

**Systematic Study on the Thermodynamic Stability of Lanthanides
and Actinides in Molten Alkali and Alkaline Earth Chlorides**

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Chapter 1 General Introduction

1.1 Introduction

1.1.1 Current status of nuclear fuel cycle

Nuclear energy has contributed to the economical developments as well as our convenient lives on the basis of stable electricity supply. About 30% and 15% of total electric power consumed in Japan and in the world, respectively, is now generated at nuclear plants, and its proportion is predicted to increase especially in developing countries like China and India. Nuclear energy is a promising option from the aspects of energy security as well as low CO₂ emission. The energy system depending on fossil fuels is vulnerable to future soaring prices of oil and natural gas and responsible to the global warming. Nuclear plants recently respond to some accessory demands of desalination of water or hydrogen production by utilizing the nuclear heat. After Fukushima accident in March this year, a radical overhaul of the energy policy in Japan including nuclear has been launched. Whatever a future direction of the policy given for nuclear energy is, efforts to resolve intrinsic technological challenges in the utilization of nuclear power are continuously necessary to advance the safety, the nonproliferation, and the management of spent fuels.

Suitable management of spent nuclear fuels being accumulated in the back-end of fuel life cycle is one of the most important issues to be solved betimes. There are two options for the spent fuel management: (1) direct disposal in geologically stable sites at depth of more than 300 meters, or (2) disposal after separation of uranium (U), plutonium (Pu), and/or part of the wastes with relatively high levels of radioactivity, namely High Level Waste (HLW), including lanthanide (Ln) fission products and minor actinides (MAs) such as neptunium (Np), americium (Am), and curium (Cm). Japan Atomic Energy Commission has committed in “framework for nuclear energy policy” to adopt the latter option and to develop nuclear fuel cycle, where U and Pu are collected from spent nuclear fuels and used again in Fast Breeder Reactor (FBR) and/or in commercialized Light Water Reactor (LWR). A conceptual design of the nuclear fuel cycle is shown in Fig. 1.1. The operation of LWRs with recycled U and Pu as MOX fuel has been started in Japan since 2010. It can help the securement of energy resources which are scarce in Japan.

The partitioning and transmutation (P&T) of MAs is another challenging task to diminish the emplacement area and the potential radiotoxicity over a thousand years of HLW disposal (Figs. 1.2 [1] and 1.3 [2]), which can simplify waste management. Technical developments to achieve the transmutation in accelerator driven subcritical system (ADS) or in molten salt reactor (MSR) are now in progress. Molten salts can be conceivable to be used as liquid reactor core for the reactors [3,4]. Molten chlorides and fluorides would be preferable for ADR and MSR utilizing fast and thermal neutrons, respectively.

Three separation concepts which satisfy all design requirements for the separation of Ln and actinide (An) elements from the spent nuclear fuels have been addressed in feasibility study on commercialized FBR cycle system (F/S) conducted by a joint project team of Japan Atomic Energy Agency (JAEA) and Japan Atomic Power Company since 1999: the advanced aqueous reprocessing, the metal electrorefining reprocessing, and the oxide electrowinning reprocessing [5]. The aqueous system based on PUREX method consists of the following steps: (1) crystallization of certain portion of U to adjust Pu concentration in nitric acid solution, (2) a solvent co-extraction of U, Pu, and Np, and (3) an extraction chromatography for MAs from the raffinate solution. Practically, this aqueous process is expected to be implemented at an early stage. The construction of facilities has been started in Rokkasyo-mura village in Aomori prefecture.

1.1.2 Pyrochemical reprocessing

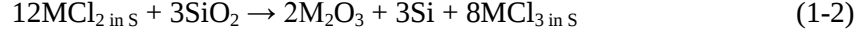
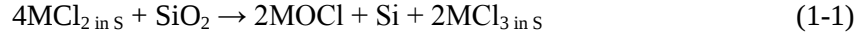
The latter two separation concepts in F/S, the metal electrorefining and the oxide electrowinning reprocessings, are the pyrochemical processes using molten salts as reaction media. The pyroreprocessing represents a promising alternative to the aqueous process for the treatment of spent metal or oxide fuels in FBR and for the separation of MAs in HLW. Pyrochemical processes offer inherent advantages in comparison with those carried out in aqueous system, *e.g.*, higher rate and efficiency of the electrolysis and wide electrochemical window of molten salts which allows variety of operation to obtain electrodeposits or alloys of actinide and rare earth metals. In addition, the pyroreprocessing processes have favorable features such as plant compactness, good solubility of target materials in molten salts, satisfactory irradiation resistance of the inorganic reactants that allows treatment of materials

with minimum prior cooling, and highly proliferation resistance without Pu isolation unlike in the PUREX method [6].

The concepts of the pyroprocessing of oxide and metallic alloy fuels were originally developed in Research Institute of Atomic Reactors (RIAR, Russia) and Argonne National Laboratory (ANL, USA), respectively. The schematics of these processes are shown in Figs. 1.4 and 1.5. In the metal electrorefining process, Ans and Lns in spent metal fuels are anodically oxidized to the trivalent, An^{3+} and Ln^{3+} , and are dissolved into molten chlorides. Majority of U is selectively collected on a solid Fe cathode by the difference in the redox potentials of the elements included, then Pu, MAs, and residual U are collected into a liquid metal, usually Cd or Bi, with some amounts of Ln fission products by electrolysis or reductive extraction. In the oxide electrowinning process, UO_2 in spent oxide fuels is oxidized to UO_2^{2+} at the first step. Simultaneously, the UO_2^{2+} ion is reduced on a cathode and deposited UO_2 coating is collected. Then, PuO_2 in the spent fuel at anode is dissolved in the melt by the chlorination, and PuO_2^{2+} is stabilized by the supply of mixed gas of O_2 and Cl_2 . Mixed oxide of UO_2 and PuO_2 (MOX) is obtained as deposits on the cathode.

Both processes require the basic knowledge about the redox properties of deposition and extraction reactions of Lns and Ans. For the MOX electrolysis, controlling the atmosphere of O_2 and Cl_2 is also necessary. In this context, there have been a dozen studies on thermochemical properties of the *f* elements for molten alkali chlorides [6-27]. Special attention must be paid to Lns since residual Lns in collected An fuels reduce the efficiency of fission and/or transmutation processes in a reactor core because of their neutronic poison effect. Chemical characteristics of Lns are often analogue to those of Ans. The analogy motivates studies on Lns since Ans are not easily examined because of high radioactivity and limitation of the usage, while the chemical similarity makes their mutual separation difficult. The advanced Ln/An separation technique is, hence, desirable, and it has been investigated using several kinds of electrodes such as Cu [7] and Al [8,9]. Some of the Ln and An elements, Nd, Sm, Eu, and Am, have divalent state in molten chlorides which is unique for the series. The separation idea utilizing the characteristics of the divalent state has been proposed as shown in Fig. 1.6 [10]. The example separation reactions of the elements in divalent state from those in trivalent are described as follows (suffixed “in S” denotes species dissolved in salt).

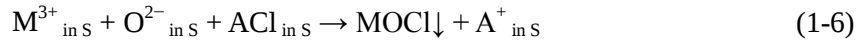
- M^{2+} reaction with other solids (oxides)



- M^{2+} disproportionation and reaction of metal fog with other solids (oxides)



- M^{3+} precipitation as M_2O_3 or $MOCl$



LiCl-KCl, NaCl-KCl, and NaCl-CsCl eutectic melts are usually chosen as solvent media by the following reasons: their melting point is rather low, structure materials containing the process melt is often less corrosive to chlorides compared with fluorides, and the solubility of Ln and An compounds are sufficient. Most of the studies have been devoted for the typical systems from an engineering prospective, and fundamental understandings on the solvation characteristics of the elements in molten salts have not been clarified sufficiently.

1.2 Current knowledge in literatures

1.2.1 Electrochemical studies

The history of studies on electrochemical behavior of Ln and An elements in molten chlorides goes back to 1950s when RIAR and ANL started to investigate the pyroprocessing scheme seriously. The accumulated knowledge has been well reviewed and reinvestigated in collaborative programs among European countries (Pyrometallurgical Processing Research Programme “PYROREP”) since 2000 [11]. The project has been undertaken to build up accurate database to assess electrochemical separation paths in molten chloride media for improved pyrochemical flow-sheets. Systematic electrochemical studies of Ln elements [12-21] and uranium [22] carried out at Research Centre for Energy, Environment and Technology, and at University of Valladolid (CIEMAT-UVA, Spain) and of the An elements (Pu [23], Am [24]) at Institute for Transuranium Elements (ITU, Germany). Electrochemical behavior of Cm in

LiCl-KCl eutectic has been investigated at RIAR [25]. In these studies, a combination of transient electrochemical techniques such as cyclic voltammetry (CV), chronopotentiometry (CP), and chronoamperometry (CA) has been used to investigate not only the mechanism of redox reactions of the elements but also transport properties of the ions. Trusty values of redox potentials as well as diffusion coefficients of An and Ln ions have been obtained. These studies were carried out mainly for LiCl-KCl eutectic melt (LiCl:KCl = 59:41 mol%), and some of them were for equimolar NaCl-CaCl₂. Comparing the results, it is suggested that heavier Ln ions with smaller ionic radius are more stabilized through the complexation in these melts [12,26].

1.2.2 Thermochemical studies

Mixing enthalpy and electric conductance of molten LnX₃-AX mixtures (A: alkali metal, X: halide) have been analyzed and discussed in terms of complex formation [27]. The results in the mixtures with low LnX₃ concentration inferred that the presence of larger A⁺ with smaller Ln³⁺ in the melts favors complex formation. Since X⁻ is more attracted to Ln³⁺ than to A⁺, larger mixing enthalpy and larger activation energy for conductivity are observed.

1.2.3 Spectroscopic studies

In parallel with thermochemical studies, attempts to acquire the knowledge about coordination structure around An and Ln ions in molten salts have been performed employing both experimental and computational methods. The microscopic knowledge is beneficial to explain the macroscopic thermochemical properties of An and Ln complexes as above and to understand the solvation characteristics in ionic liquid system. The coordination structure of trivalent Ln ions in molten halides has been investigated by using electric absorption spectrophotometry [28-32], Raman spectrophotometry [33-35], neutron diffraction (ND) [36], nuclear magnetic resonance (NMR) [37], and extended X-ray absorption fine structure (EXAFS) [38,39]. The studies give structural information of An and Ln complexes such as the number and the distance of halide anion surrounding An or Ln cations. It has been pointed out that Ln³⁺ except La³⁺, Ce³⁺, and Pr³⁺ is majorly surrounded by six chloride anions and has octahedral structure in molten ACl mixtures with low concentration of LnCl₃ [40]. The hexachloro complex, LnCl₆³⁻, is

distorted from the octahedral symmetry in the mixtures with smaller A like Li, since smaller A significantly attracts Cl^- surrounding Ln^{3+} [30,31]. La^{3+} is surrounded by seven or eight Cl^- in LiCl-rich mixtures [39,41], since La has large ionic radius and spatially, more than six Cl^- can be arranged around La^{3+} . The hexachloro complex, AnCl_6^{3-} , has been proposed for the structure of U and Np chlorides in ACl [42,43]. Systematic change in octahedral symmetry of the complex along with the change of the melt composition is of interest that has not been sufficiently investigated [44].

1.2.4 Computational studies

Molecular dynamic (MD) simulation is particularly suited for the study of ionic liquid system. The first MD studies for molten salts were built upon the rigid ion model (RIM) where ion is considered as a ball with hard sphere center of which a point charge locates. In this model, the force field is accounted from the Coulomb interaction and Van der Waals repulsion. The most successful RIM potential takes the Born-Mayer-Huggins form:

$$V(r_{ij}) = \sum_{i < j} \frac{q_i q_j}{r_{ij}} + \sum_{i < j} A^{ij} \exp(-a^{ij} r_{ij}) - \sum_{i < j} \left[\frac{C_6^{ij}}{r_{ij}^6} + \frac{C_8^{ij}}{r_{ij}^8} \right] \quad (1-8)$$

where q_i is the charge carried by the ion i , while A_{ij} , a_{ij} , C_6^{ij} , and C_8^{ij} are the parameters defining its interaction with another ion j , located at a distance r_{ij} from i . The parameters are often referred to the Fumi-Tosi potential [45,46] since the first accurate parameterization for alkali halides was performed by the authors. This hard sphere model (RIM) could well reproduce experimental data such as thermal capacity for the case of alkali chlorides, though certain differences have been found for the system with higher valence ions such as alkaline earth and lanthanide chlorides. In order to expand the applicability of MD to those systems, polarizable ion model (PIM) was developed and firstly reported in 1990s [47,48], where the polarization energy term was introduced that includes the short-range effects of an instantaneous induced dipole moment. This model is expected as a potential tool to understand microscopic structure of various kinds of molten salts with collaborative analyses of EXAFS [39] and Raman spectrophotometry [41]. PIM is also studied to reproduce thermodynamic property [49].

1.3 Conclusion

Pyrochemical reprocessing is an attractive candidate for the suitable management of spent nuclear fuels for the stable use of nuclear energy. In order to control the separation behavior of Ln and An elements from the spent nuclear fuels, their chemical characteristics in molten salt media are essential to be understood. Compared with wide variety of melt compositions for which coordination structure of the f elements has been investigated, electrochemical studies have not sufficiently addressed to the systematic understanding on their thermodynamic properties depending on the melt composition. Since association of the thermodynamic stability with the coordination structure has not been addressed sufficiently, the solvation effect of molten salts on the dissolution of the elements has not been well clarified.

Spectroelectrochemistry is a powerful method to observe and analyze both microscopic and macroscopic properties together. The equipment in our laboratory is shown in Fig. 1.7 [50]. Changes in thermodynamic stability and coordination structure depending on the melt composition are investigated by electrochemical and absorption spectrophotometric measurements, respectively. The aim of this thesis is to put these micro- and macroscopic pieces of knowledge together to assess the complexation of f elements in molten salts. To reveal the similarities and differences in solvation characteristics of f elements in molten chlorides would be helpful for Ln and An separation to be advanced.

In this context, Chapter 2 will be addressed to the systematic changes in thermodynamic and structural properties of Nd(III) complex along with the melt composition. The study starts with rather simple system of binary mixtures of molten alkali chlorides. The correlation between dependences of the properties on the cation size of solvent alkali metal is discussed.

The dependences observed in the previous chapter will be examined in ternary mixtures of molten alkali chlorides in Chapter 3. Increased component species might make ionic interaction among Nd(III) complex and alkali cations more complicated with respect to the binary mixtures.

In Chapter 4, valence change of component cations is taken into account to the dependences with alkaline earth metals in solvent melt. Chloride anions surrounding Nd^{3+} are more polarized because of high electric density of alkaline earth cations, which makes it more difficult to interpret the structural information obtained by absorption spectrophotometry.

In Chapter 5, subjected elements are expanded to other Lns (La, Ce, Pr, Tb, and Er) and U.

Their thermodynamic stability is investigated in the mixtures of LiCl and KCl, and compared with that of Nd evaluated in Chapter 2. Systematic changes in the dependence of the thermodynamic stability on the melt composition throughout the Ln series are of interest. Special attention is paid to the different bonding characteristics of $4f$ and $5f$ orbital associating with the solvation behavior of Lns and Ans in molten salts.

Chapter 6 gives general conclusions including engineering remarks of this thesis.

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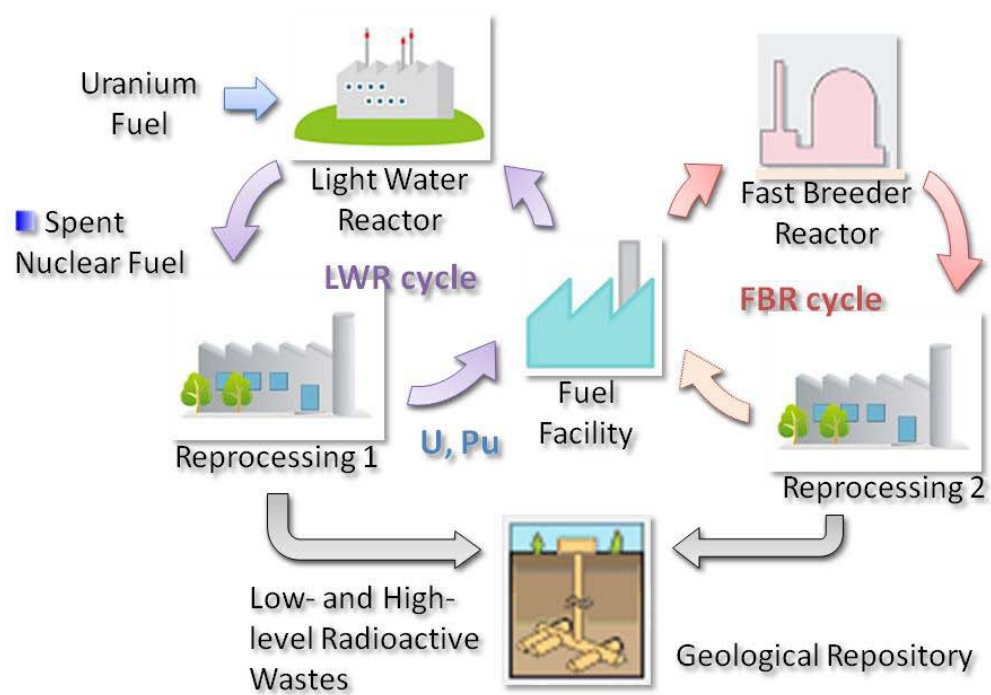


Figure 1.1 Schematic of nuclear fuel cycle.

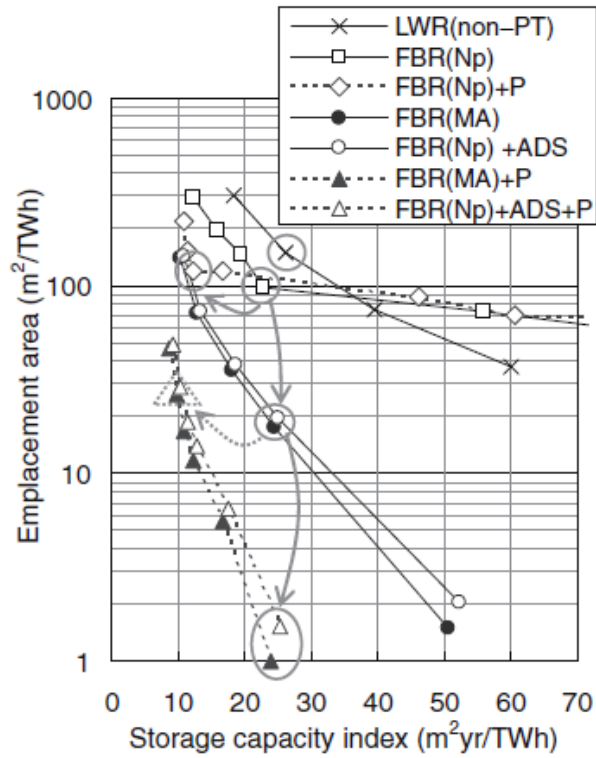


Figure 1.2 Emplacement area required for nuclear waste disposal with/without partitioning (P) and transmutation of MAs in FBR and ADS [1]. Storage capacity index is defined as the area occupied by the storage pits (m^2) multiplied by the storage period (year). Encircled parameters are representative for each scenario, while the parameter in the dotted triangle is the secondary representative for the FBR(MA)+P and FBR(Np)+ADS+P scenarios.

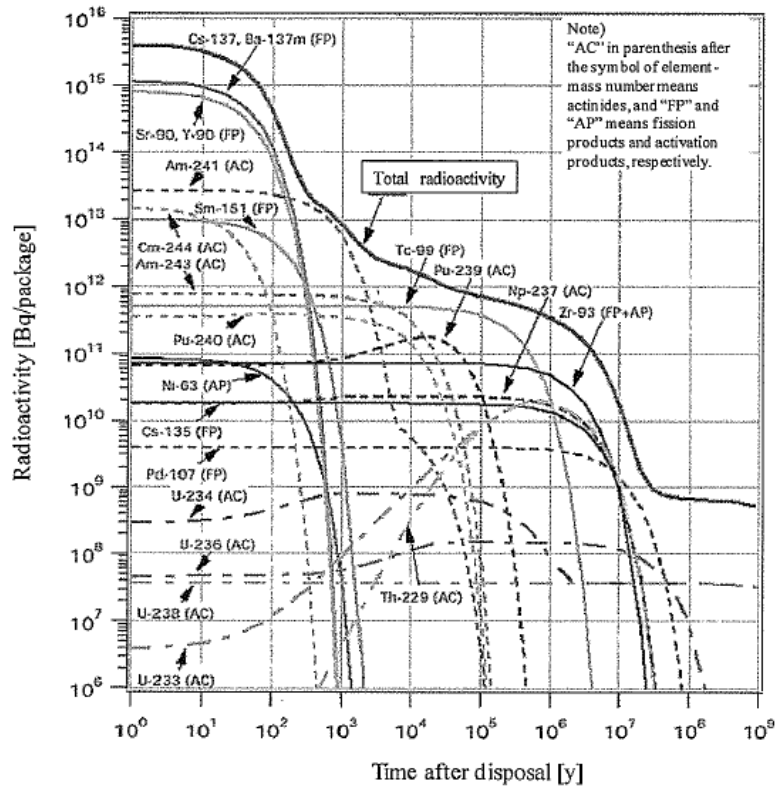


Figure 1.3 Variations in radioactivity of vitrified waste with time after emplacement in geological site [2]. Spent nuclear fuel 54 years after discharge from the reactor was assumed. Contribution of radioactivity of MAs is significant to the total radioactivity after a thousand years.

