Electromotive force study of lanthanides in liquid Bi phase

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The thermodynamic properties of Pr, Gd, Tb, Dy and Ho in liquid bismuth were determined by the electromotive force (EMF) measurement method using a cell consisting of molten chloride and liquid bismuth. The partial molar excess free energy changes of lanthanides dissolved in Bi solution and activity coefficients were determined at varying concentration and temperature. The partial excess entropy and corresponding enthalpy of lanthanides dissolved in Bi solution in a temperature range of 773K~1100K were evaluated. It was found that the excess free energy and entropy changes of trivalent lanthanides depend linearly on the 2/3 power of their metallic volume. The partial excess free energy changes of $LnCl_3$ dissolved in the salt of some trivalent lanthanides were deduced.
Keywords: electromotive force, lanthanides, activity coefficient, thermodynamic properties, systematics

1   Introduction

Implementation of partitioning and transmutation (P&T) is intended to reduce the inventories of actinides and long-lived fission products in nuclear wastes. Aqueous separation techniques (such as PUREX process) are currently employed in the nuclear fuel reprocessing industry for effective separation of minor actinides and fission products based on the separation of element by element. The conditions of a possible grouping of certain elements would achieve a compact, economic and non-proliferative recycling process and simplify the overall management. Pyrochemical process based on the liquid-liquid extraction using molten salt and liquid metal is a possible technology for the group separation of lanthanides and actinides in the irradiated fuel reprocessing industry [1,2]. However, pyrochemical process is still in basic research phase and may need great efforts and breakthroughs before being applied. In support of the establishment of this group separation process, thermodynamic behavior of lanthanides and actinides in molten salt and liquid metal are needed to be determined. The extraction and separation performance of lanthanides and actinides by the pyrometallurgical extraction system mainly depends on the standard Gibbs free energy of formation of their chlorides, but their activity coefficients in both phases greatly influence the separation efficiency as well [3]. However, there are insufficient data related to the activity coefficients of lanthanides and actinides in the liquid bismuth systems. The purpose of this study is to determine the thermodynamic quantities associated with the formation of liquid lanthanide-bismuth alloys using the EMF measurement method.
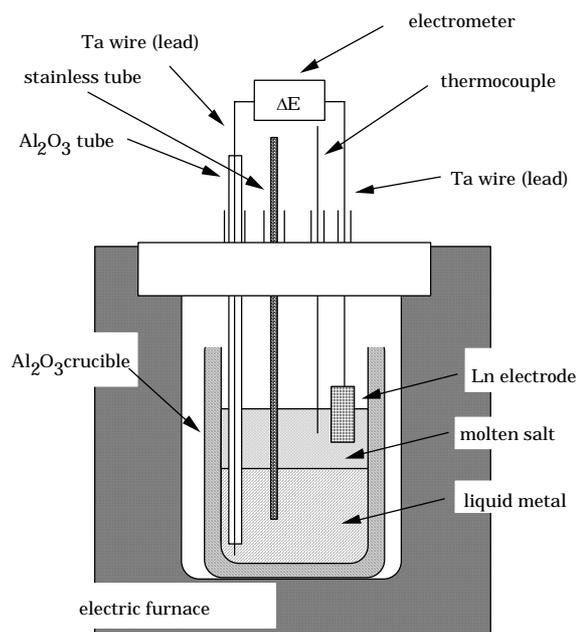
2   Experimental

The following galvanic cell was designed to measure the

Fig.1   Schematic diagram of the apparatus for electromotive force measurement

EMF values between the metallic lanthanide (Ln) and Ln solute in Bi solution.

Ln (solid) | KCl-LiCl | Ln-Bi (solution)

The apparatus of EMF measurement is shown in Fig.1. A pure lanthanide electrode was prepared by welding a tantalum lead to a small rod of 99.9% pure lanthanide metals. The alloy electrode was prepared by directly dissolving a small piece of pure lanthanide metal in pure bismuth. The electrolyte was pure KCl-LiCl eutectic (mole ratio of lithium and potassium = 51/49) purchased from Anderson Physics Laboratory Engineered Materials Inc. All other reagents used were of analytical grade purchased from Wako Pure Chemicals Co. Ltd. The experiments were carried out in a glove-box filled with purified argon whose oxygen and humidity content was kept < 1ppm. In a typical experiment, 133 grams of Bi with about 1 gram of metallic Ln was loaded into a finely sintered alumina crucible, and then about 36 grams KCl-LiCl eutectic was loaded. The crucible was heated to a desired temperature in an electric furnace. After the desired temperature was achieved, then the pure lanthanide

