 0.41$) of Am, the diffusion-controlled zone of Am can hardly be distinguished from those of La, Eu, Sm and Cm, and poor purification of Am is suggested. If constant potential electrolysis with a well controlled potential at -1.75 V is realized, extraction of Am with $>90\%$ recovery yield results in the coextraction of La, Sm and Eu with decontamination factors of 1.19, 0.963, and 0.966, respectively, which means that the recovery yields of these elements are almost the same as that of Am [4].

The insufficient separation of Eu and Sm from Am is

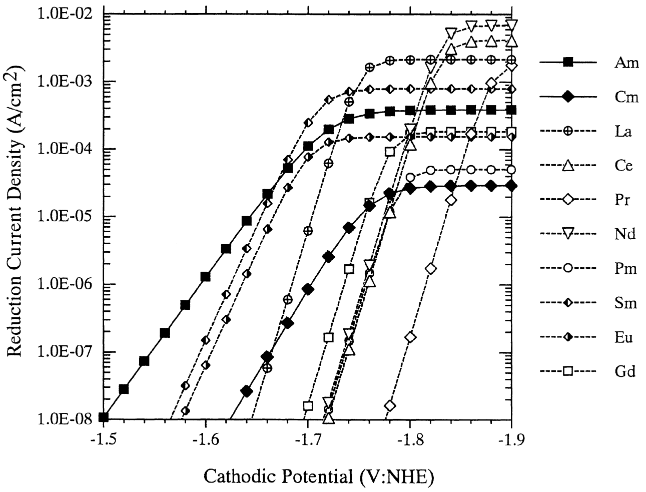


Fig. 5. Dependence of intermetallic interaction on the metallic radii of f-elements (Zn at 873 K).

due to their large amalgamation energy, as described above. However, a unique stepwise reduction mechanism may improve their separation from Am by the following technique. Because of the presence of transient intermediate di-positive cations of Eu and Sm, by adding any adequate chemical species which selectively interacts with the divalent cations, the reduction waves of Eu and Sm can be shifted to the more negative side [4]. One of the crown ethers, 18-CROWN-6(1-4-7-10-13-16-hexaoxacyclooctadecane), which has a selectivity for the ionic size of divalent cations, is expected to shift the reduction potentials to the more negative side by 0.136 and 0.127 V for Eu and Sm, respectively [13].

6. Conclusion

Using reported radiopolarography data for f-elements, the thermodynamic characteristics of aqueous electrolytic amalgamation was studied. By comparing them with the pyrochemical reductive extraction of f-elements with liquid Zn and Cd, the uniqueness of the systematics of aqueous amalgamation was demonstrated. Based on the parameters of f-element’s electrolytic amalgamation, it was shown that the effective separation of Eu and Sm from Am is difficult. To improve the separation of Eu and Sm from Am, it is proposed to stabilize the transient intermediate divalent states with organic ligands.

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