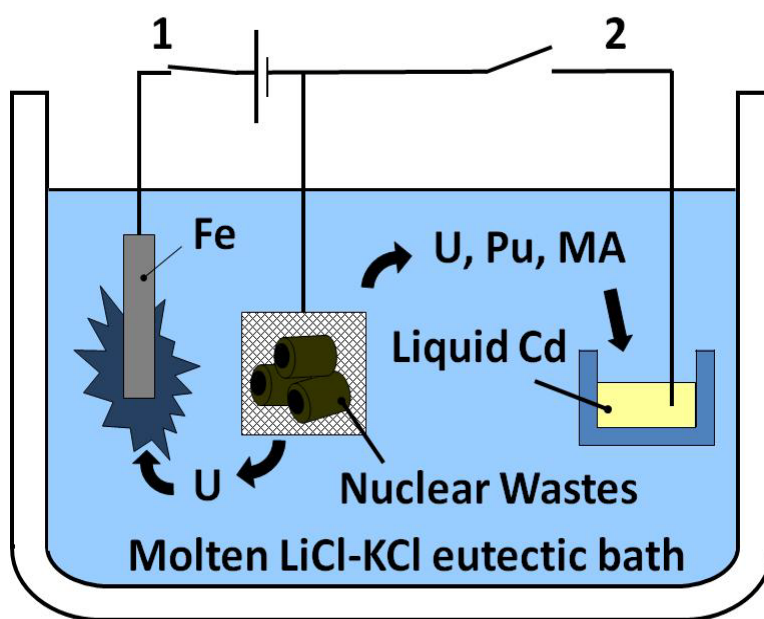


Figure 1.4 Schematic of the metal electrorefining process. Majority of U is selectively collected on a solid Fe cathode for the first step (1). Then, Pu, MAs, and residual U are collected into a liquid metal, usually Cd or Be, with some amounts of Ln fission products by electrolysis or reductive extraction (2).

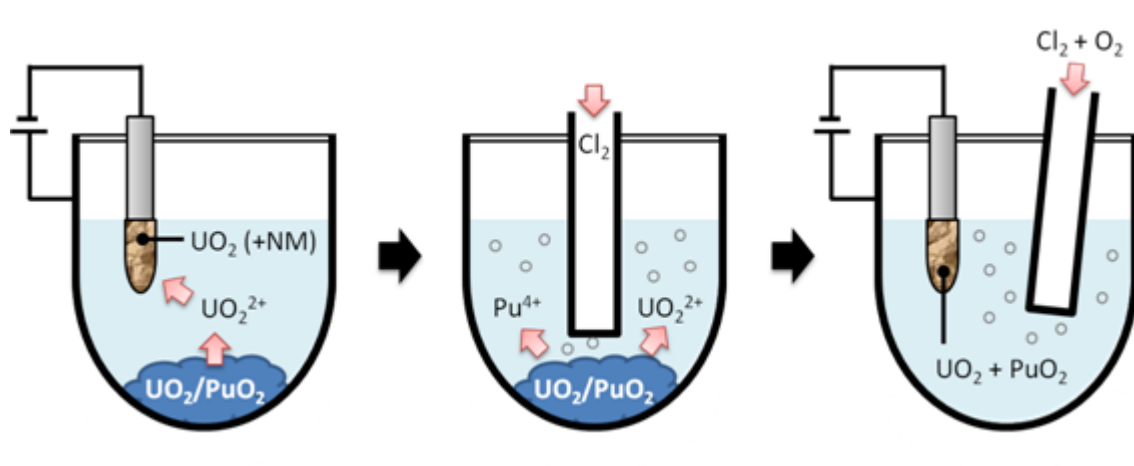


Figure 1.5 Schematic of the oxide electrowinning process.

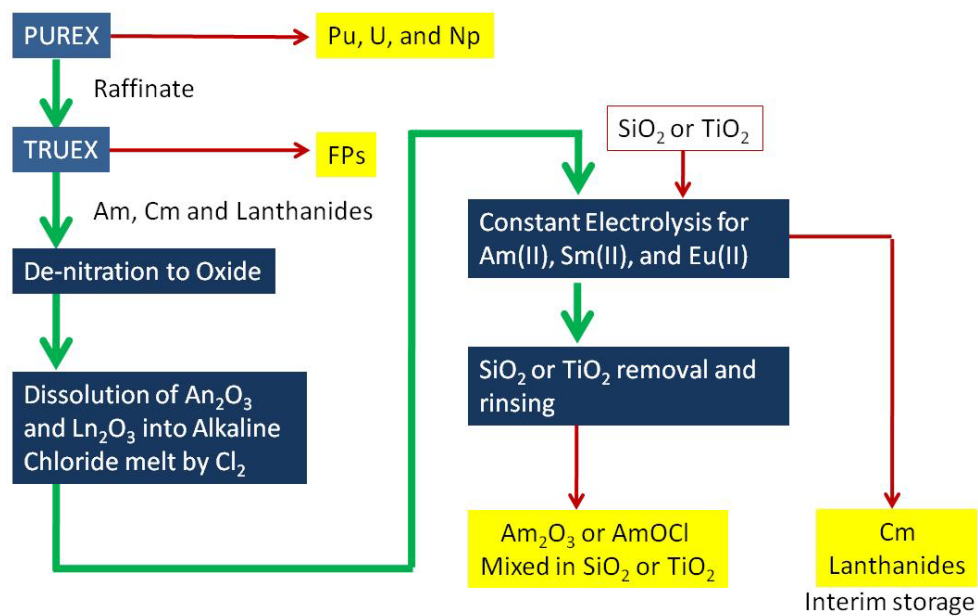


Figure 1.6 Proposed separation scheme utilizing the characteristics of divalent state of some lanthanides and americium [10].

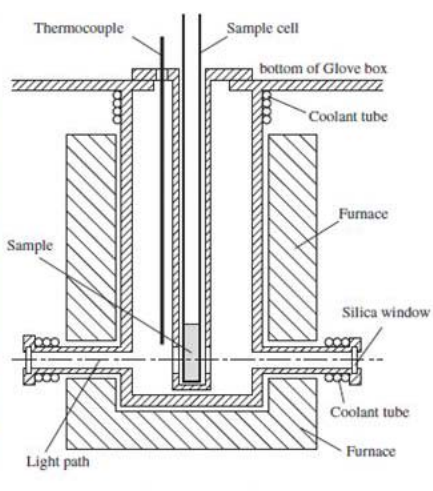


Figure 1.7 Experimental apparatus for spectroelectrochemistry. An electric furnace is connected at the bottom of glove box. The schematic is cited from the literature [50].

Chapter 2 Chemical Properties of Neodymium Ions in Binary

Mixtures of Molten Alkali Chlorides

2.1 Introduction

The present chapter deals with thermodynamic stability and coordination structure of Nd(III) complex in binary mixtures of molten alkali chlorides. As described in Chapter 1, the correlation between these macro- and microscopic properties of fission products (FPs) including lanthanides (Lns) and actinides (Ans) in molten salt media are essential to be understood to optimize the separation process.

Neodymium is one of major FP elements having larger neutron capture cross sections, and hence its removal in the pyrochemical reprocessing is desired. The reports for the electrochemical behavior of Nd in molten chlorides have been limited for LiCl-KCl [1-3], NaCl-CaCl₂ [2] and LiCl-CaCl₂ [3] eutectic melts, where its electrochemical behavior is comparably resemble to that of Am. Systematic data for the thermodynamic stability of Nd(III) complex in various alkali chlorides are necessary to assess the refining performance of Nd and might be helpful to know that of Am by analogy. Information on the coordination circumstance of solute ions is also important since it should be correlated with the stability. The predominant Nd(III) complex in molten alkali chlorides with low Nd³⁺ concentration has been confirmed to be NdCl₆³⁻ with octahedral symmetry (*O_h*) by absorption spectrophotometry [4] and Raman spectrometry [5]. The degree of the octahedral symmetry has been investigated for LiCl-CsCl mixtures employing absorption spectrum analysis, and the results reported that the NdCl₆³⁻ complex was more distorted in the melts with lower CsCl content [6].

In the present chapter, the thermodynamic stability and the coordination circumstances of the Nd(III) complex for various molten alkali chloride mixtures were investigated by electrochemical and absorption spectrum measurements, respectively. Their dependence on the melt compositions and the correlation between these macroscopic and microscopic properties were discussed.

2.2 Experimental

All experiments were carried out under an argon atmosphere, in which humidity and oxygen impurity were continuously kept less than 1 ppm. Anhydrous chlorides (99.99% purity) were purchased from Aldrich-APL LLC and used without further purification. 0.2-0.7 mol% NdCl_3 was dissolved in LiCl melt in a quartz tube. After electrochemical or spectrophotometric measurements, ACl (A = Na, K, Rb, and Cs) was added into the sample melt to change the melt composition. This procedure was repeated to the extent allowed by the melting point of alkali chloride mixtures.

An electrochemical measurement system Hz-5000 (Hokuto Denko Co.) was used for cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The sweep rate of CV for extracting peak potentials was 100 mV s^{-1} . The pulse height, period, and width of DPV were 50 mV, 100 ms, and 10 ms, respectively. A tungsten wire (99.95%, The Nilaco Co.) of 1 mm diameter, a pyrographite rod (99.99%, Tokai Carbon Co., Ltd.) of 3 mm diameter, and a Ag/Ag^+ electrode were used for the working, counter, and reference electrodes, respectively. In each measurement, the potential of chlorine gas evolution (Cl_2/Cl^-) on the pyrographite electrode [7] was determined to calibrate the Ag/Ag^+ electrode.

The electronic absorption spectra of Nd^{3+} in the melts were measured by using an UV/Vis/NIR spectrometer (V-570, JASCO). The experimental apparatus was described in [8]. The analytical light from a light source (a tungsten halogen lamp) was guided to the electric furnace with quartz windows by using optical fibers, and the light passed through the sample in a quartz tube with a 10 mm light path inside the furnace. The light which traveled through the furnace was again guided to the spectrophotometer, in which a monochromator was set in front of detectors to decrease the background noise. The light intensity for the molten alkali chloride (I_0) and that including Nd(III) (I) was measured in the wavelength range of 300-850 nm at 0.5 nm intervals and 700-550 nm at 0.1 nm intervals. The absorbance was determined to be $-\log(I/I_0)$.

All the experiments were performed at $923 \pm 3 \text{ K}$. In order to compare the results obtained in the present study with reported data [2,9], the same experiment at different temperature, $723 \pm 3 \text{ K}$, was also performed for a LiCl-KCl eutectic system.

2.3 Results and Discussion

2.3.1 Determination of redox potentials of the Nd³⁺ reduction

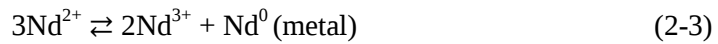
Typical cyclic voltammograms of Nd in LiCl and LiCl-KCl eutectic at 923 K are shown in Fig. 2.1. The electrochemical reduction process of Nd(III) in the eutectic has been identified to be a two-step process via Nd(II) by CV and chronopotentiometry [10],



The cathodic wave i_{C1} associated with an anodic wave i_{A1} is attributable to the soluble-soluble Nd³⁺/Nd²⁺ couple. The cathodic peak i_{C2} associated with a sharp anodic peak i_{A2} corresponds to the Nd²⁺/Nd⁰ soluble-insoluble system. All peaks were separately observed for the LiCl system, where the cathodic peak currents were proportional to the square root of the potential sweep rate and the potential difference between positive and negative peak pairs were not significant. Hence both reactions were treated as reversible.

In the present study, the overlap of i_{C1} and i_{C2} in CV (Fig. 2.1(b)) was enhanced by adding ACl (A = Na, K, Rb, or Cs) into LiCl and it could not be resolved. In order to analyze the reduction reaction 2-1, DPV was carried out, and additionally, the convolution analysis was applied to cyclic voltammograms obtained. The differential pulse voltammogram taken in the LiCl-KCl eutectic is shown in Fig. 2.2, in which the first peak was clearly obtained.

The following disproportionation reaction of Nd takes place in molten chlorides [1,2,11],



It has been reported that the reaction is completed within several minutes [1]. This is much slower than the transient time during electrochemical measurement, and hence the interference of reaction 2-3 in electrochemical analyses in the present study is considered to be insignificant.

The formal redox potential of the Nd³⁺/Nd²⁺ couple, $E^{\circ'}_{3/2}$, was determined by DPV as [12],

$$E^{\circ'}_{3/2} = E^{\circ}_{3/2} + \frac{RT}{F} \ln \frac{\gamma_{\text{Nd}^{3+}}}{\gamma_{\text{Nd}^{2+}}} = E_{\text{max}} + \frac{\Delta E}{2} - \frac{RT}{F} \ln \left(\frac{D_{\text{Nd}^{2+}}}{D_{\text{Nd}^{3+}}} \right)^{1/2} - E_{\text{ref}} \quad (2-4)$$

where $E^{\circ}_{3/2}$, E_{max} , ΔE , and E_{ref} are the standard redox potential, the peak potential of i_{C1} , the applied potential pulse height, and the potential of the Ag/Ag⁺ electrode vs. Cl₂/Cl⁻, respectively. R is the gas constant, γ the activity coefficient, T the absolute temperature, and F the Faraday

constant. The $E'^{\circ}_{3/2}$ values were constant within the analytical uncertainty of ± 10 mV in the experimental range of NdCl_3 concentration from 0.2 mol% to 0.7 mol%. This means that the ratio of activity coefficients $\gamma_{\text{Nd}^{3+}}/\gamma_{\text{Nd}^{2+}}$ is constant. D represents the diffusion coefficient of suffixed species. Due to the disproportionation reaction (reaction 2-3), it is impossible to measure an accurate diffusion property of Nd^{2+} and hence $D_{\text{Nd}^{2+}}$ is not available. In the present study, the ratio $D_{\text{Eu}^{2+}}/D_{\text{Eu}^{3+}}$ reported for europium [13] was substituted for $D_{\text{Nd}^{2+}}/D_{\text{Nd}^{3+}}$. The uncertainty of this substitution was examined to be small since both $D_{\text{Ln}^{2+}}$ and $D_{\text{Ln}^{3+}}$ decrease with the increase of atomic number and the decrease trend in Ln series is monotonic; $D_{\text{Ln}^{2+}}$ is available for Sm, Eu, and Yb [14,15] for equimolar NaCl-KCl melt, and the evaluated $D_{\text{Ln}^{2+}}/D_{\text{Ln}^{3+}}$ values were similar, so that its variation resulted in an uncertainty < 2 mV on $E'^{\circ}_{3/2}$. Moreover, the ratio $D_{\text{Nd}^{2+}}/D_{\text{Nd}^{3+}}$ for other molten chloride mixtures was assumed to be similar to the $D_{\text{Eu}^{2+}}/D_{\text{Eu}^{3+}}$ in equimolar NaCl-KCl mixture that was equal to 1.96 [13].

Convolution analysis of cyclic voltammograms [12] was used to determine $E'^{\circ}_{3/2}$ for the melts with higher MCl contents (up to 60% for the case of KCl) where the first reduction peak of Nd was not clearly obtained even by DPV. Theoretical treatment of the analysis is described in Appendix 2A at the end of this chapter.

The $E'^{\circ}_{3/2}$ values obtained for the LiCl-KCl eutectic at 723 K are shown in Table 2.1. The $E'^{\circ}_{3/2}$ values determined by DPV and convolution analysis of cyclic voltammogram agreed with each other. The literature values are shown together, in which $E'^{\circ}_{3/2}$ was determined by the convolution analysis and the D in the right side of Eq. 2-4 was not taken into account. $E'^{\circ}_{3/2}$ determined following the same method is shown in parentheses. The values agreed with the literature values [2,9].

The formal redox potential of the $\text{Nd}^{2+}/\text{Nd}^0$ couple, $E'^{\circ}_{2/0}$, was evaluated from CV as [16], which is available for reversible deposition reaction,

$$E'^{\circ}_{2/0} = E^{\circ}_{2/0} + \frac{RT}{nF} \ln \gamma_{\text{Nd}^{3+}} = E_{\text{pc}} - \frac{RT}{nF} \ln C_{\text{O}} + (0.9241)^2 \frac{RT}{nF} - E_{\text{ref}} \quad (2-5)$$

where $E^{\circ}_{2/0}$, E_{pc} , n , and C_O are the standard redox potential, the peak potential of CV cathodic peak i_{C2} , the reaction electron number ($n=2$, in the present case), and the bulk concentration, respectively. The $E^{\circ'}_{2/0}$ values were proportional to the natural logarithm of $NdCl_3$ concentration in the measured range. The obtained $E^{\circ'}_{2/0}$ values shown in Table 2.1 are consistent with the literature data [9].

It should be noted that, in this section, the Cl_2/Cl^- equilibrium potential determined by using a chlorine gas electrode [17] was used in order to obtain the precise standard potential values. In following sections, the Cl_2 evolution potential mentioned in experimental section will be used as the standard redox potential of the Cl_2/Cl^- couple, E_{ref} in Eqs. 2-4 and 2-5. Though the Cl_2 evolution potential slightly shifts from the Cl_2/Cl^- equilibrium potential, the former method is feasible for systematic study with molten salts of various components.

2.3.2 Dependence of Gibbs free energy change of Nd(III) formation on the melt composition

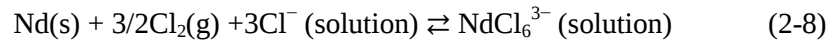
The standard redox potential of the Nd^{3+}/Nd^0 couple, $E^{\circ'}_{3/0}$, was calculated from $E^{\circ'}_{3/2}$ and $E^{\circ'}_{2/0}$ by employing the following equation,

$$E^{\circ'}_{3/0} = \frac{E^{\circ'}_{3/2} + 2E^{\circ'}_{2/0}}{3} \quad (2-6)$$

The standard Gibbs free energy change of Nd(III) formation, $\Delta G^{\circ'}_{3/0}$, was derived as,

$$\Delta G^{\circ'}_{3/0} = nFE^{\circ'}_{3/0} \quad (2-7)$$

The reaction corresponding to the $\Delta G^{\circ'}_{3/0}$ is given as the following reaction.



The $\Delta G^{\circ'}_{3/0}$ values were evaluated for various binary mixtures of alkali chloride, ACl ($A = Na, K, Rb, \text{ or } Cs$), and $LiCl$ at 973 K. It should be noted that Cl_2/Cl^- couple cannot be assumed as an absolute reference since the activity of Cl^- is not invariable for the melt compositions. The melt composition changes the chemical status of both Cl^- (solution) and $NdCl_6^{3-}$ (solution). As defined in the above reaction, the observed $\Delta G^{\circ'}_{3/0}$ values represent the difference between the Gibbs energy levels of these two.

Figure 2.3 shows $\Delta G^{\circ'}_{3/0}$ s obtained as functions of $LiCl$ content. The maximum mole fraction

of ACl was limited by following two reasons: (1) melting point of the sample and (2) cathode limit (alkali metal deposition) for electrochemical analysis. The $\Delta G^{\circ'}_{3/0}$ value increased by adding ACl into LiCl, which means that the addition of ACl makes the Nd(III) complex stable. In alkali cation series, the ionic radius is in the order of $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$, and the polarizing ability is in the inverse order. That is, the alkali cation with smaller ionic radius like Li^+ interacts with Cl^- strongly. Hence, there could be strong interaction among Li^+ and chloride ions surrounding the solute Nd^{3+} in LiCl.

For mixtures of alkali chlorides, the polarizing ability of alkali cations to Cl^- could be an average of each according to the mixing ratio. Redox potential of some chemical reactions in molten salts was reported to be correlated with the “charge density”,

$$c = \sum \chi_i \frac{z_i}{r_i^3} \quad (2-9)$$

where χ_i is the molar fraction of the i th component with the cation of radius r_i having a charge of z_i [18,19]. However, they counted solute ion as a component as well as solvent ions and in general, the ionic potential z/r , or the force z/r^2 is more rational than c as an expression of polarizing ability of solvent alkali cations.

In this study, $\Delta G^{\circ'}_{3/0}$ was found to have a strong correlation with the averaged “polarizing power” of alkali cations in the melts,

$$P = \sum \chi_i \frac{z_i}{r_i^2} \quad (2-10)$$

Ionic radius r_i for six coordinated ions [20] was used in the present study. The r_i and P_i values are shown in Table 2.2. The relationship between $\Delta G^{\circ'}_{3/0}$ and P is shown in Fig. 2.4. The relation between $\Delta G^{\circ'}_{3/0}$ and P can be expressed by a linear function for all alkali binary mixtures. The Nd(III) complex is more stable in the alkali binary mixture with smaller P , and the stability increases with a constant slope, $\delta(\Delta G^{\circ'}_{3/0})/\delta P$.

2.3.3 Coordination environment of Nd(III) complex

Absorption spectra of Nd^{3+} in molten LiCl-ACl mixtures and LiCl at 923 K were measured. A typical absorption spectrum of Nd^{3+} in the LiCl-KCl eutectic is shown in Fig. 2.5, in which an intensive absorption peak can be seen at 589 nm. This peak is assigned to be the f - f transitions

from the ground level of $^4I_{9/2}$ to the excited levels of $^4G_{5/2}$ and $^2G_{7/2}$. The $^4G_{5/2} \leftarrow ^4I_{9/2}$ transition, which is known as the hypersensitive f - f transitions, is sensitive to changes in the coordination circumstance and commonly used to examine the complexation of Nd^{3+} in solutions [6]. Figure 2.6 shows the absorption spectra of $^4G_{5/2}, ^2G_{7/2} \leftarrow ^4I_{9/2}$ transition for LiCl and some binary alkali chlorides, ranging from 562 to 625 nm wavelength. The spectra are composed of several transitions between split degenerate terms of the ground and the excited levels. The transitions between the split degenerate states are schematically shown in Fig. 2.7. According to the reported energy diagram [4], each transition shown in Fig. 2.6 was assigned. The spectrum peaks corresponding to each transition were separable using Gaussian functions, and consequently, wave numbers at each peak position were determined.

The electric field given by the symmetrical octahedral coordination of NdCl_6^{3-} promotes the splitting of the degenerate energy states, which makes the absorption peaks separable as the LiCl-CsCl system (spectrum (e) in Fig. 2.6). In the same manner, sharper absorption spectrum as the LiCl case (spectrum (a) in Fig. 2.6) where the energy splitting is depressed indicates that the symmetry of NdCl_6^{3-} is distorted in the melt. As shown in Figs. 2.6 and 2.7, the difference of peak positions I* and II is equal to the sum of energy splittings of the $^4I_{9/2}$ and $^4G_{5/2}$ states, $\Sigma\Delta E$, and hence the term of $\Sigma\Delta E$ is a useful probe to know the symmetry of NdCl_6^{3-} [6].