electron as immersed into the molten salt phase, and the EMF between the pure lanthanide electron and liquid alloy electrode as measured by an electrometer (HG-5100, Hokutodenko Co. Ltd.). After immersing the pure lanthanide electrode, the variation of EMF was monitored for longer than 10 minutes, waiting for the stabilization of EMF. In many cases, the fluctuation of EMF settled into $< \pm 2mV$ within 10 minutes after starting the measurements, and in such cases it was recognized that the electrochemical equilibrium was achieved. Measurement for Pr, Gd, Tb, Dy and Ho were performed at four different temperatures in a range of 773K~1100K. At each temperature, the concentration of lanthanide in bismuth phase was changed several times to record EMF at different concentration. For increasing the lanthanide concentration, small pieces of lanthanide metals were added. For decreasing the concentration, lanthanides were electrodeposited onto another cathode by using the liquid metal electron as an anode. After the EMF measurement, a small portion of the metal phase was sucked into a stainless steel tube as a sample. The sample was weighed and dissolved with 6N HNO_3, and then the concentration of lanthanide in bismuth was analyzed by ICP-AES (ICPS-1000III, Shimadzu Co. Ltd.).

3　Thermodynamic basis

In general, the valences of the various species in the salt phase were those expected. All of the studied lanthanides in chloride melts in contact with a metal were trivalent [4]. The following equilibrium between the salt phase and Ln-Bi solution were thus attained.

$$Ln^{3+} \text{ (in salt)} + 3e^- = Ln \text{ (in Bi solution)} \qquad (1)$$
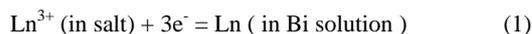
According to the Nernst's equation, the electric potential of metallic Ln (E_{Ln}) and Ln in Bi solution (E_{Ln} (in Bi)) can be expressed as the following equations, respectively.

$$E_{Ln} = E_{Ln}^0 + \frac{2.3RT}{nF} \log(a_{LnCl3}/a_{Ln}) \qquad (2)$$

$$E_{Ln}(\text{in Bi}) = E_{Ln}^0 + \frac{2.3RT}{nF} \log(a_{LnCl3}/a_{Ln-Bi}) \qquad (3)$$

Where E_{Ln}^0 is the standard potential of the couple LnCl$_3$/Ln; R the gas constant; the absolute temperature; n the valence of the lanthanide ion ($n=3$); F the Faraday constant; $_{LnCl3}$ the activity of LnCl$_3$ in molten salt; $_{Ln}$ and $_{Ln-Bi}$ the activities of metallic Ln and that of dissolved Ln in Bi solution, respectively. The EMF value between metallic Ln and Ln-Bi solution (E) can obtained via the formula $a_{Ln} = 1$ and $a_{Ln-Bi} = X_{Ln} \times \gamma_{Ln}$ as

$$E = E_{Ln}(\text{in Bi}) - E_{Ln}$$

$$= \frac{2.3RT}{3F} \log(a_{Ln}/a_{Ln-Bi})$$

$$= -\frac{2.3RT}{3F} \log _{Ln} - \frac{2.3RT}{3F} \log _{Ln} \qquad (4)$$

Where $_{Ln}$ denotes mole fraction of Ln in Bi solution, and γ_{Ln} is the activity coefficient of Ln in Bi solution. Equation (4) is the basic thermodynamic expression of this study. The Ln-Bi solution can be treated as a regular solution at lower Ln concentration, the partial molar excess Gibbs free energy changes of Ln dissolved in Bi solution ($\Delta \overline{G}_{Ln}^{ex}$) can be deduced as following [5,6]:

$$\Delta \overline{G}_{Ln}^{ex} = RT \ln \gamma_{Ln} \qquad (5)$$

The temperature dependence of formation free energy can be expressed by

$$\Delta \overline{G}_{Ln}^{ex} = \Delta \overline{H}_{Ln}^{ex} - T\Delta \overline{S}_{Ln}^{ex} \qquad (6)$$