The transition probability of the $^4G_{5/2}, ^2G_{7/2} \leftarrow ^4I_{9/2}$ transition, which is expressed as the oscillator strength f , also gives information of the coordination circumstance of NdCl_6^{3-} . f is defined as,

$$f = 4.319 \times 10^{-9} \frac{9n}{(n^2 + 2)^2} \int \varepsilon(\nu) d\nu \quad (2-11)$$

where $\varepsilon(\nu)$ is the molar absorptivity at energy ν (cm^{-1}) and n is the reflective index of the solvent medium. $\varepsilon(\nu)$ was integrated from 562 to 625 nm in the present study. The reflective indexes of single alkali chlorides are available [21]. For binary mixtures, the n value was estimated by a linear interpolation between the values of pure component melts [22]. Table 2.3 shows f , $\Sigma\Delta E$, and molar absorptivity at 589 nm for binary eutectics.

The f and $\Sigma\Delta E$ values for binary alkali chlorides obtained are shown in Fig. 2.8 as functions of LiCl mole fraction, χ_{LiCl} . $\Sigma\Delta E$ decreased with the increase of χ_{LiCl} , which suggests the distortion of the octahedral symmetry of NdCl_6^{3-} . The f values increased with χ_{LiCl} , and this also suggests the distortion proceeds. The results showed a similar trend reported for NdCl_3 in LaCl_3 -KCl

mixtures [23].

Figure 2.9 shows the dependence of f and $\Sigma\Delta E$ on the polarizing power of solvent cations, P . The f values increased with P , while $\Sigma\Delta E$ linearly decreased with the increase of P . Different ACl-LiCl systems show different increasing rates of f (Fig. 2.9(a)), while the decreasing rates and absolute values of $\Sigma\Delta E$ are similar for all ACl-LiCl systems (Fig. 2.9(b)). The factors influencing f in molten alkali chlorides are: (a) the distortions from octahedral symmetry, and, (b) the electron donating ability of the chloride anion [24]. Figure 2.9(b) suggests that $\Sigma\Delta E$ correlated with the factor (a) [6] is simply controlled by P for molten alkali chloride systems. On the other hand, f varies for different ACl-LiCl systems at the low χ_{LiCl} region, which suggests that the factor (b) is also important.

Figure 2.10 shows f as a function of $\Sigma\Delta E$. The f value similarly decreased with the increase of $\Sigma\Delta E$ in every mixtures near $\chi_{\text{Li}}=1$, but it was clearly different depending on the mixed cations in the region of higher $\Sigma\Delta E$; the f value was smaller in the sequence of $\text{K}^+ \rightarrow \text{Cs}^+$. These cations have lower polarizing power that enlarges the electron donating ability of Cl^- in the same sequence. This suggests that the effect of factor (b) gradually emerges at the low χ_{LiCl} region.

The discussion above is also suggestive that the local structure around Nd^{3+} significantly correlates with the bulk thermodynamic stability since both $\Sigma\Delta E$ and $\Delta G^{\circ'}_{3/0}$ depend well upon P . Figure 2.11 shows the relationship between $\Sigma\Delta E$ and $\Delta G^{\circ'}_{3/0}$ in which $\Delta G^{\circ'}_{3/0}$ decreases with the increase of $\Sigma\Delta E$. From these results, it can be concluded that the polarizing power of solvent cations controls the degree of distortion from octahedral symmetry of ligand chloride structure which is correlated with the thermodynamic stability of NdCl_6^{3-} complex in molten alkali chlorides.

2.4 Conclusion

The $\Delta G^{\circ'}_{3/0}$ value decreased by adding ACl ($A = \text{Na}, \text{K}, \text{Rb}, \text{or Cs}$) into LiCl. This means that the Nd(III) complex is more stable in the alkali chloride mixtures with larger averaged cationic radius. $\Delta G^{\circ'}_{3/0}$ is correlated with the polarizing power of solvent cations, P .

The change in the oscillator strength of the ${}^4G_{5/2}, {}^2G_{7/2} \leftarrow {}^4I_{9/2}$ transition and $\Sigma\Delta E$ suggested that the octahedral symmetry of the NdCl_6^{3-} complex is more distorted in the melts of higher LiCl

content. The degree of distortion is correlated with increasing P .

The P controls the local structure around Nd^{3+} and the degree of its distortion from octahedral symmetry is correlated with thermodynamic stability of NdCl_6^{3-} complex in molten alkali chlorides.

Appendix 2A Convolution analysis of CV [12]

The reaction $\text{O} + ne \rightleftharpoons \text{R}$ is considered assuming semi-infinite linear diffusion and a solution initially containing only species O. When one can assume that the reaction is reversible (diffusion controlled), the equations governing this case are

$$\begin{aligned} \frac{\partial C_{\text{O}}(x,t)}{\partial t} &= D_{\text{O}} \frac{\partial^2 C_{\text{O}}(x,t)}{\partial x^2} & \frac{\partial C_{\text{R}}(x,t)}{\partial t} &= D_{\text{R}} \frac{\partial^2 C_{\text{R}}(x,t)}{\partial x^2} \\ C_{\text{O}}(x,0) &= C_{\text{O}}^* & C_{\text{R}}(x,0) &= 0 \\ \lim_{x \rightarrow \infty} C_{\text{O}}(x,t) &= C_{\text{O}}^* & \lim_{x \rightarrow \infty} C_{\text{R}}(x,t) &= 0 \end{aligned} \quad (2\text{A-1})$$

where C and D represent the concentration and the diffusion coefficient of the species O and R, respectively. x and t are the distance from electrode surface and the time, respectively. Laplace transformation of the diffusion equations and application of the initial and semi-infinite conditions leads to

$$\begin{aligned} \bar{C}_{\text{O}}(x,s) &= \frac{C_{\text{O}}^*}{s} + A(s) \exp \left[- \left(\frac{s}{D_{\text{O}}} \right)^{1/2} x \right] \\ \bar{C}_{\text{R}}(x,s) &= B(s) \exp \left[- \left(\frac{s}{D_{\text{R}}} \right)^{1/2} x \right] \end{aligned} \quad (2\text{A-2})$$

The electron flux at the electrode surface is proportional to the current:

$$i(t) = nFAD_{\text{O}} \left[\frac{\partial C_{\text{O}}(x,t)}{\partial x} \right]_{x=0} = -nFAD_{\text{R}} \left[\frac{\partial C_{\text{R}}(x,t)}{\partial x} \right]_{x=0} \quad (2\text{A-3})$$

which is transformed to

$$\bar{i}(s) = nFAD_{\text{O}} \left[\frac{\partial \bar{C}_{\text{O}}(x,s)}{\partial x} \right]_{x=0} = -nFAD_{\text{R}} \left[\frac{\partial \bar{C}_{\text{R}}(x,s)}{\partial x} \right]_{x=0} \quad (2\text{A-4})$$

where F and A are the Faraday constant and the surface area of the electrode, respectively.

From the combination of these equations and the Laplace inversing, it is obtained

$$C_O(0,t) = C_O^* - \frac{1}{nFAD_O^{1/2}} \left[\frac{1}{\pi^{1/2}} \int_0^t \frac{i(u)}{(t-u)^{1/2}} du \right] \quad (2A-5)$$

$$C_R(0,t) = \frac{1}{nFAD_R^{1/2}} \left[\frac{1}{\pi^{1/2}} \int_0^t \frac{i(u)}{(t-u)^{1/2}} du \right] \quad (2A-6)$$

If the term in brackets, which represents a particular (convolutive) transformation of the experimental $i(t)$ data, is defined as $I(t)$, then the equations becomes

$$C_O(0,t) = C_O^* - \frac{I(t)}{nFAD_O^{1/2}} \quad C_R(0,t) = \frac{I(t)}{nFAD_R^{1/2}} \quad (2A-7)$$

where

$$I(t) = \frac{1}{\pi^{1/2}} \int_0^t \frac{i(u)}{(t-u)^{1/2}} du \quad (2A-8)$$

This integral can be considered as the *semi-integral* of $i(t)$ as $\frac{d^{-1/2}}{dt^{-1/2}} i(t) = I(t)$.

Under the condition where $C_O(0,t) = 0$ (i.e., under purely diffusion-controlled conditions), $I(t)$ reaches its limiting or maximum value, I_l , which is

$$I_l = nFAD_O^{1/2} C_O^* \quad (2A-9)$$

Then,

$$C_O(0,t) = \frac{[I_l - I(t)]}{nFAD_O^{1/2}} \quad (2A-10)$$

At the cathodic sweep of CV with the electrode initially held at a potential E_i , where no electrode reaction occurs, the potential changes linearly with the sweep rate v ($V s^{-1}$):

$$E(t) = E_i - vt \quad (2A-11)$$

Under the assumption of the reversible reaction, C_O and C_R immediately adjust to the ratio dictated by the Nernst equation:

$$\frac{C_O(0,t)}{C_R(0,t)} = \exp \left[\frac{nF}{RT} (E_i - vt - E^0) \right] \quad (2A-12)$$

The application of semi-integral equations of C_O and C_R yields

$$E(t) = E^{\circ'} + \frac{RT}{nF} \ln \left(\frac{D_R}{D_O} \right)^{1/2} + \frac{RT}{nF} \ln \frac{I_l - I(t)}{I(t)} = E_{1/2} + \frac{RT}{nF} \ln \frac{I_l - I(t)}{I(t)} \quad (2A-13)$$

where $E_{1/2}$ is called the half wave potential.

For the analyses of sampled i - t data by CVs, one convenient algorithm, which follows directly from the definition of $I(t)$, is

$$I(t) = I(k\Delta t) = \frac{1}{\pi^{1/2}} \sum_{j=1}^{j=k} \frac{i(j\Delta t - 1/2\Delta t)\Delta t}{\sqrt{k\Delta t - j\Delta t + 1/2\Delta t}} = \frac{1}{\pi^{1/2}} \sum_{j=1}^{j=k} \frac{i(j\Delta t - 1/2\Delta t)\Delta t^{1/2}}{\sqrt{k - j + 1/2}} \quad (2A-14)$$

$E_{1/2}$ is obtained by reading out the $E(k\Delta t)$ value when t satisfy the condition of $\ln \frac{I_l - I(\Delta t)}{I(\Delta t)} =$

0. It should be noted that the theoretical potential difference between E_i and $E_{1/2}$ is equal to $5RT/nF$. In the present study, E_i was chosen to adjust the potential difference to be $5RT/nF$ with $E_{1/2}$ calculated.

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Table 2.1 Formal redox potentials of Nd in LiCl-KCl eutectic at 723 K.

	Method		
	CV	DPV	
$E^{\circ'}_{3/2}$ (V vs. Cl_2/Cl^-)	-3.122 ± 0.010 (-3.097)	-3.122 ± 0.010 (-3.097)	[this study]
	-3.089 ± 0.001		[2]
	-3.098 ± 0.010		[9]
$E^{\circ'}_{2/0}$	-3.142 ± 0.010		[this study]
	-3.206 ± 0.003		[2]
	-3.120 ± 0.015		[9]

Table 2.2 Ionic radius and polarizing power of cations.

	Ionic radius r / Å [20]	Polarizing power P^a
Li ⁺	0.76	1.73
Na ⁺	1.02	0.96
K ⁺	1.38	0.53
Rb ⁺	1.52	0.43
Cs ⁺	1.67	0.36
Nd ³⁺	1.36	1.62

^a See Eq. 2-10.

Table 2.3 Sum of splittings of electronic energy levels, molar absorptivity at 589 nm, and the oscillator strength of hypersensitive transitions

Spectrum	Medium (molar ratio)	ϵ_{589} ($\text{M}^{-1} \text{cm}^{-1}$)	$f (\times 10^6)$	$\Sigma(\Delta E)^a$ (cm^{-1})
(a)	LiCl	15.2	23.5	421
(b)	LiCl-NaCl (70:30)	14.5	23.2	432
(c)	LiCl-KCl (59:41)	12.4	23.1	454
(d)	LiCl-CsCl (60:40)	10.7	21.1	460
(e)	LiCl-CsCl (40:60)	9.35	18.8	463

^a $\Delta E(^4I_{9/2}) + \Delta E(^4G_{5/2})$. Peak positions were analyzed by dividing the raw spectrum into four simple Gaussian functions.

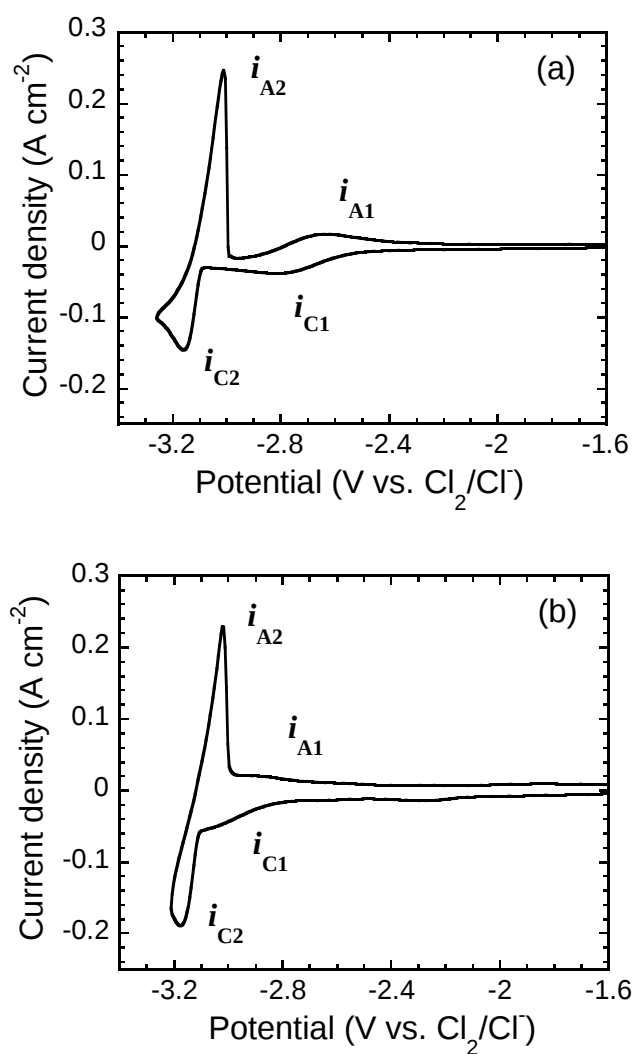


Figure 2.1 Cyclic voltammograms of Nd in alkali chlorides at 923 K. Potential sweep rate of CV was 100 mV s^{-1} . (a) LiCl system. Concentration of NdCl_3 in LiCl was 0.60 mol%. (b) LiCl-KCl eutectic system. Concentration of NdCl_3 in LiCl-KCl was 0.47 mol%.

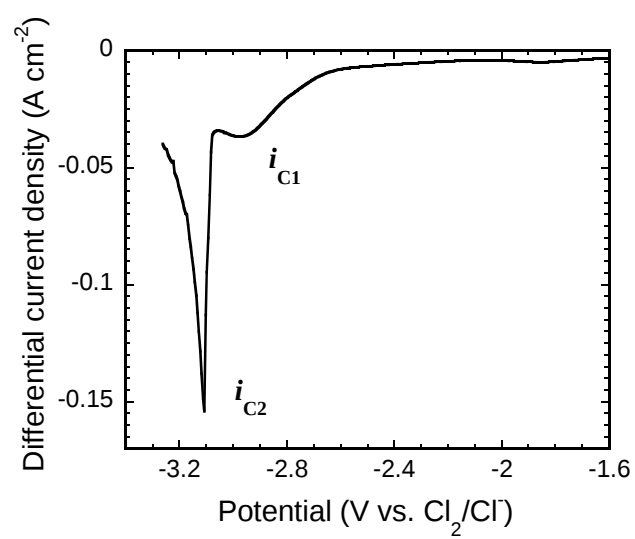


Figure 2.2 Differential pulse voltammogram of Nd in LiCl-KCl eutectic melt at 923 K. The pulse height, period, and width of DPV were 50 mV, 100 ms, and 10 ms, respectively. Concentration of NdCl_3 was 0.47 mol%.

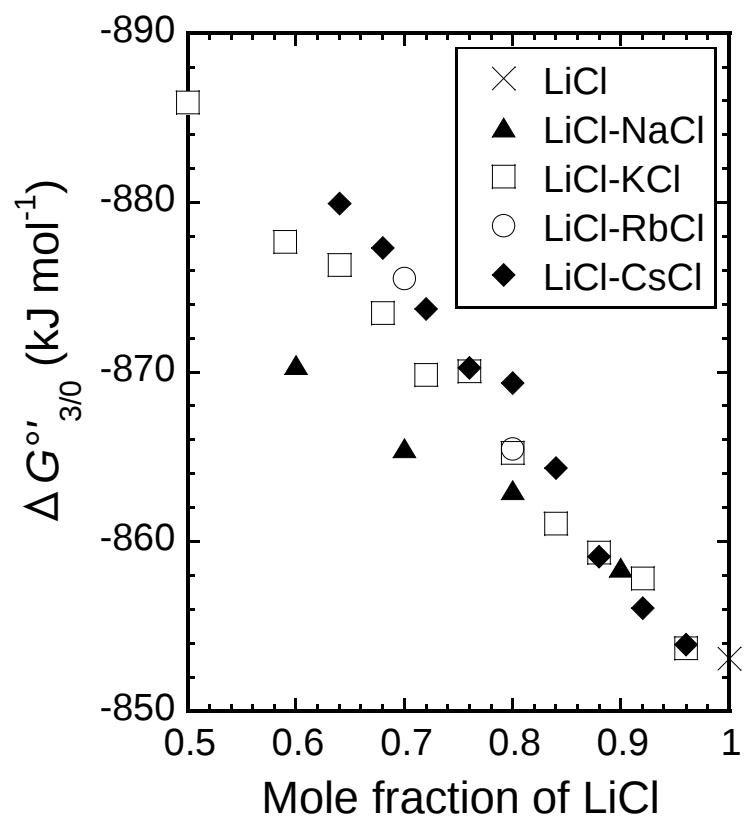


Figure 2.3 Dependence of Gibbs free energy change of Nd(III) formation on the melt composition.

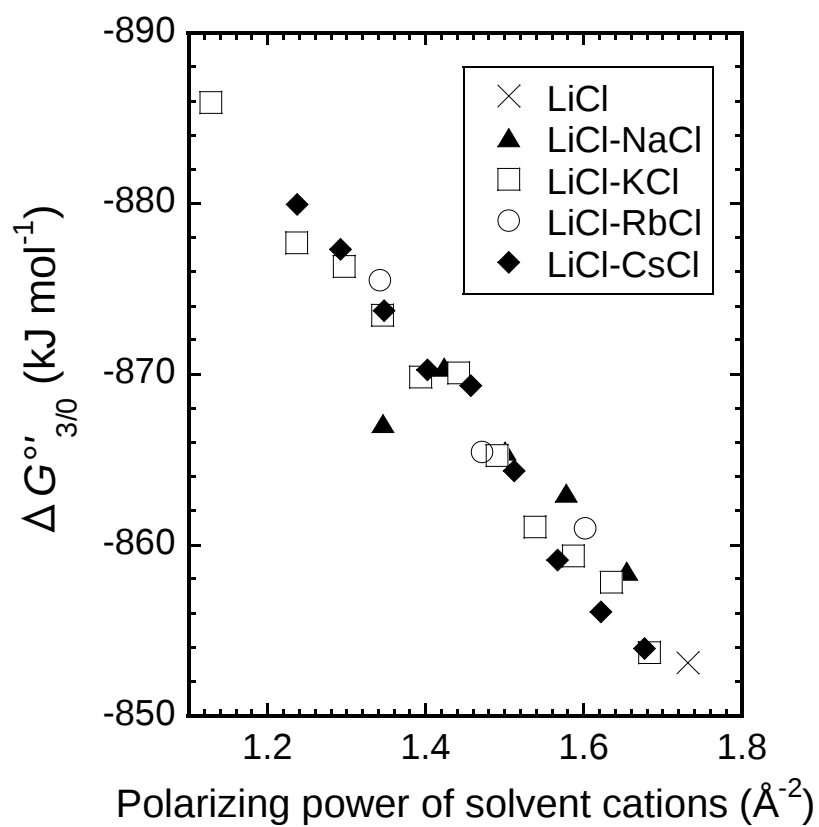


Figure 2.4 Dependence of Gibbs free energy change of Nd(III) formation on the polarizing power of solvent cations.

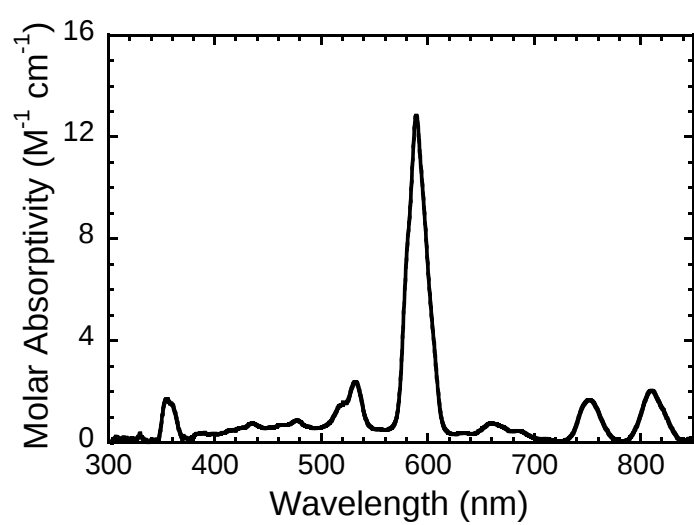


Figure 2.5 Absorption spectra of Nd³⁺ in LiCl-KCl eutectic melt at 923 K.