Where $\Delta \overline{H}_{Ln}^{ex}$ is the partial excess enthalpy change of Ln dissolved in Bi solution, and $\Delta \overline{S}_{Ln}^{ex}$ is the corresponding excess entropy change. Combining equations (5) and (6), the following equation is yielded.

$$\log \gamma_{Ln} = \frac{\Delta \overline{H}_{Ln}^{ex} - T\Delta \overline{S}_{Ln}^{ex}}{2.3RT} = \frac{-\Delta \overline{S}_{Ln}^{ex}}{2.3R} + \frac{\Delta \overline{H}_{Ln}^{ex}}{2.3RT} \qquad (7)$$

In this experiment, Ln concentrations in the Bi solution were very low (mole fraction $< 0.01\%$), thus the activity coefficient of Bi is treated as 1. The standard Gibbs free energy of formation of liquid Ln-Bi alloys (ΔG_f^0, the standard state here means the pressure) can be shown that

$$\Delta G_f^0 = \Delta \overline{G}_{Ln}^{ex} + \Delta G_{Ln}^{fusion} \qquad (8)$$

Where ΔG_{Ln}^{fusion} is the fusion energy of Ln, which can obtain from literature [7].

4　Results and discussion

For all the elements and temperatures tested, the observed E showed a roughly linear dependence on $\log X_{Ln}$ as shown in Fig.2. The variation of E approximately obeys equation (4). The lines drawn in Fig.2 are those of theoretical slopes ($\frac{2.3RT}{3F}$) that were obtained by applying the least squares fitting method to the experimental data of every temperature. It could find that less Ln dissolved in Bi solution obeys Henry's law. The term ($-\frac{2.3RT}{3F} \log \gamma_{Ln}$) in equation (4) is a constant over the tested concentration and temperature ranges, suggesting that the activity coefficients of Ln in Bi solution are constant in the experimental concentration ranges at a given temperature. The activity coefficients can be calculated from equation (4), using the values of E and $_{Ln}$ obtained in this study along with temperature and other constants. The errors of $\log \gamma_{Ln}$ involve all the errors associated with the measurement. Major components of the errors are those accompanied by: (1) chemical analysis, from 10% for $X_{Ln} = 10^{-6}$ to 2% for $X_{Ln} = 10^{-2}$; (2) temperature measurement, constantly $\pm 1K$; and (3) EMF
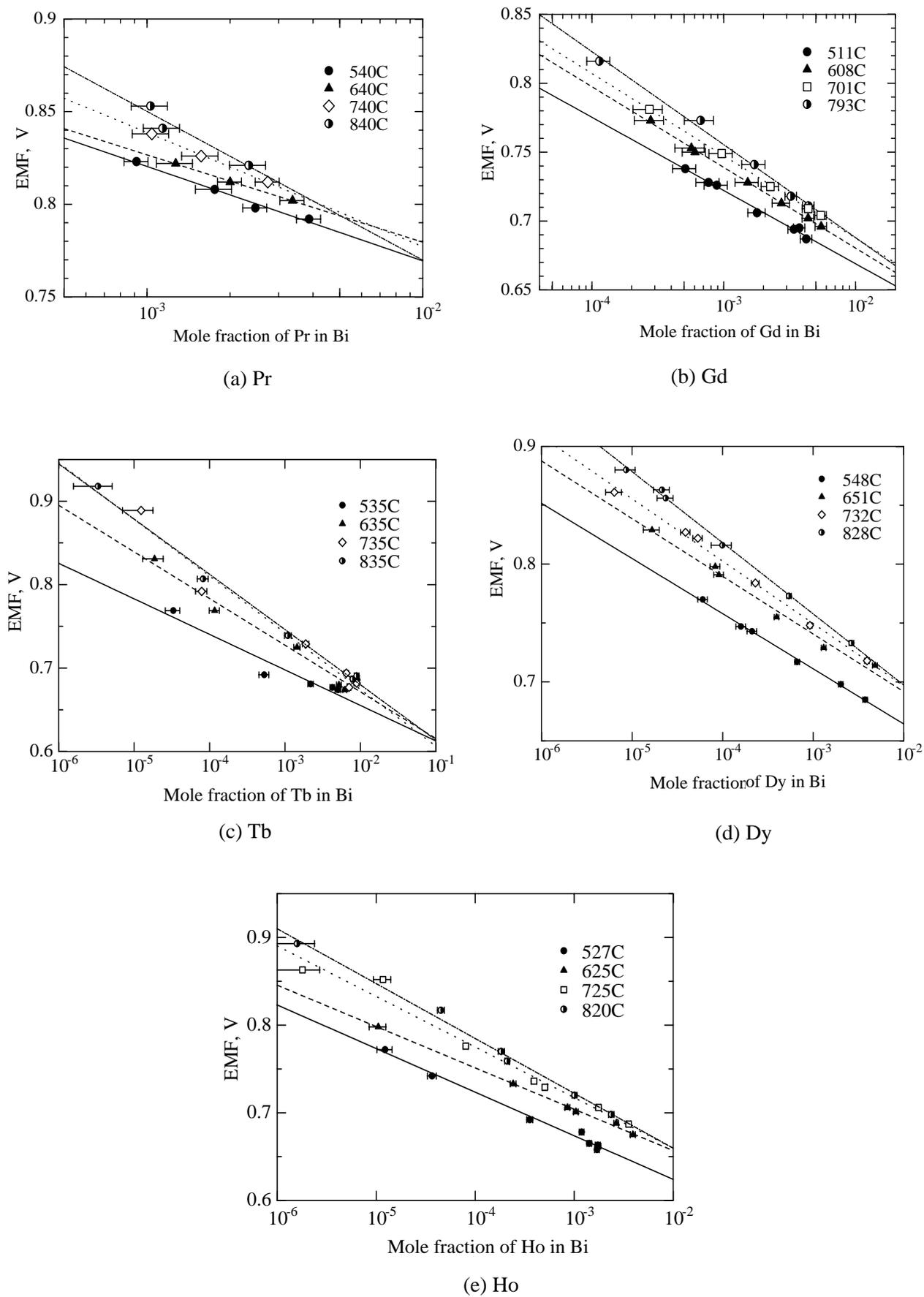
(a) Pr