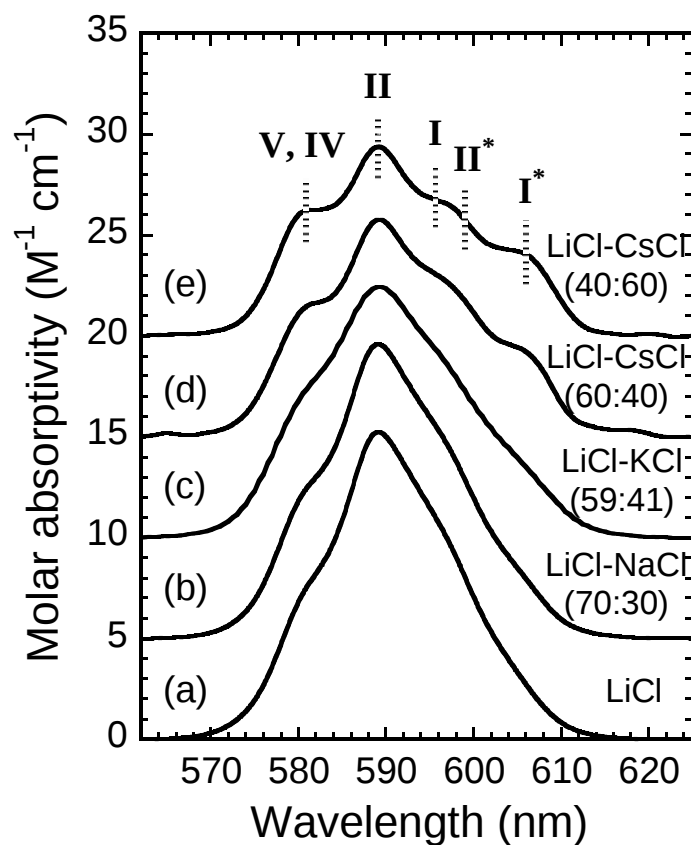


Figure 2.6 Electronic absorption spectra of Nd^{3+} in molten alkali chlorides at 923K. (a) LiCl system. (b) 70 mol% LiCl and 30 mol% NaCl system. (c) LiCl-KCl eutectic system. (d) 60 mol% LiCl and 40 mol% CsCl system. (e) 40 mol% LiCl and 60 mol% CsCl system.

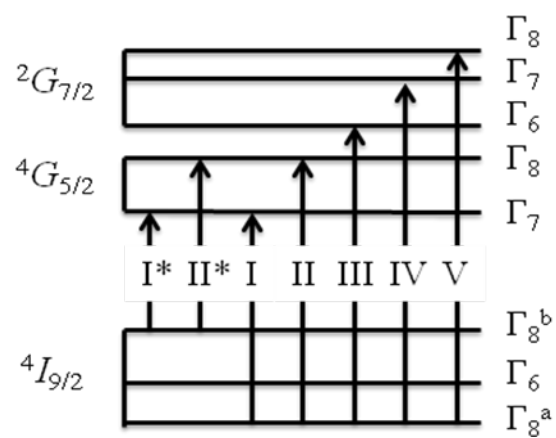


Figure 2.7 Diagram of hypersensitive transitions of NdCl_6^{3-} . The diagram was quoted from the literature [4].

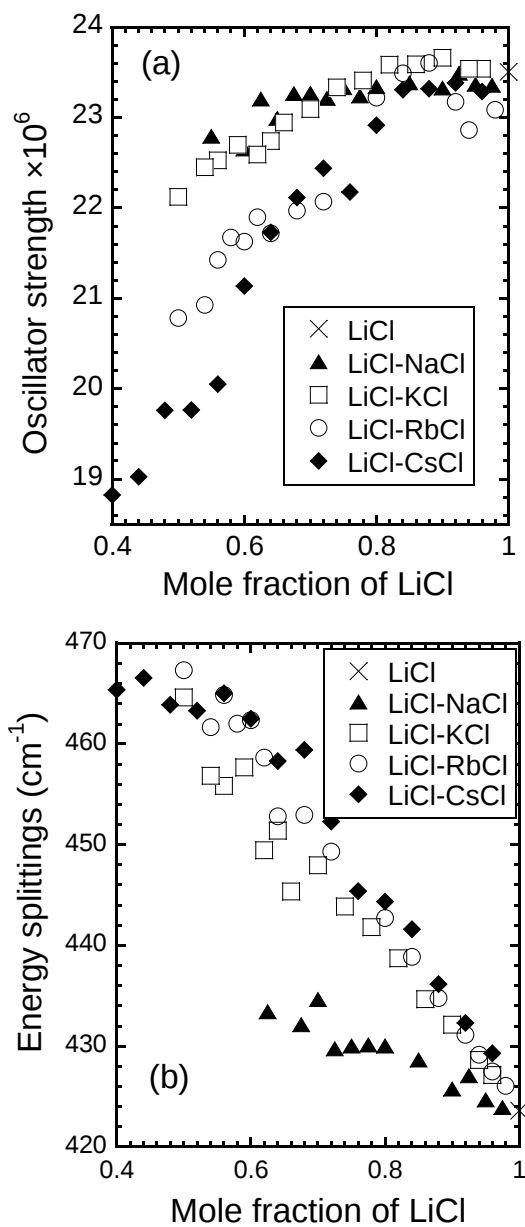


Figure 2.8 Dependence of oscillator strength and energy splittings of hypersensitive transition of Nd^{3+} on the melt composition. (a) Oscillator strength. (b) Energy splittings.

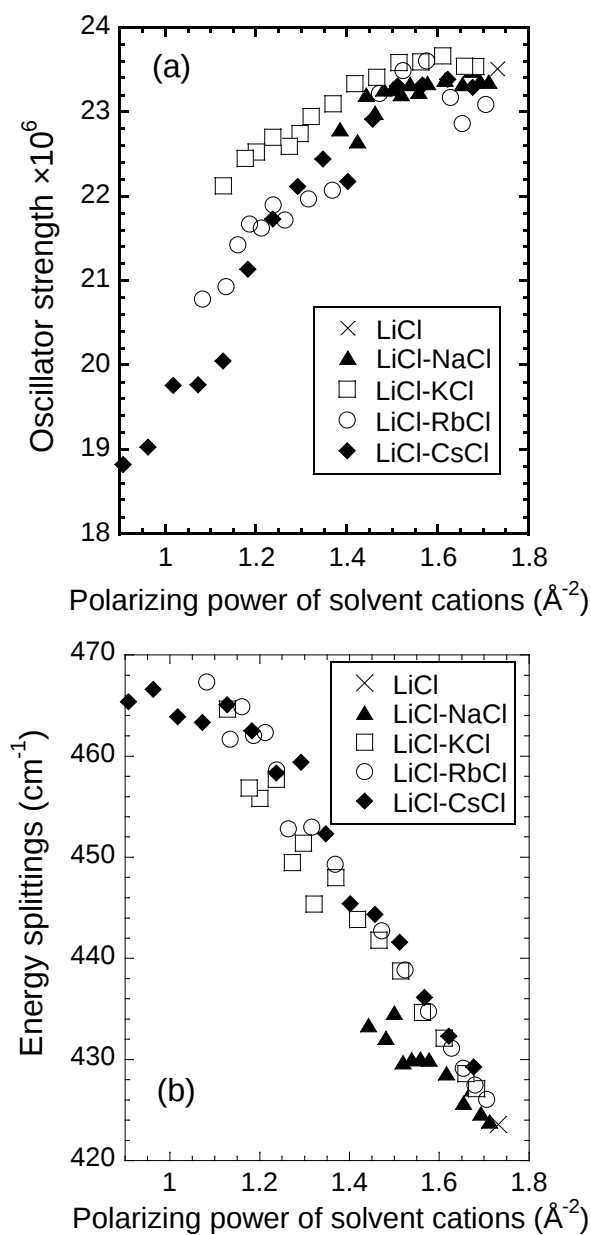


Figure 2.9 Dependence of oscillator strength and energy splittings of hypersensitive transition of Nd^{3+} on the polarizing power of solvent cations. (a) Oscillator strength. (b) Energy splittings.

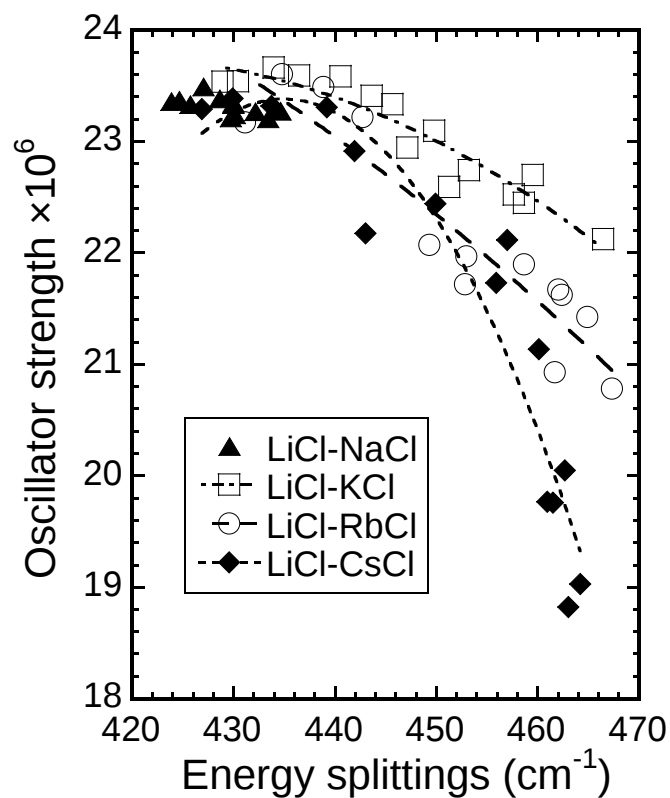


Figure 2.10 Dependence of oscillator strength on energy splittings. Dashed, dashed-dotted, and dashed-two dotted lines are quadratic approximated curves of dots for LiCl-KCl, LiCl-RbCl, and LiCl-CsCl systems, respectively.

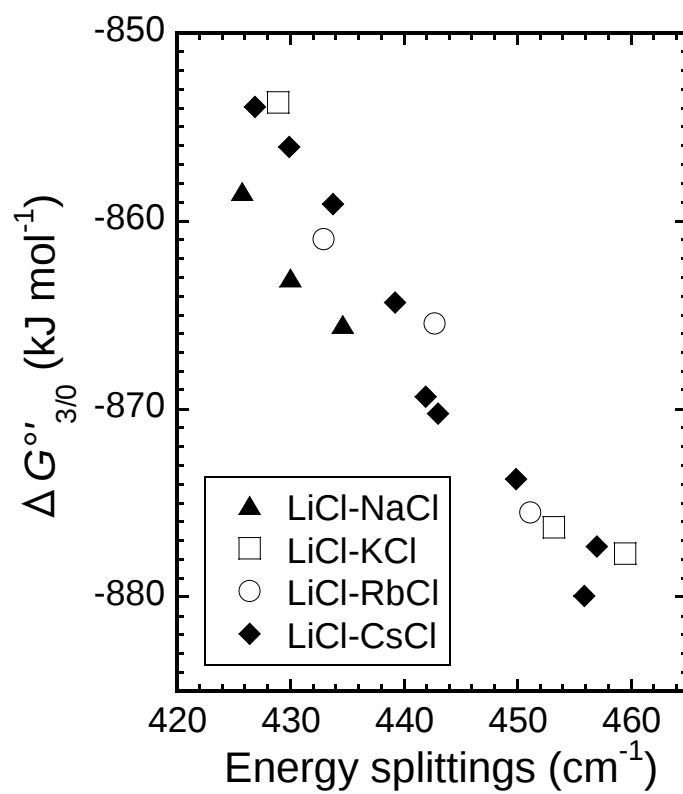


Figure 2.11 Relationship between Gibbs free energy change of Nd(III) formation and energy splittings.

Chapter 3 Thermodynamic Stability of Nd(III) Complex in Ternary Mixtures of Molten Alkali Chlorides

3.1 Introduction

The present chapter deals with the thermodynamic stability of Nd(III) complex in ternary mixtures of alkali chlorides. The thermodynamic stability was closely correlated with the averaged polarizing power of solvent cations for binary mixtures of alkali chlorides as described in Chapter 2. It is of interest whether the thermodynamic stability of Nd(III) complex in ternary mixtures can be explained by the same function of ionic radius of solvent alkali cations. Additional alkali cation might make ionic interaction among Nd(III) complex and alkali cations more complicated.

As mentioned in Chapter 2, The electrochemical behavior of Nd ions has been reported only for binary mixtures of alkali chlorides [1-5], LiCl-AECl₂ (AE = Ca, Sr, and Ba) [3,4] and NaCl-CaCl₂ [5], where Nd³⁺ is reduced to metal by two steps via divalent as follows:



Thermodynamic properties of Nd in ternary mixtures, on the other hand, have not been investigated. Some ternary mixtures possess lower melting point, *e.g.*, 619 K for LiCl-NaCl-KCl (55:9:36 mol%) and 538 K for LiCl-KCl-CsCl (58:13:29 mol%) eutectics [6], compared with that of a typical binary system, LiCl-KCl eutectic melt (59:41 mol%) at 628 K. This feature may be suitable for the reprocessing at moderate operation temperature. In this context, the electrochemical behavior of Nd in ternary molten mixtures of alkali chlorides was investigated in the present chapter.

3.2 Experimental

All experiments were carried out under an Ar atmosphere (O₂ and H₂O < 1 ppm). Anhydrous chlorides (99.99% purity) were purchased from Aldrich-APL LLC and used without further purification. 0.3-0.6 mol% NdCl₃ was dissolved in various ternary mixtures of alkali chlorides,

where equimolar NaCl-KCl or KCl-CsCl mixture (31:69 mol%) was added into LiCl melt. Experimental temperature was controlled in the range from 623 to 923 ± 3 K.

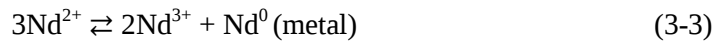
An electrochemical measurement system Hz-5000 (Hokuto Denko Co.) was used for cyclic voltammetry (CV) and the differential pulse voltammetry (DPV). The sweep rate of CV for extracting peak potentials was 100 mV s^{-1} . The pulse height, period, and width of DPV were 50 mV, 100 ms, and 10 ms, respectively. A tungsten wire (99.9%, The Nilaco Co.) of 1 mm diameter, a pyrographite rod (99.99%, Tokai Carbon Co., Ltd.) of 3 mm diameter, and a Ag/Ag⁺ electrode were used for the working, counter, and reference electrodes, respectively. In each measurement, the potential of chlorine gas evolution (Cl₂/Cl⁻) on the pyrographite electrode [7] was determined to calibrate the Ag/Ag⁺ electrode.

3.3 Results and Discussion

3.3.1 Determination of Gibbs free energy change of Nd(III) formation

Figure 3.1(a) shows typical cyclic voltammograms of Nd in molten LiCl-KCl-CsCl mixtures at 923 K. The cathodic wave i_{C1} associated with an anodic wave i_{A1} is attributable to the soluble-soluble Nd³⁺/Nd²⁺ couple. The cathodic peak i_{C2} with a sharp anodic peak i_{A2} corresponds to the Nd²⁺/Nd⁰ soluble-insoluble system. Decrease of current densities was due to the concentration of Nd³⁺. All peaks were clearly observed for pure LiCl system, while the overlap of i_{C1} and i_{C2} in voltammograms was enhanced by adding ACl (A = K, Cs) into LiCl and it could not be resolved. In order to obtain sharp wave i_{C1} , DPV was performed. The result in LiCl-KCl-CsCl mixtures at 923 K is shown in Fig. 3.1(b), in which the first peak was clearly obtained until LiCl mole fraction, χ_{LiCl} , is more than 0.7. The convolution analysis [8] was applied for cyclic voltammograms.

The disproportionation reaction of Nd takes place in molten chlorides [1,5,9],



Its interference in the following analyses is considered to be insignificant as discussed in section 2.3.1.

The formal redox potential of the Nd³⁺/Nd²⁺ couple, $E^{\circ'}_{3/2}$, was determined by DPV [8] and by the convolution analysis of CV [8] in the case of $0.58 \leq \chi_{\text{LiCl}} \leq 0.7$. Detailed analytical procedure

of DPV is same as explained in the previous chapter. The values of density of the melt and diffusion coefficient of Nd^{3+} , $D_{\text{Nd}^{3+}}$, in the melt are required for the convolution analysis. The former was reported for LiCl-KCl-CsCl eutectic in the temperature from 573 to 723 K [10]. The data were extrapolated to the experimental temperatures. The density for LiCl-NaCl-KCl (50:25:25 mol%) was evaluated by averaging those of equimolar LiCl-NaCl and LiCl-KCl at 920 K [11]. For other mixtures, the value was estimated by a linear interpolation between the values of pure LiCl and the above ternary melts. The value of $D_{\text{Nd}^{3+}}$ for LiCl-KCl eutectic melt [12] was used for all systems. Though it changes depending on the melt composition [13], uncertainty would be ± 10 mV on the $E^{\circ'}_{3/2}$ value.

The formal redox potential of the $\text{Nd}^{2+}/\text{Nd}^0$ couple, $E^{\circ'}_{2/0}$, was evaluated from CV [14]. The formal redox potential of the $\text{Nd}^{3+}/\text{Nd}^0$ couple, $E^{\circ'}_{3/0}$, was calculated from $E^{\circ'}_{3/2}$ and $E^{\circ'}_{2/0}$ by employing the following equation,

$$E^{\circ'}_{3/0} = \frac{E^{\circ'}_{3/2} + 2E^{\circ'}_{2/0}}{3} \quad (3-4)$$

The Gibbs energy change of Nd(III) formation, $\Delta G^{\circ'}_{3/0}$, was derived as,

$$\Delta G^{\circ'}_{3/0} = nFE^{\circ'}_{3/0} \quad (3-5)$$

3.3.2 Dependence of $\Delta G^{\circ'}_{3/0}$ on the melt composition

The obtained $\Delta G^{\circ'}_{3/0}$ values for LiCl-KCl-CsCl and LiCl-NaCl-KCl systems are shown in Fig. 3.2 with those for binary alkali mixtures [2]. The value decreases with χ_{LiCl} , which means that Nd(III) complex was stabilized by the increase of averaged radius of solvent alkali cations (Li < Na < K < Cs). It is reported that the thermodynamic stability of Nd(III) complex showed linear correlation with the polarizing power of solvent cations, P , which is defined as,

$$P = \sum \chi \frac{z}{r^2} \quad (3-6)$$

where χ , z , and r are the mole fraction, the valence, and the ionic radii of solvent alkali cations. As shown in Fig. 3.2(b), the present results are on the similar slope vs. P . The correlation between the thermodynamic stability and the symmetry of the octahedral coordination structure of Nd(III) complex, NdCl_6^{3-} , has been pointed out for binary mixtures of alkali chlorides [2].

The interaction between the complex and ions in outer coordination spheres would be more complicated in ternary mixtures than that in binary mixtures because of the increase of ion species. The present results suggest that the interaction of alkali cations to the structure as well as the thermodynamic stability of the complex is averaged.

3.3.3 Temperature dependence of $\Delta G^{\circ}_{3/0}$ for LiCl-KCl-CsCl eutectic

CVs of Nd for the LiCl-KCl-CsCl eutectic melt were carried out at different temperatures from 673 to 923 K, from which $\Delta G^{\circ}_{3/0}$ values were evaluated as shown in Fig. 3.3. Enthalpy and entropy terms, ΔH and ΔS , can be derived from the temperature dependence of $\Delta G^{\circ}_{3/0}$ as,

$$\Delta G = \Delta H - T\Delta S \quad (3-7)$$

ΔH and ΔS obtained in this study were -1065 kJ and -0.201 kJ K⁻¹, respectively. These values are comparable to the reported ones for the LiCl-KCl eutectic melt: $\Delta H = -1061.2$ kJ and $\Delta S = -0.222$ kJ K⁻¹ [5].

The lower limit of experimental temperature was 673 K, even higher than the melting point of this system. At lower temperature than 673 K, the melt was separated into two phases in transparent (upside) and in denser green (downside). This means that most of Nd³⁺ ions were concentrated at the bottom of the melt. The concentration of Nd³⁺ in the transparent phase was analyzed by absorption spectrophotometry to be about 0.02 M, *i.e.*, 85% of Nd³⁺ ions initially added were settled at the bottom. Adequate electrochemical measurements, hence, could not be performed.

3.4 Conclusion

Thermodynamic stability of Nd(III) complex in ternary mixtures of molten alkali chlorides was proportional to the polarizing power of solvent alkali cations. The slope was similar to that for binary mixtures of alkali chlorides. The result suggests that the interaction of surrounding alkali cations to the complex can be averaged to determine the octahedral symmetry of the complex, NdCl₆³⁻. It was confirmed that the operating temperature of electrorefining process can be decreased to 673 K by using ternary molten salt media, 100 K lower than that assumed for general pyroprocess. The lower temperature limit of 673 K is even higher than the melting

point of the LiCl-KCl-CsCl eutectic melt at 538 K due to unexpected phase separation.

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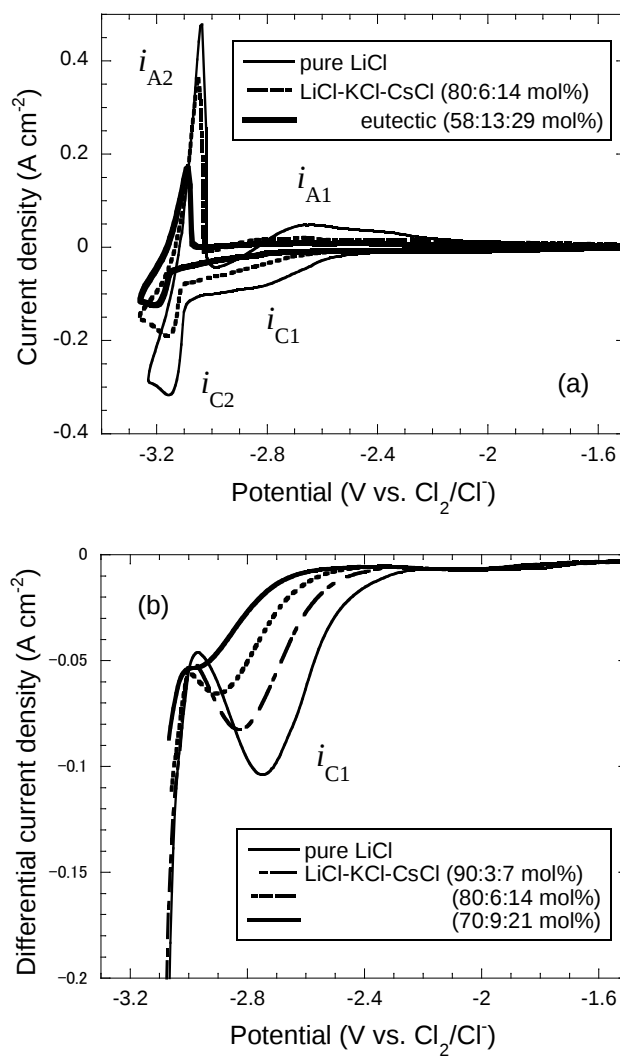


Figure 3.1 Cyclic voltammograms and differential pulse voltammograms of Nd for molten LiCl-KCl-CsCl mixtures at 923 K. (a) Cyclic voltammograms. (b) differential pulse voltammograms.

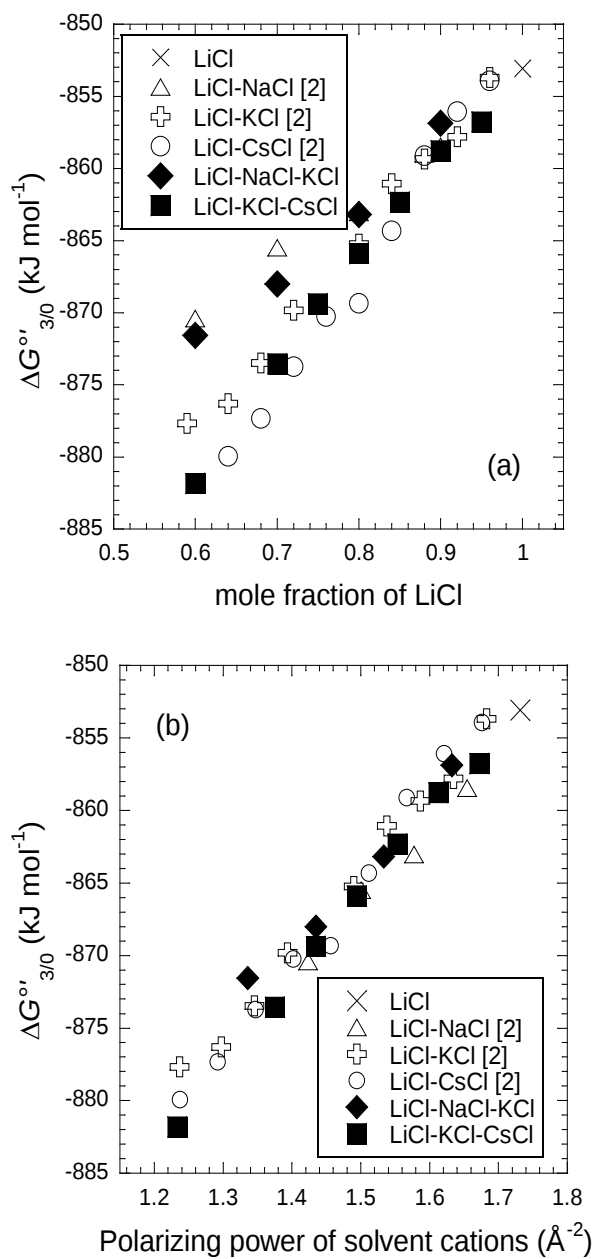


Figure 3.2 Dependences of $\Delta G^{\circ'}_{3/0}$ of Nd on mole fraction of LiCl and polarizing power of solvent cations for binary and ternary systems at 923 K. (a) Dependences of $\Delta G^{\circ'}_{3/0}$ on mole fraction of LiCl. (b) Dependences of $\Delta G^{\circ'}_{3/0}$ on polarizing power of solvent cations.

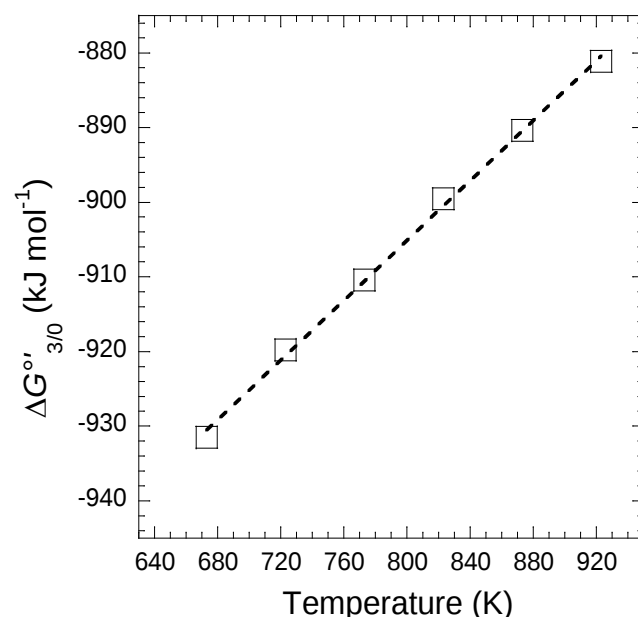


Figure 3.3 Temperature dependence of $\Delta G^{\circ'}_{3/0}$ of Nd in LiCl-KCl-CsCl eutectic melt.

Chapter 4 Chemical Properties of Neodymium Ions in Binary

Mixtures of LiCl and Alkaline Earth Chlorides

4.1 Introduction

The present chapter deals with thermodynamic stability and coordination structure of Nd(III) complex in binary mixtures of LiCl and alkaline earth chlorides. It was pointed out in Chapter 2 and Chapter 3 that thermodynamic stability shows linear correlation with the polarizing power of solvent alkali cations. The polarizing power can be evaluated simply by averaging those of each alkali cation, which assumes that the coordination environment outside the Nd(III) complex is homogeneous. Ionic atmosphere with a certain length (so called Debye length) is formed around a solute ion in aqueous solution that usually spreads further from the first hydration sphere. Coulomb interaction between the complex and ions outside the first coordination sphere might be more complicated in the molten salts with alkaline earth chloride, since solvent matrix of alkaline earth chlorides is not as simple as that of alkali chlorides having lattice structure.

This chapter continues to deal with Nd whose redox behavior in molten chlorides resembles to that of americium [1]. Since Nd is one of fission products and acts as a neutron absorber in nuclear reactor, decontamination of Nd from recycled fuel is required. The chemical properties of Nd in various types of molten chlorides are, hence, necessary to be well understood.

The thermodynamic properties and coordination structure of Nd ions in molten chlorides have been studied by electrochemical [2-4] and spectrophotometric methods [5,6], respectively. The former method has been applied for Nd(III) complex in LiCl-KCl [2-4], NaCl-CaCl₂ [2], and LiCl-CaCl₂ [4] eutectic melts, while the latter for Nd³⁺ in alkali chloride mixtures [5], CaCl₂ [5], and LaCl₃-KCl mixtures [6]. In order to clarify the correlation between the macroscopic and microscopic properties obtained by these two different analytical methods, the electrochemical and spectrometric properties of Nd(III) ions were systematically investigated for various molten binary mixtures of LiCl and an alkaline earth chloride, CaCl₂, SrCl₂, or BaCl₂.

4.2 Experimental

All experiments were carried out under an argon atmosphere in a glove box, where humidity and oxygen impurity were continuously kept less than 1 ppm. Anhydrous chlorides (99.99% purity, Aldrich-APL LLC) were used without further purification. 0.2-0.7 mol% NdCl_3 was dissolved in various binary mixtures of LiCl and AECl_2 ($\text{AE} = \text{Ca}, \text{Sr}, \text{or Ba}$) in a quartz tube.

Cyclic voltammetry (CV) and the differential pulse voltammetry (DPV) were performed with an electrochemical measurement system Hz-5000 (Hokuto Denko Co.). The potential scanning rate of CV for extracting peak potentials was 100mV s^{-1} . The pulse height, period, and width of DPV were 50 mV, 100 ms, and 10 ms, respectively. A tungsten wire (99.9% purity, The Nilaco Co.) of 1 mm diameter, a pyrographite rod (99.99% purity, Tokai Carbon Co., Ltd.) of 3 mm diameter, and a Ag/Ag^+ (1 mol% in solvent melt) electrode were used for the working, counter, and reference electrodes, respectively. In each measurement, the potential of chlorine gas evolution (Cl_2/Cl^-) on the pyrographite electrode was determined to calibrate the Ag/Ag^+ electrode [7].

The electronic absorption spectra of Nd^{3+} in the melts were measured by using an UV/Vis/NIR spectrometer (V-570, JASCO). The experimental apparatus and procedure were described in the literature [8]. The light, which was guided to the electric furnace with quartz windows by using optical fibers, passed through the melted sample in a quartz rectangular tube with a 10 mm light path set at the middle of the furnace, and was guided again to the spectrometer. The transmitted light intensity for the molten alkali chloride (I_0) and that including Nd(III) (I) was measured in the wavelength range from 550 to 700 nm at 0.1 nm intervals. The absorbance was determined to be $-\log(I/I_0)$. All the experiments were performed at 923 ± 2 K.

4.3 Results and Discussion

4.3.1 Thermodynamic stability of Nd(III) complex in molten LiCl-AECl_2 binary mixtures

Figure 4.1 shows cyclic voltammograms obtained for Nd in molten LiCl-CaCl_2 (mole fraction of $\text{LiCl}:\text{CaCl}_2$ is 64:36) and LiCl-BaCl_2 (mole fraction of $\text{LiCl}:\text{BaCl}_2$ is 76:24) at 923 K. These binary mixtures are almost the eutectics. Nd(III) ion is reduced to Nd metal by two-step

reaction via Nd^{2+} ,



In Figs. 4.1(a) and 4.1(b), cathodic current i_{C1} associated with anodic peak i_{A1} is attributable to the $\text{Nd}^{3+}/\text{Nd}^{2+}$ redox couple, and the other sharp peak pair, i_{C2} and i_{A2} , correspond to the $\text{Nd}^{2+}/\text{Nd}^0$ redox couple. Both reactions were examined to be reversible [9].

$\text{Nd}(\text{II})$ is known to disproportionate as [2,3,10],



However, the disproportionation reaction is reported to take several minutes to complete [3] that are significantly long compared with the transient time during electrochemical measurements. The disproportionation reaction 4-3 was not taken into account in this study.

DPV was applied for the case that cathodic peak i_{C1} could not be resolved in cyclic voltammogram due to the overlap of reduction waves of reactions 4-1 and 4-2. Figure 4.2 shows a differential pulse voltammogram obtained for LiCl-BaCl_2 eutectic melt. In the present study, the standard redox potential of the $\text{Nd}^{3+}/\text{Nd}^{2+}$ couple, $E'^{\circ}_{3/2}$, was determined by DPV. $E'^{\circ}_{3/2}$ is defined as [11],

$$E'^{\circ}_{3/2} = E^{\circ}_{3/2} + \frac{RT}{F} \ln \frac{\gamma_{\text{Nd}^{3+}}}{\gamma_{\text{Nd}^{2+}}} = E_{\text{max}} + \frac{\Delta E}{2} - \frac{RT}{F} \ln \left(\frac{D_{\text{Nd}^{2+}}}{D_{\text{Nd}^{3+}}} \right)^{1/2} - E_{\text{ref}} \quad (4-4)$$

where $E^{\circ}_{3/2}$, E_{max} , ΔE , and E_{ref} are the standard redox potential, the peak potential of DPV peak i_{C1} , the applied potential pulse height, and the potential of the Ag/Ag^+ electrode vs. Cl_2/Cl^- , respectively. R is the gas constant, T the absolute temperature, and F the Faraday constant. D represents the diffusion coefficient of suffixed species. Diffusion coefficient of Nd^{2+} in molten chlorides is not available, and hence, $D_{\text{Eu}^{2+}}/D_{\text{Eu}^{3+}}$ reported for europium for equimolar NaCl-KCl melt at 923 K [12] was substituted for $D_{\text{Nd}^{2+}}/D_{\text{Nd}^{3+}}$. The value of the ratio adopted in this study was 1.96.

The formal redox potential of the $\text{Nd}^{2+}/\text{Nd}^0$ couple, $E'^{\circ}_{2/0}$, was determined from CV peak potentials by using the following theoretical equation [13]:

$$E^{\circ'}_{2/0} = E^{\circ}_{2/0} + \frac{RT}{nF} \log \gamma_{\text{Nd}^{3+}} = E_{\text{pc}} - \frac{RT}{nF} \log C_{\text{O}} + (0.9241)^2 \frac{RT}{nF} - E_{\text{ref}} \quad (4-5)$$

where n , $E^{\circ}_{2/0}$, E_{pc} , and C_{O} are the reaction electron number, the standard redox potential, the peak potential of CV cathodic peak i_{C2} , and the bulk concentration, respectively.

The formal redox potential of the $\text{Nd}^{3+}/\text{Nd}^0$ couple, $E^{\circ'}_{3/0}$, was calculated from $E^{\circ'}_{3/2}$ and $E^{\circ'}_{2/0}$ by employing the following equation,

$$E^{\circ'}_{3/0} = \frac{E^{\circ'}_{3/2} + 2E^{\circ'}_{2/0}}{3} \quad (4-6)$$

The Gibbs free energy change of Nd(III) formation, $\Delta G^{\circ'}_{3/0}$, was derived as,

$$\Delta G^{\circ'}_{3/0} = nFE^{\circ'}_{3/0} \quad (4-7)$$

Figure 4.3 shows changes of $\Delta G^{\circ'}_{3/0}$ by adding an alkaline earth chloride into LiCl. In the case of CaCl_2 and SrCl_2 , $\Delta G^{\circ'}_{3/0}$ increased with the decrease of mole fraction of LiCl, χ_{Li} , which suggests that the thermodynamic stability of Nd(III) complex decreased. On the other hand, the addition of BaCl_2 decreased $\Delta G^{\circ'}_{3/0}$. This suggests the stabilization of the Nd(III) complex.

The Coulomb force of the solvent cations is basically determined by the valence, z , and the ionic radius, r , and this could be a factor to control $\Delta G^{\circ'}_{3/0}$. The Coulomb force is expressed as z/r or z/r^2 . In this study, It was found that $\Delta G^{\circ'}_{3/0}$ has the linear correlation with the averaged “polarizing power” of solvent cations, P , which is defined as

$$P = \sum \chi_i \frac{z_i}{r_i^2} \quad (4-8)$$

Suffixed symbol i represents the solvent cations, Li^+ and an alkaline earth cation (Ca^{2+} , Sr^{2+} , or Ba^{2+}). Ionic radius r_i for six coordinated ions [14] was used in the present study. The r_i and P_i values are shown in Table 4.1. The dependence of $\Delta G^{\circ'}_{3/0}$ on P is shown in Fig. 4.4. The $\Delta G^{\circ'}_{3/0}$ value determined in the previous study for the LiCl-KCl eutectic [4] is shown together. $\Delta G^{\circ'}_{3/0}$ was clearly proportional to P . $\Delta G^{\circ'}_{3/0}$ for the LiCl-KCl eutectic [4] can be extrapolated from other data determined in the present study. It is concluded that the Nd(III) complex is more stable in binary alkali and alkaline earth chloride mixtures with smaller P , and the stability increases with a constant slope, $\delta(\Delta G^{\circ'}_{3/0})/\delta P$.

4.3.2 Coordination environment of Nd(III) complex

Absorption spectra of Nd^{3+} in molten LiCl-CaCl_2 , LiCl-SrCl_2 , and LiCl-BaCl_2 mixtures and LiCl at 923 K were measured. Typical spectra of Nd^{3+} for LiCl and for binary mixtures near eutectic composition of each system are shown in Fig. 4.5. The absorption peak assigned to the hypersensitive $f-f$ transition from the ground level of $^4I_{9/2}$ to the excited levels of $^4G_{5/2}$ accompanied with the $^2G_{7/2} \leftarrow ^4I_{9/2}$ transition was observed at the wave length of 589 nm. The reported energy diagram [15] is shown in Fig. 4.6. It should be noted that a different interpretation of the energy diagram has been reported [6]. The absorption peak at 589 nm can be resolved into small peaks corresponding to each transition using Gaussian functions as indicated upon Fig. 4.5. According to the diagram, the difference of peak positions I* and II is equal to the sum of energy splittings of the $^4I_{9/2}$ and $^4G_{5/2}$ states, $\Sigma\Delta E$, which is a useful probe to know the octahedral symmetry of the predominant hexachloro Nd(III) complex for molten chlorides, NdCl_6^{3-} [5].

The transition probability of the $^4G_{5/2}, ^2G_{7/2} \leftarrow ^4I_{9/2}$ transition, which is expressed as the oscillator strength, gives information on the coordination environment of NdCl_6^{3-} . Oscillator strength f is defined as,

$$f = 4.319 \times 10^{-9} \frac{9n}{(n^2 + 2)^2} \int \varepsilon(\nu) d\nu \quad (4-9)$$

where $\varepsilon(\nu)$ is the molar absorptivity at energy ν (cm^{-1}) and n is the reflective index of the solvent medium. $\varepsilon(\nu)$ was integrated from 562 to 625 nm in the present study. The reflective indexes for binary mixtures were estimated by a linear interpolation between the values of pure component melts [16,17].

The past spectrophotometric studies [5,6,18] on Ln^{3+} in molten chlorides explain that the f values are sensitive to two factors: (a) the distortions from octahedral symmetry of LnCl_6^{3-} and (b) the electron donating ability of the coordinated chloride anion, while $\Sigma\Delta E$ is mostly associated with the factor (a). With the structure of NdCl_6^{3-} approaching to the octahedral symmetry, the symmetrical (O_h) ligand field decreases f . Simultaneously, the symmetrical ligand field enhances the energy splitting of the electronic energy levels, which results in the increase of $\Sigma\Delta E$. For alkali chloride series, it has been reported that the increase of f and the decrease of $\Sigma\Delta E$ indicate that the symmetrical octahedral structure is more distorted in the

melts with lower averaged solvent cations' size [5], *i.e.*, with higher P .

In contrast to the alkali chloride systems, the complicated trends were observed in this study for the mixtures containing alkaline earth chloride. The relationships of f vs. P and $\Sigma\Delta E$ vs. P are shown in Fig. 4.7. In Fig. 4.7(a), f decreases with the increase of P for LiCl-CaCl₂ systems, which is the inverse trend to alkali chloride systems. The decrease trend of $\Sigma\Delta E$ with the increase of P for alkali chloride systems also turns to be unclear for LiCl-CaCl₂ and LiCl-SrCl₂ systems and to be inverse for LiCl-BaCl₂ systems (Fig. 4.7(b)). These discrepancies suggest that the ligand field of NdCl₆³⁻ is not determined simply by P for the mixtures with alkaline earth chlorides.

It can be pointed out that the reason to cause the phenomena is the structural characteristics of solvent alkaline earth chlorides. The structure of CaCl₂, SrCl₂, and BaCl₂ has been studied by neutron diffraction [19-21] and molecular dynamic (MD) simulation [20,21]. The structural order of cations and anions in pure BaCl₂ is not rigid [19]. This suggests that addition of BaCl₂ into LiCl makes the melt structure irregular, which may expand the interactive electric field of solvent cations to the center Nd³⁺. As the result, the inhomogeneous ligand field could be formed and $\Sigma\Delta E$ decreased at low P region.

Regarding to the inverse trend of f for LiCl-CaCl₂ systems, the strengthened electron donating ability of chloride anions to Nd³⁺ (factor (b)) could be a reason. The ionic polarizability of chloride ions plays an important role for molten CaCl₂ to reproduce experimental data from EXAFS by MD simulation [20,21]. The polarizability should have a correlation with their electron donating ability. The structure of molten alkali chlorides can be simulated with rigid ion model partly because of the linear alignment of anions and cations in lattice structure. The MD simulation with polarizable ion model, however, showed that chloride anions in alkaline earth chlorides with smaller cations like Ca²⁺ tend to form non-linear bridging sites between a pair of cations [20]. Simply, this means that the angle of cation-anion-cation bridging is not 180°. This model is coincident with the bond-bending structure proposed for ZnCl₂ [22]. An addition of CaCl₂ into LiCl would not change coordination numbers of Ca²⁺ and Li⁺ [23], while it may cause the bending of cation-anion-cation bridging. The bond-bending structure enables effective screening of cation-cation repulsion [20]. If the screening effect works for the cations around NdCl₆³⁻, electron donating ability of Cl⁻ to Nd³⁺ would increase.

In the chloride mixtures including alkaline earth ions, the NdCl_6^{3-} complex seems to be sensitive on the arrangement of cations as well as anions even far from Nd^{3+} . The interaction between the complex and distant ions is of interest. Length of ionic atmosphere induced around a solute ion for aqueous system is represented by the well-known parameter, so-called Debye length. A similar parameter has been proposed for molten salt system of single component [24,25]. Extension of the theory to multi-component systems and progress of computational techniques are desirable challenges for the future.

4.4 Conclusion

The $\Delta G^{\circ}_{3/0}$ value was found to be strongly correlated with the polarizing power of solvent cations, P , which was systematically controlled by adding an alkaline earth chloride, CaCl_2 , SrCl_2 , or BaCl_2 into LiCl . The Nd(III) complex is more stable in the melts with lower P . Trends of the oscillator strength and the energy splittings upon P , on the other hand, could not be explained simply by the distortion of the octahedral structure of Nd(III) complex. This indicates that the coordination environments further from second neighbor have considerable effects on the structural change in ligand field of Nd(III) complex for the mixtures including alkaline earth chloride. The stabilized ligand structure around solute ion in molten salts relates to the thermodynamic stability should be carefully investigated.

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Table 4.1 Ionic radius and polarizing power of cations.

	Ionic radius r / Å	Polarizing power P^a
Li⁺	0.76	1.73
Ca²⁺	1.00	2.00
Sr²⁺	1.18	1.44
Ba²⁺	1.35	1.10
Nd³⁺	1.36	1.62

^a See Eq. 4-8.