(b) Gd

(c) Tb

(d) Dy

(e) Ho

Fig.2　Concentration dependence of the EMF

Table 1   Activity coefficients of Ln in liquid Bi

| Ln	$\log\gamma_{Ln} = a + b/T$		γ values at 873K
	a	$-b$	
La [1]	0.94	11158	1.44E-12
Ce [1]	2.03	11400	9.37E-12
Pr	1.60 ± 0.376	11290 ± 378	4.61E-12
Nd [1]	1.90	11074	1.64E-11
Gd	1.58 ± 0.358	9933 ± 345	1.59E-10
Tb	1.72 ± 0.586	9870 ± 585	2.51E-10
Dy	2.03 ± 0.037	10219 ± 37	2.11E-10
Ho	1.96 ± 0.284	9686 ± 280	7.42E-10
Er [1]	1.23	8593	2.44E-09

(1) Reference[8]

measurement, constantly ±2mV. An example of the observed dependence of $\log\gamma_{Ln}$ on $\log X_{Ln}$ is given in Fig.3, where the independence of $\log\gamma_{Ln}$ on $\log X_{Ln}$ is clearly seen. The same results can also be obtained for other studied lanthanides.

There is a considerable increase in the activity coefficient on the temperature. For determining the $\Delta\overline{H}_{Ln}^{ex}$ and $\Delta\overline{S}_{Ln}^{ex}$ by temperature dependence of $\log\gamma_{Ln}$, plotting $\log\gamma_{Ln}$ on $1/T$ was performed according to the equation (7), as shown in Fig.4. The lines in the Fig.4 show the results of the least squares fitting treatment, which gave quite satisfactory agreement to the data. By writing the linear functions as