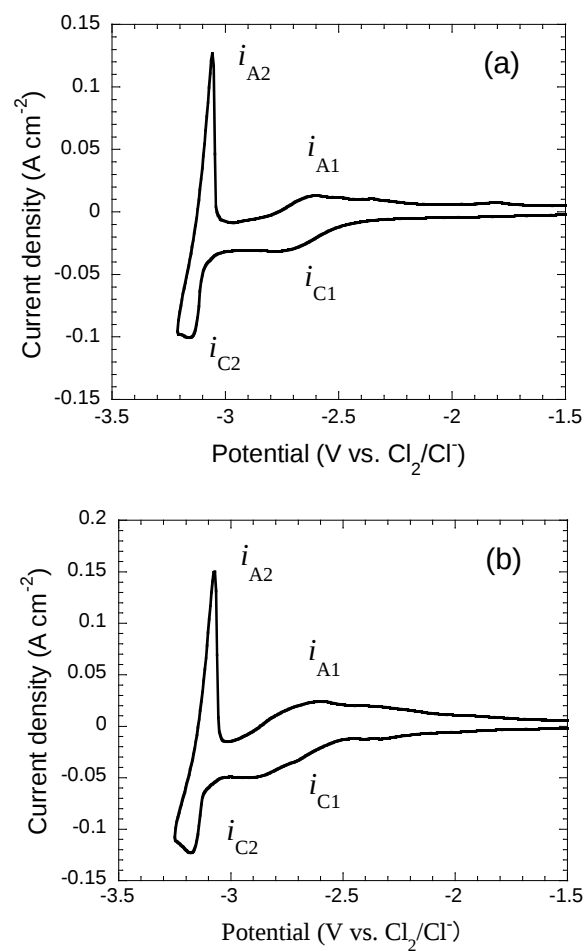


Figure 4.1 Cyclic voltammograms of Nd in binary mixtures of LiCl and an alkaline earth chloride at 923 K. Potential sweep rate of CV was 100 mV s⁻¹. (a) LiCl-CaCl₂ (64:36 mol%) system. Concentration of NdCl₃ was 0.354 mol%. (b) LiCl-BaCl₂ (76:24 mol%) system. Concentration of NdCl₃ was 0.466 mol%.

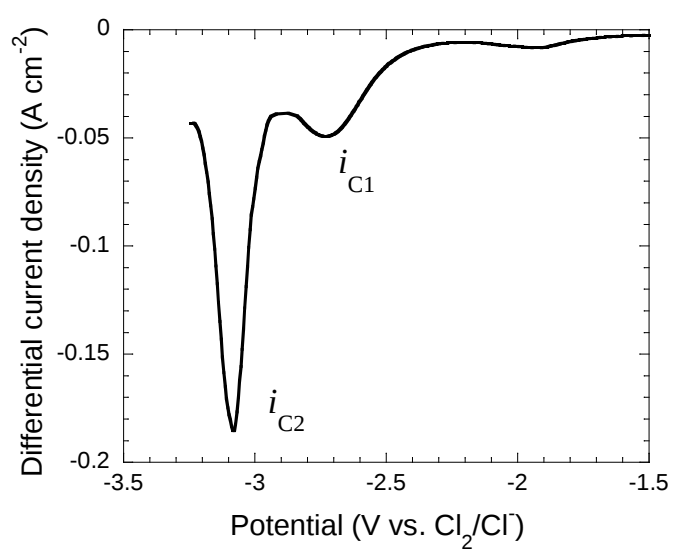


Figure 4.2. Differential pulse voltammogram in LiCl-BaCl₂ (76:24 mol%) melt at 923 K. The pulse height, period, and width of DPV were 50 mV, 100 ms, and 10 ms, respectively. Concentration of NdCl₃ was 0.466 mol%.

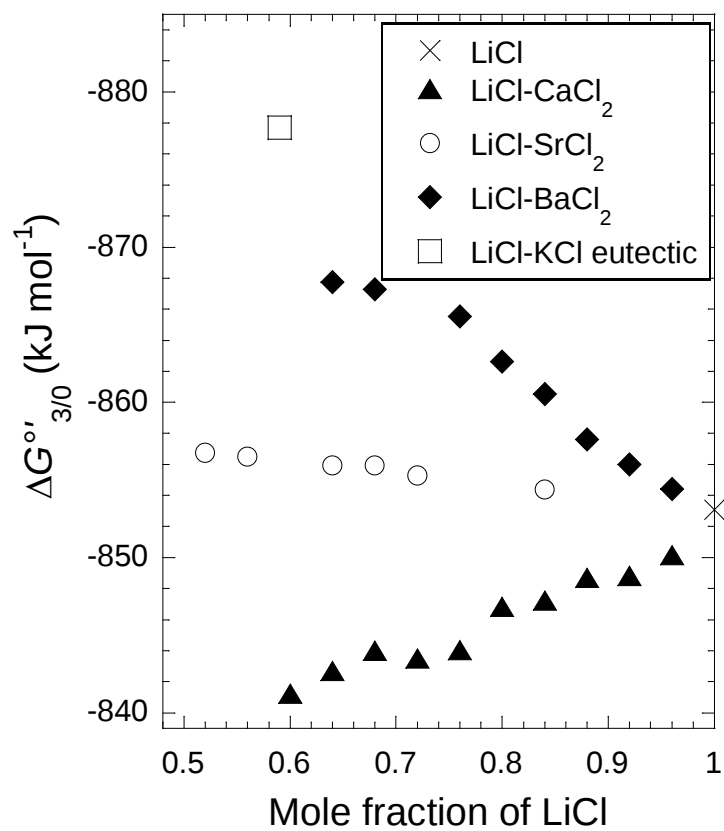


Figure 4.3 Dependence of Gibbs free energy change of Nd(III) formation on the melt compositions.

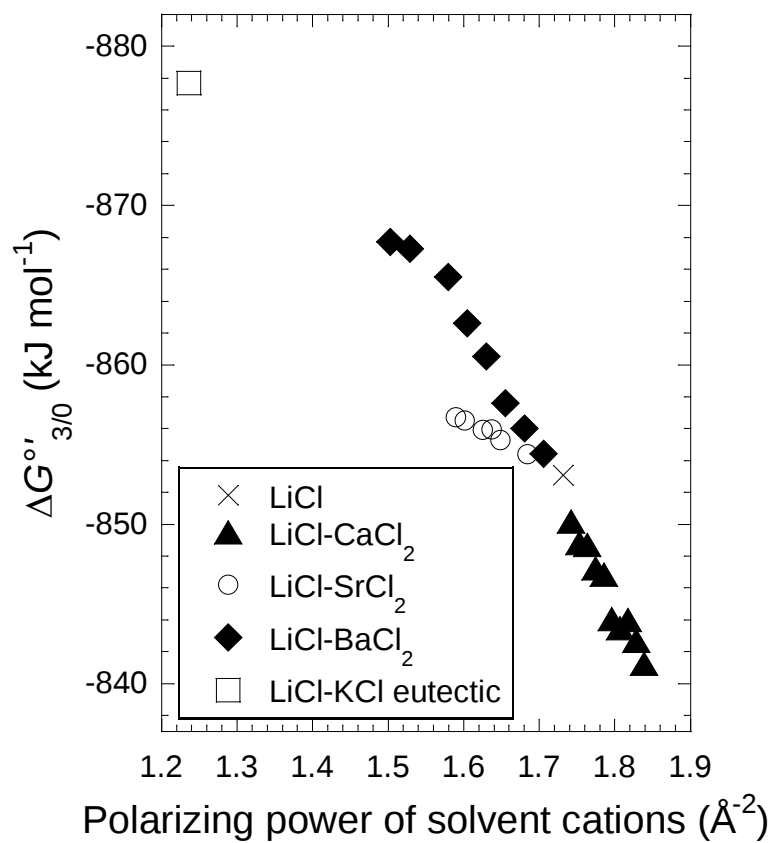


Figure 4.4 Dependence of Gibbs free energy change of Nd(III) formation on polarizing power of solvent cations.

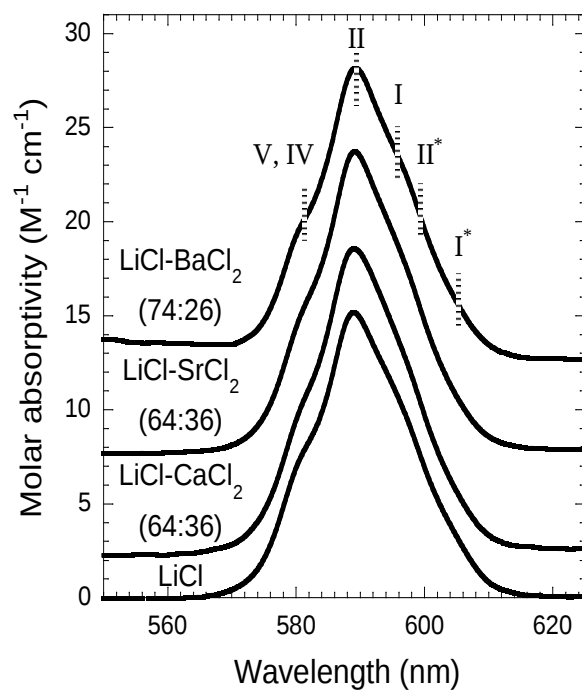


Figure 4.5 Absorption spectra of Nd^{3+} . The spectra were taken for LiCl , LiCl-CaCl_2 (64:36 mol%), LiCl-SrCl_2 (64:36 mol%), and LiCl-BaCl_2 (74:26 mol%) systems.

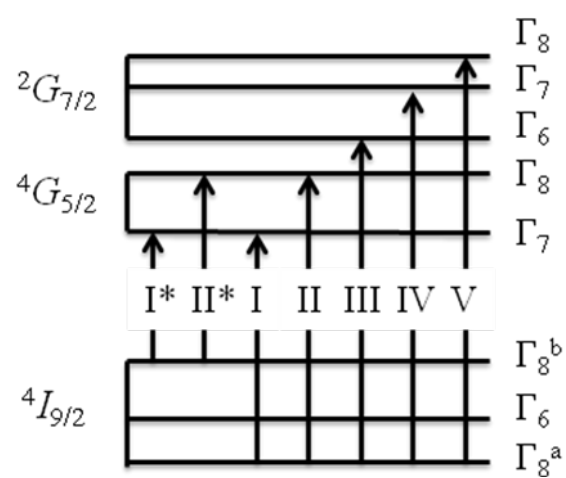


Figure 4.6 Diagram of hypersensitive transitions of NdCl_6^{3-} . The diagram was referred from the literature [15].

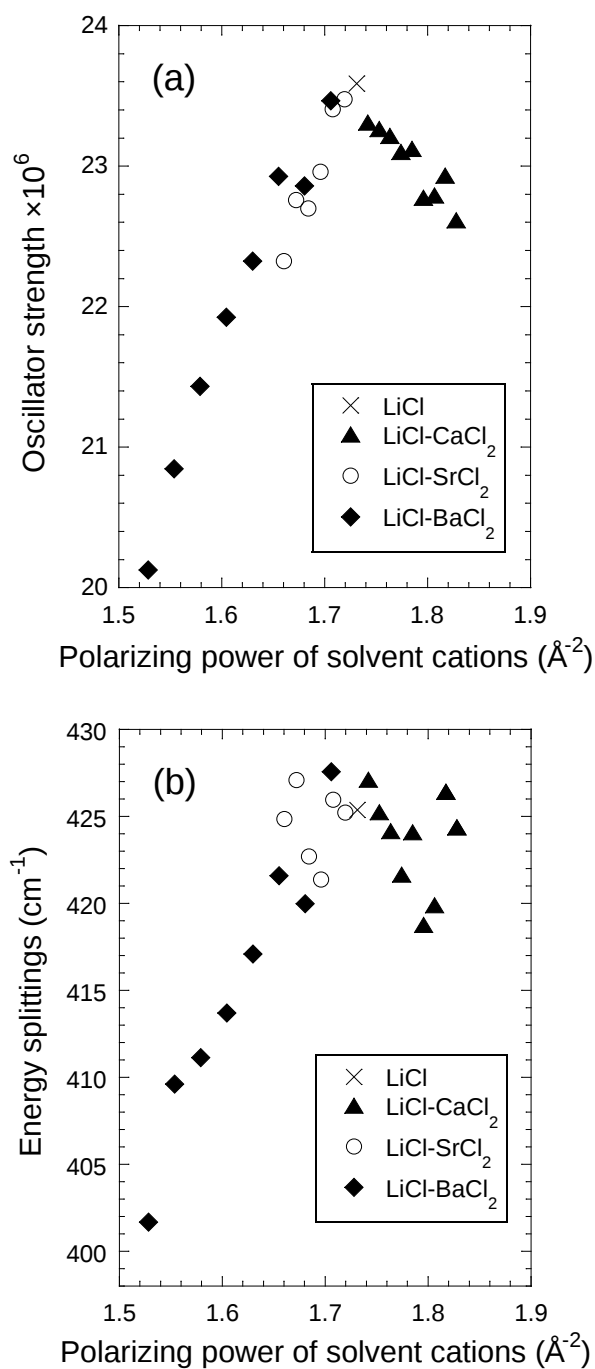


Figure 4.7 The relationships among oscillator strength, energy splittings, and polarizing power of solvent cations. (a) Oscillator strength and the polarizing power. (b) Energy splittings and the polarizing power.

Chapter 5 Thermodynamic Stability of Trivalent Lanthanides and Actinides in Molten Mixtures of LiCl and KCl

5.1 Introduction

This chapter deals with thermodynamic stability of Ln(III) and An(III) complexes in molten alkali chloride mixtures. In the previous chapters, it was clarified that thermodynamic stability of Nd(III) complex shows a linear dependence on the polarizing power of solvent cations, and is correlated with the octahedral symmetry of hexachloro complex, NdCl_6^{3-} , for molten alkali chloride. The linear dependence should be examined for other Lns and U. Ionic radius of Lns changes systematically through the series, which means that Coulomb attraction of Ln^{3+} to chloride ions surrounding it is different from each other. The change should result in differences in their solvation characteristics. Furthermore, Lns and Ans are $4f$ and $5f$ elements, respectively. As mentioned in Chapter 1, the solvation characteristics of the f elements are different because of unique physicochemical characteristics of each f orbital. These differences give suggestions for the mutual separation of Lns as well as the Ln/An separation.

Electrochemical behavior for Ln and An ions have been investigated for LiCl-KCl eutectic (59:41 mol%) [1-5], NaCl-2CsCl [4,6], equimolar NaCl-KCl [6,7], and NaCl-CaCl₂ [5,8] mixtures. Compared with extensive studies on the coordination environment around Ln and An ions in various molten chlorides well summarized in the literature [9], electrochemical studies have been almost limited for the typical compositions above. Systematic thermodynamic study from a perspective of the melt composition is desirable for connecting the knowledge of microscopic coordination structure to the understanding of macroscopic thermochemical properties. In Chapter 2, the thermodynamic stability of Nd(III) complex in various binary mixtures of molten alkali chlorides was investigated. The Gibbs free energy change of Nd(III) complex, $\Delta G^{\circ'}_{3/0}$, in molten LiCl-KCl decreased with the increase of mole fraction of KCl, χ_K . An addition of KCl, $\chi_K = 0.59$, to LiCl stabilized $\Delta G^{\circ'}_{3/0}$ about 20 kJ mol⁻¹. $\Delta G^{\circ'}_{3/0}$ showed a linear dependence on the polarizing power of component alkali cations of solvent melts, simply the inverse of squared ionic radius of alkali cations. The octahedral symmetry of hexachloro Nd(III) complex, NdCl_6^{3-} , was also correlated with the polarizing power. It is of interest

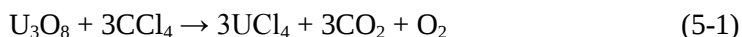
whether the similar dependence and correlation are observed for other Lns and Ans. The systematic study carried out in the present chapter enables us to access the separation performance among trivalent *f* elements in molten chlorides.

In this context, thermodynamic stability of Ln(III) (Ln = La, Pr, Ce, Tb, and Er) and U(III) ions in molten LiCl-KCl system was investigated by electrochemical methods. Difference in dependence of their thermodynamic stability on the melt composition and correlation between the stability and the coordination structure around the solute ions, were discussed.

5.2 Experimental

All experiments were carried out under an argon atmosphere in a glove box, where humidity and oxygen impurity were continuously kept less than 1 ppm. Anhydrous chlorides (99.99% purity, Aldrich-APL LLC) were used without further purification. LnCl₃ (Ln = La, Pr, Ce, Tb, and Er) was dissolved in LiCl melt in a quartz tube. After electrochemical measurement, weighed KCl granules were added to the LiCl sample. This procedure was repeated to change the mole fraction of LiCl and KCl. Electrochemical measurements were carried out at 923 ± 2 K for LiCl-KCl mixtures with $\chi_K = 0-0.65$ containing 0.2-0.7 mol% LnCl₃. Cyclic voltammetry (CV) was performed with an electrochemical measurement system Hz-5000 (Hokuto Denko Co.). The potential scanning rate of CV for extracting peak potentials was 100mV s⁻¹. A tungsten wire (99.9% purity, The Nilaco Co.) of 1 mm diameter, a pyrographite rod (99.99% purity, Tokai Carbon Co., Ltd.) of 3 mm diameter, and a Ag/Ag⁺ (1 mol% AgCl in solvent melt) electrode were used for the working, counter, and reference electrodes, respectively. At each composition of LiCl-KCl mixture, the potential of chlorine gas evolution (Cl₂/Cl⁻) on the pyrographite electrode was determined to calibrate the Ag/Ag⁺ electrode [10].

Anhydrous UCl₄ was synthesized from U₃O₈ by reaction with CCl₄ at 673 K [11]. The reaction principle is described as:



The obtained powder was refined by vacuum distillation at 923 K. To obtain UCl₃ solution, 1.7 mol% UCl₄ was dissolved in pure LiCl melt at 923 K and was totally reduced by controlled potential electrolysis following the procedure described in a literature [12]. The Ag/Ag⁺

electrode was used for a counter electrode for the electrolysis to prevent cyclic redox reaction which can reproduce U^{4+} on an unshielded counter electrode by oxidizing U^{3+} formed at a cathode.

5.3 Results and Discussion

5.3.1 Determination of redox potential of the Ln^{3+}/Ln^0 and U^{3+}/U^0 couples

$Ln(III)$ and $U(III)$ ions are reduced to metal by one step, and hence, a couple of redox reaction corresponding to the deposition and dissolution of Ln and U was observed in cyclic voltammograms as shown in Fig.5.1.

The formal redox potential of the M^{3+}/M^0 couple ($M = La, Ce, Pr, Tb, Er$, and U), $E^{\circ'}_{3/0}$, was determined from CV peak potentials by using the following theoretical equation for the reversible reaction [13]:

$$E^{\circ'}_{3/0} = E^{\circ}_{3/0} + \log \gamma = E_{pc} - \frac{RT}{nF} \log C_O + (0.9241)^2 \frac{RT}{nF} - E_{ref} \quad (5-2)$$

where R , T , F , n and γ are the gas constant, the absolute temperature, the Faraday constant, the reaction electron number, and the activity coefficient, respectively. $E^{\circ}_{3/0}$, E_{pc} , E_{ref} , and C_O denote the standard redox potential of the M^{3+}/M^0 couple, the peak potential of CV cathodic peak, the potential of the Ag/Ag^+ electrode vs. Cl_2/Cl^- , and the bulk concentration, respectively. Nucleation overpotential at the initial stage of deposition on a W electrode has been observed for the deposition reaction of Gd [14], Tb [15], and Er [16]. The nucleation overpotential may cause irreversibility of the deposition and dissolution reaction. The potential difference between cathodic and anodic peaks in voltammograms obtained in the present study was less than 0.10 V. This is close to that in soluble-soluble reversible reaction (0.06 V).

In order to assess the accuracy of data obtained in the present study, $E^{\circ'}_{3/0}$ of the La^{3+}/La^0 and the U^{3+}/U^0 couples for $LiCl-KCl$ eutectic melt at 723 K is shown in Table 5.1. The literature values [3,5,17-23] are shown together. The E_{ref} value reported in the literature [24] was used in Eq. 5-2 instead of the Cl_2 evolution potential. $E^{\circ'}_{3/0}$ has been determined by CV [20] being same as this study, or by electromotive force (emf) measurement [3,5,17-19,21-23]. The results obtained in this study are identical with the literature values [20] determined by CV within

experimental errors. Variations of emf data reported are about 50 mV. The present results also agree with the literature values [3,5,17-19,21-23] within the uncertainty of 50 mV.

5.3.2 Thermodynamic stability of Ln(III) complexes in molten LiCl-KCl system

The Gibbs free energy change of Ln(III) and U(III) formation, $\Delta G^{\circ'}_{3/0}$, is derived as,

$$\Delta G^{\circ'}_{3/0} = nFE^{\circ'}_{3/0} \quad (5-3)$$

The $\Delta G^{\circ'}_{3/0}$ values obtained are shown in Fig. 5.2. $\Delta G^{\circ'}_{3/0}$ of Nd determined in the previous study [25] is shown together. The negative values of $\Delta G^{\circ'}_{3/0}$ for any cases increased with the mole fraction of KCl, χ_K , which means that Ln(III) and U(III) complexes were thermodynamically stabilized by adding K^+ which has larger ionic radius than that of Li^+ .

For Nd, it has been pointed out in previous chapters and reported in the literatures [25,26] that $\Delta G^{\circ'}_{3/0}$ shows linear dependence on the averaged polarizing power of component cations of solvent melt, P , which is defined as

$$P = \sum \chi_i \frac{z_i}{r_i^2} \quad (5-4)$$

where z and r are the valence and the ionic radius, respectively, and suffixed symbol i represents the solvent cations, Li^+ and K^+ in this case. The correlation between $\Delta G^{\circ'}_{3/0}$ and P is shown in Fig. 5.2(b). $\Delta G^{\circ'}_{3/0}$ has been correlated with the octahedral symmetry of Nd(III) complex, $NdCl_6^{3-}$, in alkali chloride mixtures [25]. The octahedral structure is more distorted and the complex is more unstable in the mixtures with higher P (lower χ_K).