$$\log\gamma_{Ln} = a + b/T \qquad (9)$$

Where a and b are determined constants. Table 1 provides the values of a and b. A systematic increase of the activity
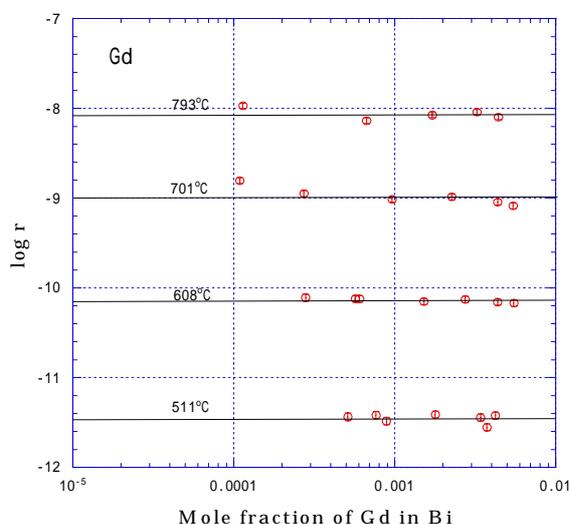
Fig.3 Activity coefficient of Gd in Bi solution
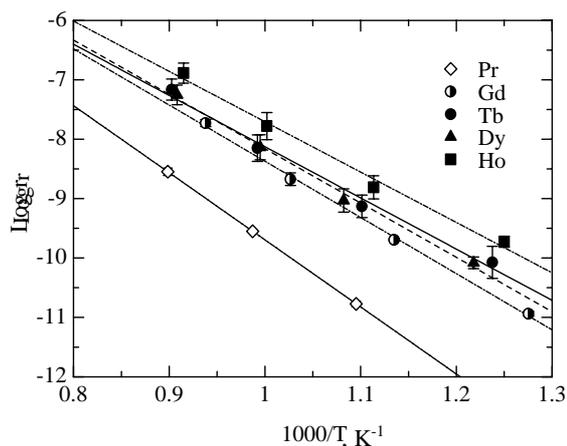
Fig.4   Temperature effects on the activity coefficient

coefficient in Bi solution along with atomic number can be found at a given temperature. Combining equation (7) and (9), $\Delta\overline{H}_{Ln}^{ex}$ and $\Delta\overline{S}_{Ln}^{ex}$ are given by the following equations:

$$\Delta\overline{H}_{Ln}^{ex} = 2.3\mathrm{R} \times b \qquad (10)$$

$$\Delta\overline{S}_{Ln}^{ex} = -2.3\mathrm{R} \times a \qquad (11)$$

The $\Delta\overline{G}_{Ln}^{ex}$ can be calculated at a given temperature from equation (5), using γ_{Ln} values. Table 2 summarized the results of thermodynamic properties related to Ln dissolved in Bi solution at 873K.

The systematic variation of the major thermodynamic quantities along with the lanthanide series is an important research topic in order to understand the reductive extraction behavior of Ln [3]. In the liquid alloy, it is presumably considered that the solute metal forms a chemical complex with the solvent metals, *i.e.* a cluster, and this is considered to be responsible for the thermodynamic excess stabilization of the solute metals [9]. Thus, the excess partial molar quantities of the solute metals in the solvent metals should reflect the degree of chemical bondings associated with the formation of the clusters. In most case of the compounds of lanthanides, their chemical stabilities scarcely depend on the number of 4f-electrons, thus tend to show monotonic variations along the lanthanides series [10]. Fig.5 shows plots of $\Delta\overline{G}_{Ln}^{ex}$ & $\Delta\overline{H}_{Ln}^{ex}$ vs. $V^{2/3}$ (V is the atomic molar volume, cm^3/mol) [11]. A linear dependence of $\Delta\overline{G}_{Ln}^{ex}$ and $\Delta\overline{H}_{Ln}^{ex}$ on $V^{2/3}$ for trivalent lanthanides at 873K was observed, which is agreed with theoretical calculation results by Miedema's model [3,11]. Such a linear relationship can be used to predict the thermodynamic properties of other unknown lanthanides. The developing reductive extraction process of trivalent lanthanides with the use of metallic Li as a reductant is described as the following reaction [2,3]:

$$\mathrm{LnCl_3\,(in\,salt) + 3Li\,(in\,Bi) \leftrightarrow Ln\,(in\,Bi) + 3LiCl\,(in\,salt)} \qquad (12)$$