In Fig. 5.2(b), $\Delta G^{\circ'}_{3/0}$ s of Er and Tb show linear dependences on P as being similar to the Nd case, which indicates that Er(III) and Tb(III) complexes also possess the octahedral symmetry and the coordination structure would be more distorted by increasing P .

The $\Delta G^{\circ'}_{3/0}$ values of La and Ce, on the other hand, are not proportional to P , and their dependence on the melt composition is less sensitive in higher P region. The ionic radius of Ln^{3+} [27] decreases in the order of $La > Pr > Ce > Nd > Er > Tb$ because of the lanthanide contraction. Spacially, Cl^- ions more than six can be arranged around Ln^{3+} having larger ionic radius like La^{3+} . It has been reported that seven to eight Cl^- ions surround La^{3+} in $LiCl-LaCl_3$ systems with larger χ_{Li} [28,29]. In the present study, the number of Cl^- ions around Ln^{3+} , N , in $LnCl_N^{3-N}$ would be >6 for Ln having larger ionic radius such as La^{3+} and Ce^{3+} at higher P .

The linear increase of $\Delta G^{\circ'}_{3/0}$ with P shown in Fig. 5.2(b) suggests that the LnCl_N^{3-N} complex keeps $N = 6$ but its octahedral symmetry is distorted. The linearity was not kept at higher P for La and Ce. This suggests that LnCl_N^{3-N} complexes with $N > 6$ exist. The structural change was possible and taken place in order to depress the increase of $\Delta G^{\circ'}_{3/0}$.

5.3.3 Dependence of $\Delta G^{\circ'}_{3/0}$ of U(III) and Ln(III) complexes on solute ionic radius

The $\Delta G^{\circ'}_{3/0}$ values of U(III) complex are compared with those of Ln(III) complexes in Fig. 5.2 on the same scale. The $\Delta G^{\circ'}_{3/0}$ values of U(III) complex are more positive than those of Ln(III) complexes. This is due to larger potential difference between solid metal and trivalent gas states, ΔG^{ion} , of U than that of Ln. An energy diagram is simply shown in Fig. 5.3. The Gibbs free energy change of sublimation, ΔG_{sub} , of U is 76 kJ mol^{-1} more positive than that of La at 923 K [30]. The ionization potential, $IP(3+)$, from U to U^{3+} is 171 kJ mol^{-1} more positive than that from La to La^{3+} [31]. The sum of ΔG^{ion} and $\Delta G^{\circ'}_{3/0}$, ΔG_{sum} , was, hence, calculated to discuss the stabilization of Ln(III) and U(III) complexes with a standard state of $\text{M}^{3+}(\text{g})$ at 923 K. It should be noted that ΔG is a function of enthalpy and entropy, $\Delta H - T\Delta S$. Strictly, the energy diagram shown in Fig. 5.3 should be interpreted with ΔH . Sum of $T\Delta S$ in $\Delta G^{\circ'}_{3/0}$ and ΔG_{sub} of Ln and U vary in the range of $305 \pm 30 \text{ kJ mol}^{-1}$ [5,20,30,32] without a specific trend. For some other LiCl-KCl mixtures with $\chi_{\text{K}} = 0-0.6$, temperature dependence of $\Delta G^{\circ'}_{3/0}$ of La, Nd, and U was examined in the temperature range from the melting point + 50 K to 923 K in this study. The results are summarized in Table 5.2. Changes in ΔH and ΔS on the melt composition for other alkali and alkaline earth chloride systems are addressed in Appendix 5A. The difference in $T\Delta S$ for the LiCl-KCl mixtures was ranged within 40 kJ mol^{-1} at 923 K. Compared with ΔG_{sum} values of $4500-5000 \text{ kJ mol}^{-1}$, the $T\Delta S$ term can be considered not to mislead the following discussions.

ΔG_{sum} of Ln(III) complexes shown in Fig. 5.4 becomes negative in the order of ionic radius of Ln ion, $\text{La} > \text{Pr} > \text{Ce} > \text{Nd} > \text{Er} > \text{Tb}$, which indicates that Ln^{3+} with smaller ionic radius is more stabilized by coordination of Cl^- ions in molten LiCl-KCl. Since smaller Ln cations possess higher charge density, Cl^- ions attract it stronger. This observation agrees with other thermochemical and structural studies which report that the decrease of ionic radius increases

the strength of cation-anion interactions and smaller Ln cations were strongly packed by surrounding Cl^- ions [33,34].

ΔG_{sum} of U, on the other hand, is more negative than that of La, though their ionic radii are almost same [27]. The reason may be the covalent characteristic of $5f$ orbitals. Lns are $4f$ elements and U is a $5f$ element. $4f$ shells are known to be contracted more than $5f$ shells, and an extension of $5f$ orbitals is responsible for the existence of covalency in the An compounds [35]. The covalency of actinides has also been recognized in theoretical [36,37] and experimental [38] studies for aqueous systems. In molten chloride media, covalent characteristics may exist in the bonding of U^{3+} and Cl^- ions. This may result in a higher stability of U(III) complex compared with La(III) complex though their structures are similar.

For LiCl-KCl eutectic system, $\Delta G^{\circ'}_{3/0}$ of trivalent complexes was reported for other Ans, Np [3], Pu [3], Am [39], and Cm [40]. The ΔG_{sum} values were evaluated by using thermochemical data [41] and ionization potentials [31]. They are shown in Fig. 5.5. Smaller An ions are generally more stabilized in the melt as for Ln series. Clear discrepancy of ΔG_{sum} of An from the trend of Ln are observed for lighter Ans such as U and Np. $5f$ orbital is more contracted with the increase of An atomic number and the characteristic of covalency would decrease, which may result in the decrease of the discrepancy. ΔG_{sum} s of Am and Cm are almost close to that of Nd with similar ionic radius. This trend is observed noticeably for ΔG_{sum} in molten chlorides rather than hydration enthalpies of Ln and An ions ($\text{M}^{3+}(\text{g}) \rightarrow \text{M}^{3+}(\text{aq})$) [31].

5.3.4 Dependence of $\Delta G^{\circ'}_{3/0}$ of U(III) and Ln(III) complexes on the melt composition

Reverting to Fig. 5.2(b), $\Delta G^{\circ'}_{3/0}$ values of U(III) complex show good linearity on P . U^{3+} has large ionic radius comparable to that of La^{3+} [27] and structural properties of U in molten salts are analogue to that of La [9]. As mentioned above, LaCl_N^{3-N} complex with $N = 6$ becomes stable and predominant in the melts with smaller P , *i.e.*, larger solvent alkali cations. A neutron diffraction study carried out for $\text{UCl}_3\text{-ACl}$ ($A = \text{Li, Na, K, and Cs}$) system observed considerable changes on the arrangement of Cl^- around U^{3+} by adding ACl to UCl_3 and the changes were more significant for larger A [43]. The octahedral UCl_6^{3-} complex has been reported for pure LiCl and LiCl- BeCl_2 mixture [44,45]. It is, thus, inferred that N of UCl_N^{3-N}

would be 6 for LiCl-KCl mixtures used in this study, where $\Delta G^{\circ'}_{3/0}$ of U(III) complex would be controlled by the same manner of the octahedral symmetry as heavier Ln(III) complexes.

The dependence of $\Delta G^{\circ'}_{3/0}$ on P is, however, less sensitive than that of Ln(III) complexes as shown in Fig. 5.2(b). The dependences of $E^{\circ'}_{3/0}$, $E^{\circ'}_{3/2}$, and $E^{\circ'}_{2/0}$ of U and heavier Lns (Nd, Tb, and Er) on P are summarized in Table 5.3. $E^{\circ'}_{3/0}$ s of U show a slope with smaller gradient compared with that of Tb and Er. This may be explained by the covalent characteristic of 5f elements. Simply, less ionic interaction among U^{3+} and surrounding ions can make the change in ionic environment of alkali cations around the complex less significant to its stability. Or generally, the covalent bonding is structurally more rigid than the ionic bonding. The octahedral structure of hexachloro U(III) complex may be more rigid than that of Ln(III) complexes, and the symmetry of the U(III) complex can be less distorted by the increase of P . As a consequence, the stability of U(III) complex is less sensitive on the melt composition, and the potential difference between U(III) and Ln(III) complexes would be wider in the melts with lower P , *e.g.*, NaCl-2CsCl.

Based on Table 5.3, changes of the redox potentials of Ans with the melt composition are predicted as described in Fig. 5.6. Slopes of the linear function of $E^{\circ'}_{3/0}$ of Np, Pu, and Cm on P was estimated to be 0.16, 0.18, and 0.20, respectively, since the covalent character of 5f orbital becomes less significant with the increase of the atomic number of Ans. Slopes of $E^{\circ'}_{3/2}$ and $E^{\circ'}_{2/0}$ of Am was estimated to be 0.5 and 0.02, respectively, as same as those of Nd. $E^{\circ'}_{3/0}$ of Np, Pu, and Cm and the redox potential of the Th^{4+}/Th^0 couple for LiCl-KCl eutectic ($P = 1.237$) were derived from the literatures [3,39,40,46]. Figure 5.6 suggests that Am and Cm are collected separately by using molten chloride mixtures with P as high as 1.8, where potential differences among $E^{\circ'}_{3/2}$ of Am and $E^{\circ'}_{3/0}$ s of Cm and Lns would be significant enough for electrolytic isolations.

5.3.5 The activity coefficient of Ln(III) and U(III) ions in molten LiCl-KCl eutectic system

The activity coefficient of MCl_3 ($M = \text{Ln and U}$) in the studied melts, γ_{MCl_3} , could be

calculated by the following equation [5]:

$$\log \gamma_{\text{MCl}_3} = \frac{\Delta G^{\circ'}_{3/0} - \Delta G^*_{\text{SCliq}}}{2.3RT} \quad (5-5)$$

The hypothetical supercooled liquid state (suffix of SCliq) was chosen as the reference state here. The $\Delta G^*_{\text{SCliq}}$ value corresponds to the energy change of the following reaction at 923 K:



$\Delta G^*_{\text{SCliq}}$ was derived [47] from the values of the enthalpy of formation of MCl_3 , the enthalpy of transition and fusion, and the heat capacity of the solid and liquid phases of M metals [48], LnCl_3 [49], UCl_3 [20] and Cl_2 gas [50]. The calculated values of $\Delta G^*_{\text{SCliq}}$ of MCl_3 are shown in Table 5.4 with $\Delta G^{\circ'}_{3/0}$ and $\log \gamma_{\text{MCl}_3}$ of M(III) complexes in the LiCl-KCl eutectic melt ($\chi_{\text{K}} = 0.41$) at 923 K. The error range of $\log \gamma_{\text{MCl}_3}$ is ± 0.08 . The values of $\log \gamma_{\text{MCl}_3}$ in the table are plotted vs. ionic radius of each M(III) ions as shown in Fig. 5.7. A general correlation is observed that $\log \gamma_{\text{MCl}_3}$ increases systematically with ionic radius. This suggests that the stabilization effect on Ln and An trichlorides in molten alkali chlorides is controlled by the ionic radius of the central ion through the electrostatic interactions as mentioned in section 5.3.3. The systematic dependence on the ionic radius is, however, fluctuated for larger Lns. This is not due to $\Delta G^{\circ'}_{3/0}$ uniquely determined but $\Delta G^*_{\text{SCliq}}$. The octahedral symmetry of LnCl_6^{3-} is almost retained in the eutectic melt as mentioned in section 5.3.2. In the case of Ln trichlorides, larger Ln group crystallizes in UCl_3 -type structure where the Ln cation is surrounded by 9 chlorines while smaller Ln group crystallizes in AlCl_3 -type structure where the Ln cation is surrounded by only 6 chlorines [9]. The structural difference would hold in the liquid phase of pure LnCl_3 . This implies the standard states traditionally taken (SCliq) are in different thermodynamic conditions depending on the Ln compounds.

The covalent characteristic of 5f electron of U is not pronounced in $\log \gamma_{\text{MCl}_3}$ compared with La since the effect would be present in both $\Delta G^*_{\text{SCliq}}$ and $\Delta G^{\circ'}_{3/0}$ and be offset.

In Fig. 5.8, ratio of γ_{MCl_3} standardized by γ_{LaCl_3} is shown and compared with those evaluated from molecular dynamic (MD) simulation [51]. The ratio for La which is not shown in the figure is zero. Logarithm of $\gamma_{\text{MCl}_3} / \gamma_{\text{LaCl}_3}$ by MD decreases with the ionic radius, which

agrees with the trend of that obtained from this study. MD is a potential tool to acquire the information about the coordination structure around Ln and An ions in molten salts. Collaborative work of empirical and computational studies will be of interest to cultivate our understandings of the coordination chemistry of the *f* elements.

5.4 Conclusion

The $\Delta G^{\circ'}_{3/0}$ values of smaller Ln(III) complexes like Tb and Er linearly increased with *P* due to the distortion of octahedral symmetry of LnCl_6^{3-} . The linearity was not kept for larger Ln(III) complexes such as La and Ce in the mixtures with higher *P* where the number of Cl^- around Ln^{3+} would be more than six. The thermodynamic stability of U(III) complex was less sensitive on the melt composition than that of Ln(III) complexes, which implies the difference between the bonding characteristics of *4f* and *5f* orbitals with Cl^- s surrounding Ln^{3+} and U^{3+} , respectively. The values of $\log \gamma$ increased systematically with ionic radius of a solute Ln(III) or U(III) ion in LiCl-KCl eutectic melt. The solvation effect would be more significant for smaller Ln(III) cations in alkali chloride mixtures.

Appendix 5A Dependence of enthalpy and entropy changes of Nd(III) and U(III) formation on the melt composition

Temperature dependence of $\Delta G^{\circ'}_{3/0}$ of Nd(III) and U(III) complexes was investigated to determine ΔH and ΔS . Experimental set-up was same as described in section 5.2. Experimental temperature was changed in the range from the melting point of each molten salt medium plus 50 K to 973 K. Since the temperature range was only 50 K for pure LiCl melt, ΔH and ΔS determined for LiCl may be less precise compared with those in other melts. The Cl_2 evolution potential adopted for E_{ref} for the determination of $\Delta G^{\circ'}_{3/0}$ has a certain difference with the Cl_2/Cl^- potential [24].

As discussed in section 5.3.3, ΔG is a function of enthalpy and entropy, $\Delta H - T\Delta S$, and the energy diagram should be interpreted with ΔH strictly. The values of ΔH and ΔS obtained for La, Nd, and U for LiCl-KCl mixture has already been shown in Table 5.2, where ΔH for Nd and U

are more negative than that of La. This results from smaller ionic radius of Nd and stronger covalent character of 5f orbital of U as discussed in section 5.3.3 with $\Delta G^{\circ'}_{3/0}$. ΔH and ΔS of Nd(III) and U(III) complexes for other alkali and alkaline earth chloride mixtures are plotted against P in Figs. 5A.1 and 5A.2. In Fig. 5A.1, generally, ΔH decreases and ΔS increases with the decrease of P . It should be pointed out that the different trend is observed for LiCl-CaCl₂ mixtures, which is similar to the results of oscillator strength of Nd³⁺ as discussed in section 4.3. The discrepancies of ΔH and ΔS could be offset for $\Delta G^{\circ'}_{3/0}$ showing uniform dependence on P for both alkali and alkaline earth chloride mixtures. Similar trends were observed for U as shown in Fig. 5A.2.

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Table 5.1 The values of $E^{\circ'}_{3/0}$ of the $\text{La}^{3+}/\text{La}^0$ and U^{3+}/U^0 couples for LiCl-KCl eutectic melt at 723 K.

$E^{\circ'}_{3/0}$ (V vs. Cl_2/Cl^-)		
$\text{La}^{3+}/\text{La}^0$	-3.183 ± 0.005	This study
	-3.183 ± 0.022	[5]
	-3.177	[17]
	-3.159	[18]
	-3.206	[19]
U^{3+}/U^0	-2.534 ± 0.005	This study
	-2.543 ± 0.01	[20]
	-2.500	[3]
	-2.550	[21]
	-2.490	[22]
	-2.495	[23]

Table 5.2 The evaluated values of ΔH and ΔS of La(III), Nd(III), and U(III) complexes in LiCl-KCl mixtures.

KCl mole fraction	La		Nd		U	
	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS
0.0	-1017.2	147.4	-1005.7	156.4	-828.07	141.5
0.2	-1052.4	176.7	-1017.1	157.5	-839.28	143.7
0.41	-1067.1	183.0	-1044.3	166.8	-861.03	157.2
0.5			-1052.2	174.8		
0.6	-1065.7	171.8			-869.49	155.7

The units of ΔH and ΔS are kJ mol^{-1} and $\text{J mol}^{-1} \text{K}^{-1}$, respectively.

It should be noted that the Cl_2 evolution potential adopted for E_{ref} for the determination of $\Delta G^{\circ}_{3/0\text{S}}$ in this table is positive by 0.055 V relative to the Cl_2/Cl^- potential [25] for LiCl-KCl eutectic melt at 923 K.

Table 5.3. Linear approximation equations of the redox potential of the $\text{Nd}^{3+}/\text{Nd}^{2+}$, $\text{Nd}^{2+}/\text{Nd}^0$, and M^{3+}/M^0 couples ($\text{M} = \text{Tb}, \text{Er}, \text{and U}$) on P at 923 K.

Redox couple	Linear approximation equation (V vs. Cl_2/Cl^-)
$\text{Nd}^{3+}/\text{Nd}^{2+}$	$0.5024P - 3.579$
$\text{Nd}^{2+}/\text{Nd}^0$	$0.0233P - 3.024$
$\text{Tb}^{3+}/\text{Tb}^0$	$0.2071P - 3.234$
$\text{Er}^{3+}/\text{Er}^0$	$0.2138P - 3.238$
U^{3+}/U^0	$0.1370P - 2.590$

*It should be noted that the potential difference between the Cl_2/Cl^- potential [25] and Cl_2 evaporation potential adopted for E_{ref} in the present study was estimated equally for all mixtures to be 55 mV, the value for LiCl-KCl eutectic system at 923 K.

Table 5.4 The evaluated values of $\Delta G^*_{\text{SCLIq}}$, $\Delta G^{\circ'}_{3/0}$, and $\log \gamma_{\text{MCl}_3}$ of Ln(III) and U(III) complexes in LiCl-KCl eutectic melt at 923 K.

	$\Delta G^*_{\text{SCLIq}} \text{ (kJ mol}^{-1}\text{)}$	$\Delta G^{\circ'}_{3/0} \text{ (kJ mol}^{-1}\text{)}$	$\log \gamma$
La	−837.0	−881.0	−2.49
Ce	−828.5	−867.2	−2.19
Pr	−826.3	−865.1	−2.20
Nd	−811.3	−861.8	−2.86
Tb	−794.9	−862.2	−3.81
Er	−783.5	−858.5	−4.25
U	−660.4	−700.4	−2.27

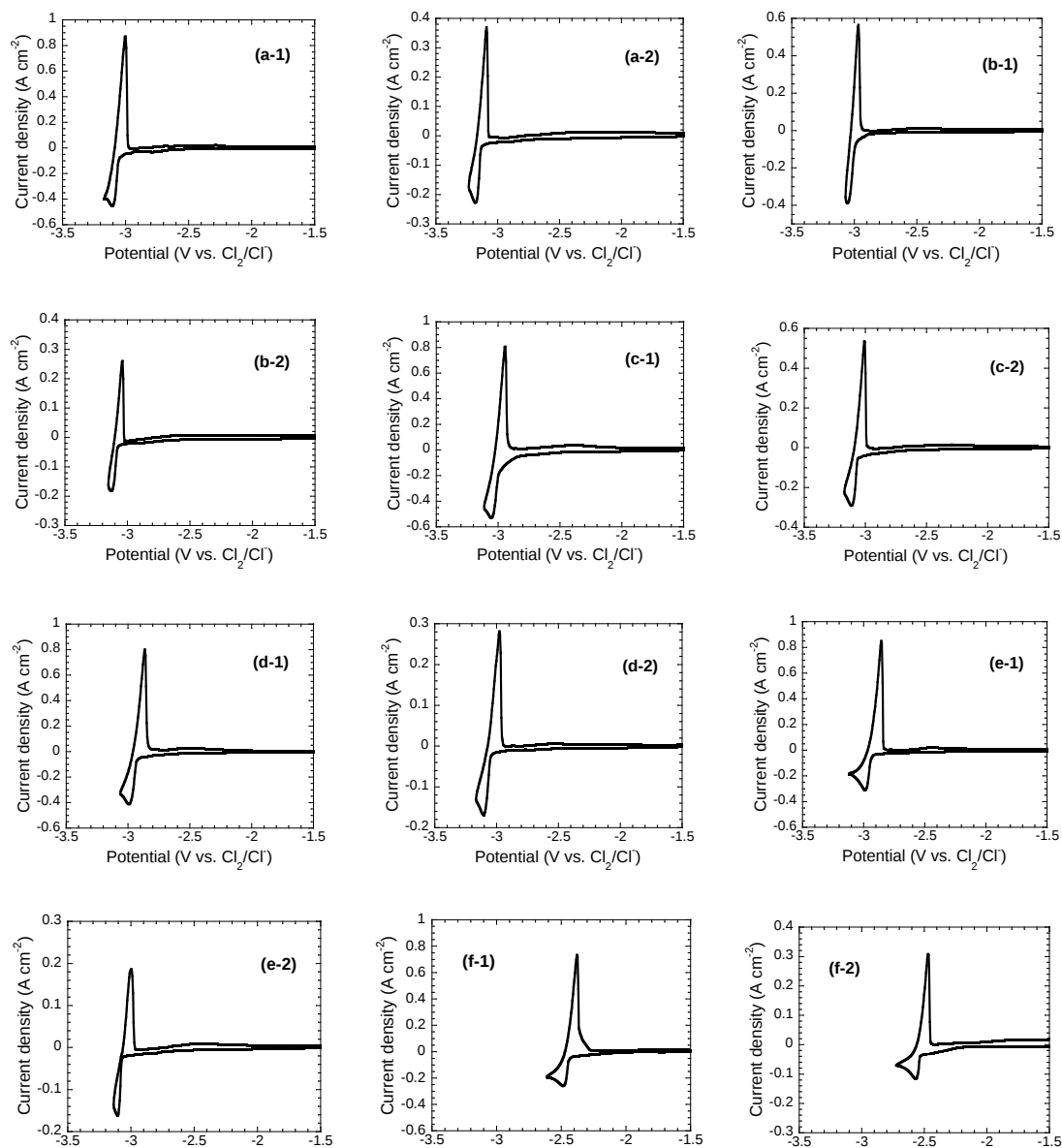


Figure 5.1 Cyclic voltammograms of Ln and U in LiCl and LiCl-KCl eutectic melts at 923 K. Potential sweep rate of CV was 100 mV s^{-1} . (a-1) 0.225 M La^{3+} in LiCl. (a-2) 0.105 M La^{3+} in LiCl-KCl eutectic. (b-1) 0.221 M Ce^{3+} in LiCl. (b-2) 0.149 M Ce^{3+} in LiCl-KCl eutectic. (c-1) 0.216 M Pr^{3+} in LiCl. (c-2) 0.167 M Pr^{3+} in LiCl-KCl eutectic. (d-1) 0.231 M Tb^{3+} in LiCl. (d-2) 0.153 M Tb^{3+} in LiCl-KCl eutectic. (e-1) 0.218 M Er^{3+} in LiCl. (e-2) 0.102 M Er^{3+} in LiCl-KCl eutectic. (f-1) 0.142 M U^{3+} in LiCl. (f-2) 0.067 M U^{3+} in LiCl-KCl eutectic.