Table 2 The changes in the partial molar thermodynamic properties at 873K

Ln	ΔG_f, kJ.mol^{-1}			$\Delta \overline{H}_{Ln}^{ex}$ kJ.mol^{-1}	$\Delta \overline{S}_{Ln}^{ex}$ J.K^{-1}mol^{-1}
	$\Delta \overline{G}_{Ln}^{ex}$	ΔG_{Ln}^{fusion} (1)	ΔG_f^0		
La	-197.67	2.43	-195.24	-213.37	-17.97
Ce	-184.10	1.33	-182.77	-217.99	-38.82
Pr	-189.26 ± 4.57	2.28	-186.98 ± 4.57	-215.89 ± 7.23	-30.51 ± 7.19
Nd	-180.04	2.63	-177.41	-211.76	-36.33
Gd	-163.56 ± 5.90	5.77	-157.79 ± 5.90	-189.94 ± 6.60	-30.21 ± 6.84
Tb	-160.27 ± 6.86	5.75	-154.52 ± 6.86	-188.32 ± 11.19	-32.13 ± 11.21
Dy	-161.52 ± 0.94	5.01	-156.51 ± 0.94	-195.41 ± 0.71	-38.82 ± 0.71
Ho	-152.41 ± 4.15	7.55	-144.86 ± 4.15	-184.80 ± 5.35	-37.10 ± 5.43
Er	-143.78	9.97	-133.81	-164.32	-23.52

1): Reference [7].
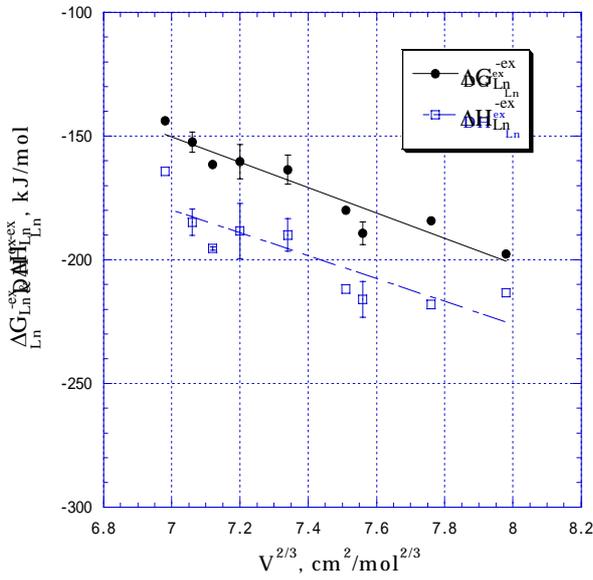
Fig. 5 $\Delta \overline{G}_{Ln}^{ex}$ **&** $\Delta \overline{H}_{Ln}^{ex}$ **vs. V$^{2/3}$**

Fig.6 $\Delta \overline{G}_{LnCl_3}^{ex}$ **vs. 1/R**

The extractability of Ln can be expressed as the sum of formation free energy of products and reactants [2,3].

$$\log(D_{Ln}/D_{Li}^3) =$$
$$-\frac{1}{2.3RT}\Delta \overline{G}_{Ln}^{ex} + \frac{1}{2.3RT}\{\Delta G_f^0(LnCl_3, liquid)$$
$$+ \Delta \overline{G}^{ex}(LnCl_3, in\ salt)\} + \cent \qquad (13)$$

Where $\log(D_{Ln}/D_{Li}^3)$ denotes the extractability of Ln (D_{Ln} and D_{Li} are the distribution ratio of Ln and Li in two phases, respectively); $\Delta G_f^0(LnCl_3,$ liquid) the formation free energy of liquid LnCl$_3$; $\Delta \overline{G}_{LnCl_3}^{ex}$ the partial excess free energy change of LnCl$_3$ dissolved in the salt; $\cent$ the constant related with formation free energy of LiCl and Li in molten salt and liquid Bi phases. At a given temperature, the extractability of Ln can be estimated by the thermodynamic quantities in equation (13). The $\Delta \overline{G}_{Ln}^{ex}$ values can be directly determined by the EMF measurement as this study expressed. In contrast, the
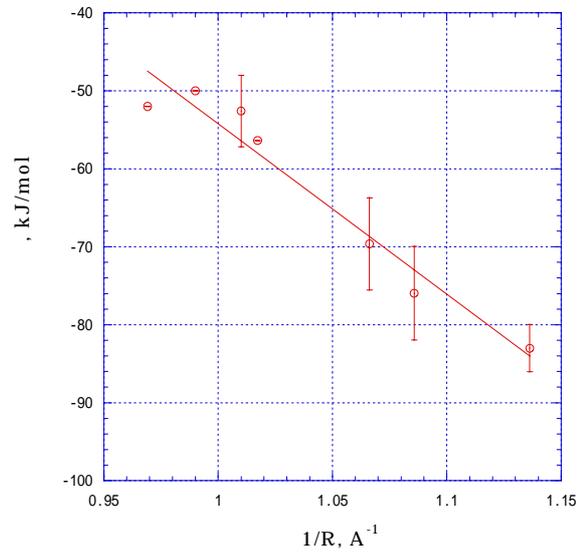
values of $\Delta \overline{G}_{LnCl_3}^{ex}$ are difficult to be measured by EMF, especially at higher temperature than about 773K. In fact, there are few reference electrodes to be easily adapted. Thus, the theoretical study of Ln extractability is severely limited because of the insufficient data of $\Delta \overline{G}_{LnCl_3}^{ex}$.

The $\Delta \overline{G}_{Ln}^{ex}$ values of some lanthanides have been obtained in this study and literatures, the $\log(D_M/D_{Li}^3)$ values of some lanthanides have been obtained in previous studies, and the values of ΔG_f^0 (LnCl$_3$, liquid) and $\cent$ are available in the published database [3,7]. Then, the values of $\Delta \overline{G}_{LnCl_3}^{ex}$ of some lanthanides can be obtained from equation (13). Table 3 presents the calculated results of $\Delta \overline{G}_{LnCl_3}^{ex}$ at 873K. The relationship between the $\Delta \overline{G}_{LnCl_3}^{ex}$ values of some trivalent lanthanides and their ionic radius (R) is shown in Fig.6. A linear dependence of $\Delta \overline{G}_{LnCl_3}^{ex}$ on 1/R was observed. Regardless of its physical meanings, this linearity of $\Delta \overline{G}_{LnCl_3}^{ex}$, i.e. that of $\Delta \overline{G}_{Ln}^{ex}$ and $\Delta \overline{H}_{Ln}^{ex}$ as well, is useful for the assessment of the characteristic extraction behaviors of lanthanides by liquid Bi.

Table 3 Calculation values of $\Delta\overline{G}_{LnCl_3}^{ex}$ for some trivalent lanthanides at 873K

Ln	$\log(D_{Ln}/D_{Li}^3)$ [1]	$\Delta\overline{G}_{Ln}^{ex}$	ΔG_f^0 (LnCl$_3$, liquid) [3]	¢ [1]	$\Delta\overline{G}_{LnCl_3}^{ex}$
La	6.605 ± 0.063	-197.67	-845.2	810	-52.21
Ce	6.713 ± 0.099	-184.10	-832.4	810	-49.64
Pr	6.911 ± 0.067	-189.26 ± 4.57	-834.6	810	-52.29 ± 4.57
Nd	6.648 ± 0.250	-180.04	-822.3	810	-57.76
Pm					
Sm	3.492 ± 0.322	-192.35 [2]	-675.2	810	
Eu	2.617 ± 0.099	-135.20 [2]	-661.4	810	
Gd	6.478 ± 0.111	-163.56 ± 5.90	-795.8	810	-69.62 ± 5.90
Tb	6.389 ± 0.123	-160.27 ± 6.86	-784.4	810	-79.21 ± 6.86
Dy		-161.52 ± 0.94	-777.2	810	
Ho		-152.41 ± 4.15	-783.9	810	
Er		-143.78 [2]	-774.4	810	
Tm	5.708 ± 0.102	-153.46 ± 3.04	-768.6	810	-82.95 ± 3.04
Yb	2.568 ± 0.093		-645.8	810	
Lu			-780.4	810	

Unit: kJ/mol
[1]: Reference [3].   [2]: Reference [8].   [3]: Reference [7].

5 Conclusions

The EMF measurement method was used to determine the thermodynamic quantities of Pr, Gd, Tb, Dy and Ho in Bi solution. The temperature dependence of their activity coefficients was investigated, and then $\Delta\overline{H}_{Ln}^{ex}$ and $\Delta\overline{S}_{Ln}^{ex}$ were obtained. There has a linear dependence of $\Delta\overline{G}_{Ln}^{ex}$ and $\Delta\overline{H}_{Ln}^{ex}$ values for trivalent lanthanides on the $V^{2/3}$. The calculation of $\Delta\overline{G}_{LnCl_3}^{ex}$ of some trivalent lanthanides was evaluated and a systematic variation of $\Delta\overline{G}_{LnCl_3}^{ex}$ values along with their ionic radii was found.

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