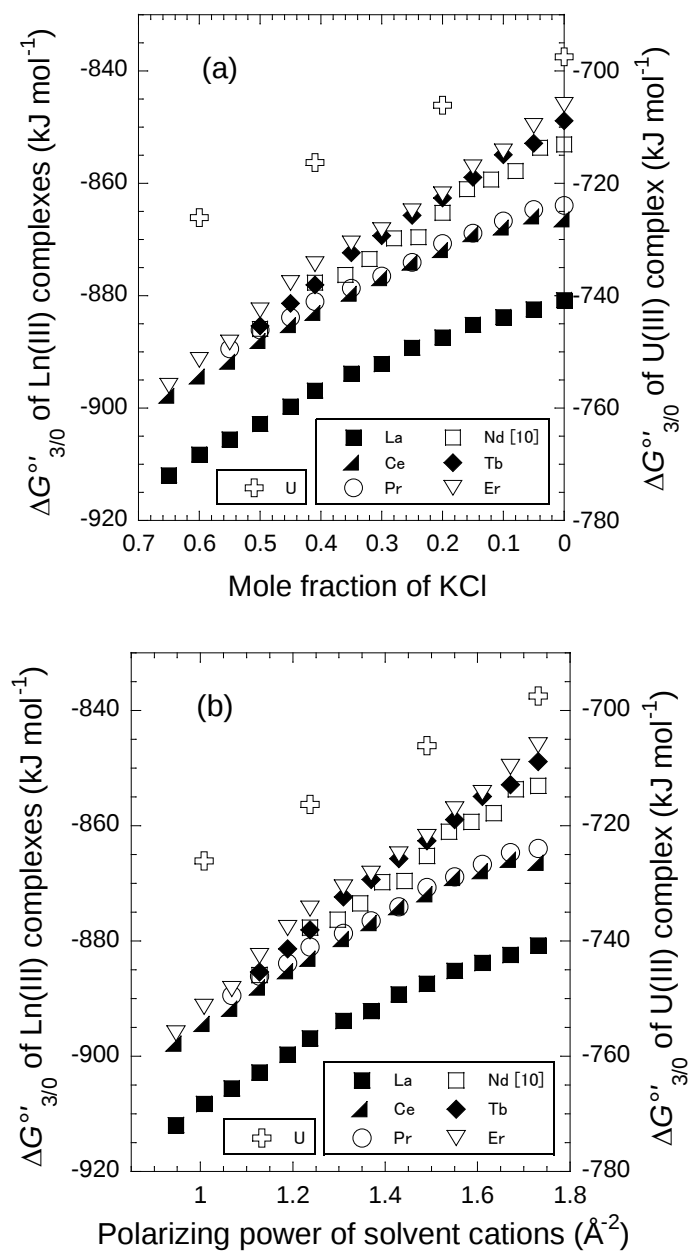


Figure 5.2 Dependence of $\Delta G^{\circ'}_{3/0}$ of Ln(III) and U(III) complexes on the melt composition. (a) $\Delta G^{\circ'}_{3/0}$ vs. mole fraction of KCl. (b) $\Delta G^{\circ'}_{3/0}$ vs. polarizing power of solvent cations.

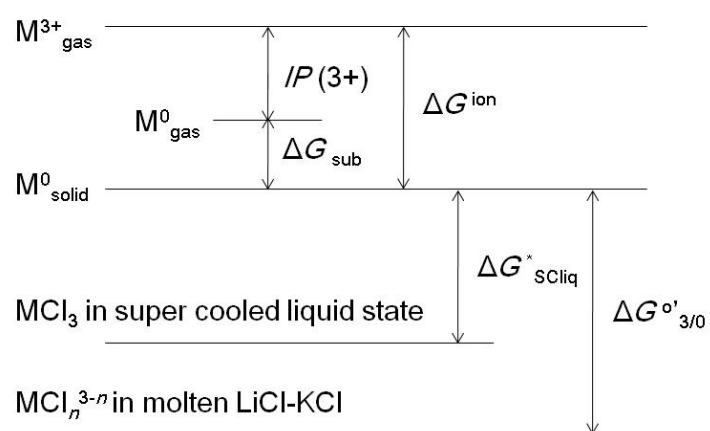


Figure 5.3 Energy diagram. M represents Ln and U. Symbols of ΔG^{ion} , ΔG_{sub} , and $IP(3+)$ means Gibbs free energy changes of the reaction from solid to trivalent gas states, that of sublimation, and the ionization potential from metal to trivalent, respectively.

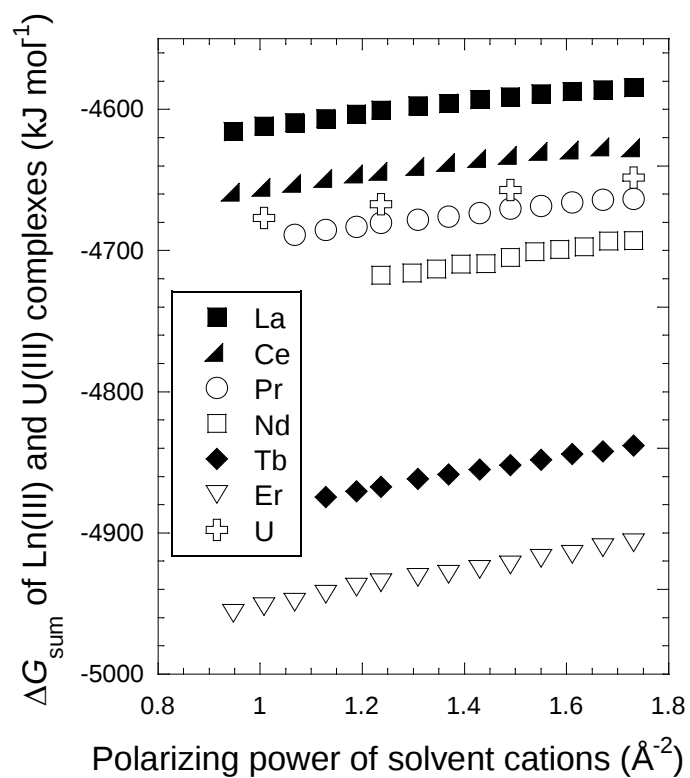


Figure 5.4 The sum of ΔG_{ion} and $\Delta G^{\circ}_{3/0}$ of Ln(III) and U(III) complexes in various LiCl-KCl mixtures. The temperature was 923 K.

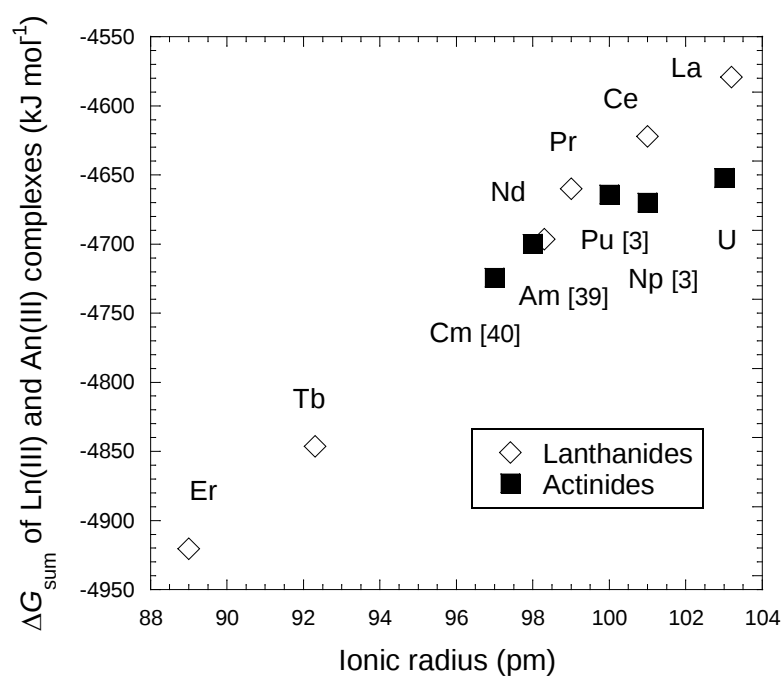


Figure 5.5 The sum of ΔG_{ion} and $\Delta G^{\circ'}_{3/0}$ of Ln(III) and An(III) complexes in LiCl-KCl eutectic melt at 923 K.

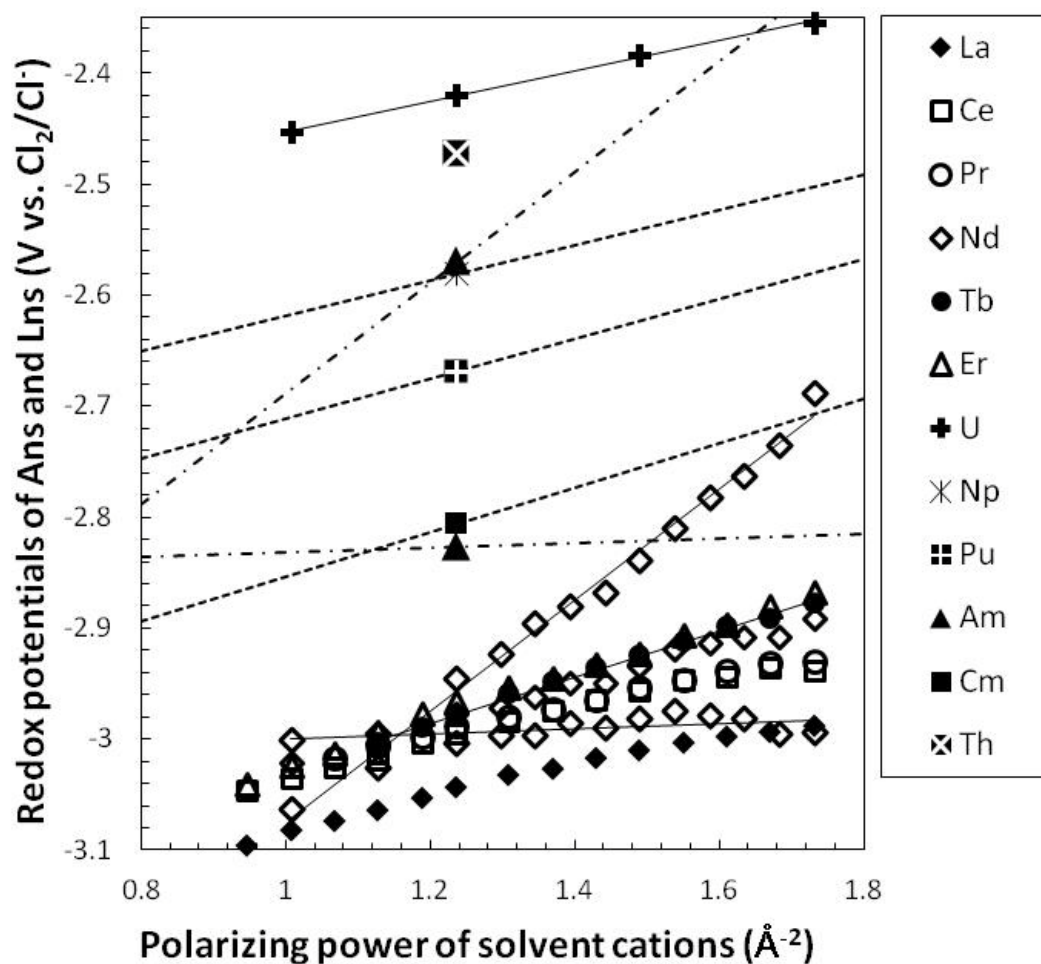


Figure 5.6 Dependence of the redox potentials of Ans and Lns on P . $E'^{o'}_{3/2}$ and $E'^{o'}_{2/0}$ of Nd and $E'^{o'}_{3/0}$ of M (M = La, Ce, Pr, Tb, Er, and U) were determined in this study. Solid lines are their approximate curves. Broken lines indicate approximate curves of $E'^{o'}_{3/2}$ and $E'^{o'}_{2/0}$ of Am and $E'^{o'}_{3/0}$ of An (An = Np, Pu, and Cm) predicted.

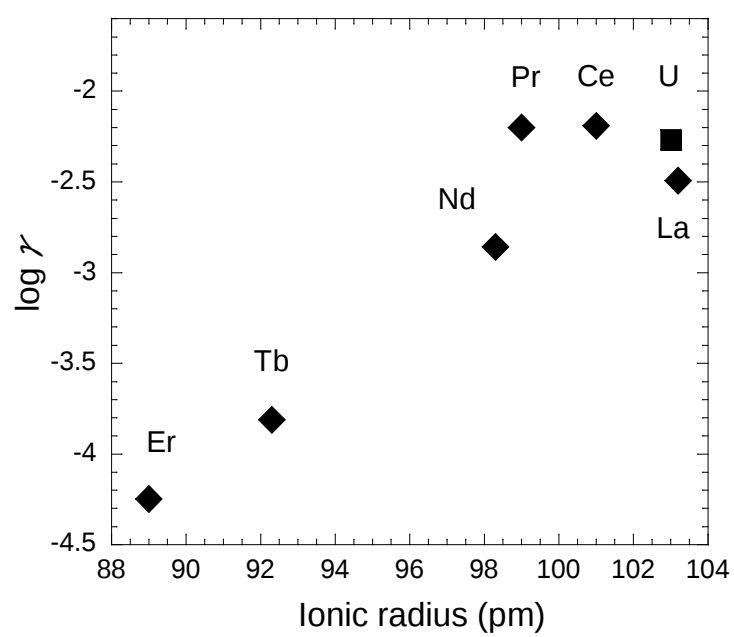


Figure 5.7 Activity coefficients of Ln^{3+} and U^{3+} in LiCl-KCl eutectic melt at 923 K.

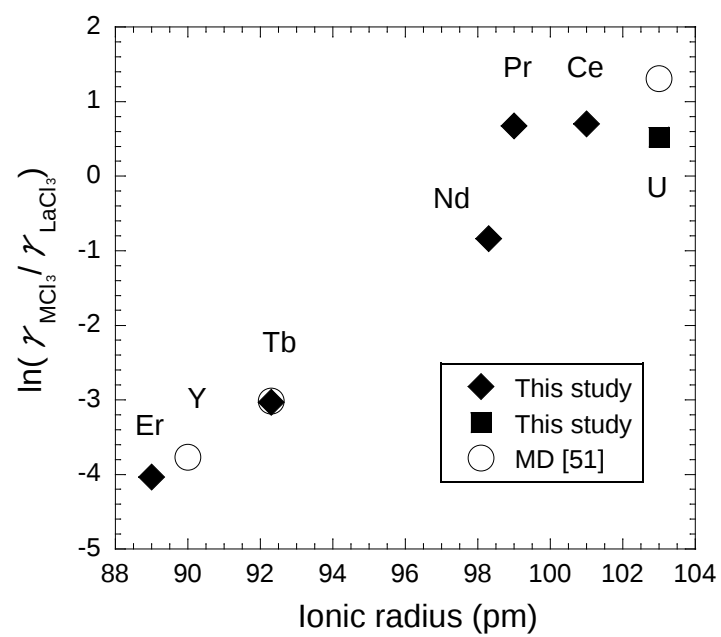


Figure 5.8 The correlation between $\ln(\gamma_{\text{MCl}_3} / \gamma_{\text{LaCl}_3})$ and ionic radius of Ln^{3+} and U^{3+} .

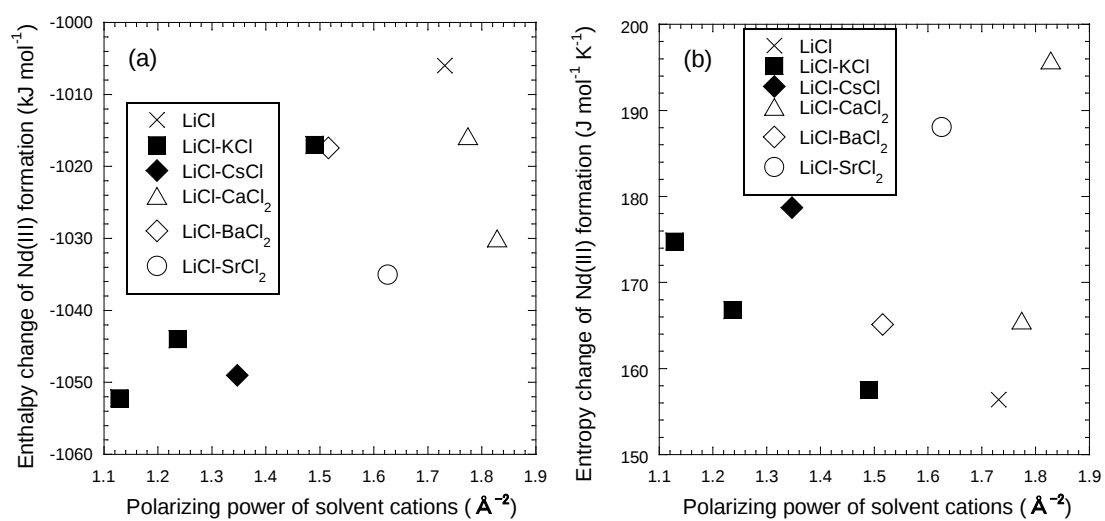


Figure 5A.1 Enthalpy and entropy changes of Nd(III) formation for various molten alkali and alkaline earth chloride mixtures. (a) Enthalpy change. (b) Entropy change.

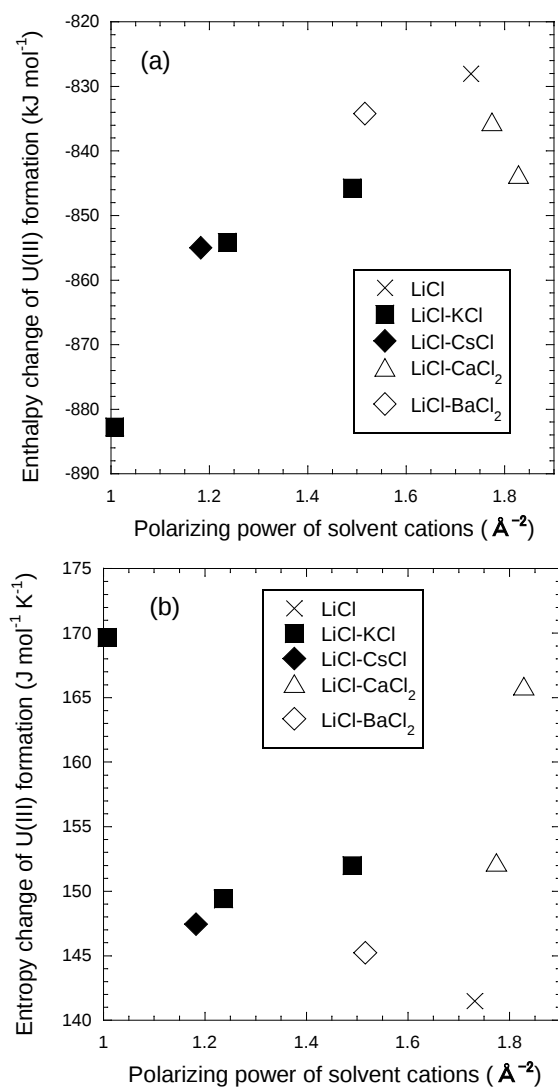


Figure 5A.2 Enthalpy and entropy changes of U(III) formation for various molten alkali and alkaline earth chloride mixtures. (a) Enthalpy change. (b) Entropy change.

Chapter 6 General Conclusion

In this thesis, thermodynamic stability and coordination environment of Ln(III) and An(III) complexes in various molten chloride mixtures were investigated by electrochemical transient techniques and absorption spectrophotometry, respectively. Systematic changes of the thermodynamic stability on the melt composition as well as the solute species of 4f and 5f elements were clarified. The changes were successfully explained with the information of coordination structure obtained. The strength of Coulomb interaction of solvent cations to the Ln(III) and An(III) complexes is the basic factor to control the solvation effect of molten salt media on the thermodynamic stability of the complexes, and it can be evaluated by the polarizing power of solvent cations, $P = \sum \chi(z/r^2)$, where χ , z , and r are the mole fraction, the valence, and the ionic radius of solvent cations, respectively. The thermodynamic stability of Ln's hexachloro complex linearly increased with the decrease of P . The dependence on P changed when increase of the number of chloride ions surrounding Ln^{3+} is taken place for light Lns with larger ionic radius in the melts with higher P . Trivalent ions of lighter Ans, especially U^{3+} , were more stabilized by the dissolution in molten chlorides than Lns with similar ionic radius, which implies that covalent character of 5f orbital exists in the electrostatic bonding between An^{3+} and surrounding chloride ions.

In Chapter 2 and Chapter 3, it was clarified that the thermodynamic stability of Nd(III) complex shows linear correlation with P in molten alkali chlorides. The complex was more stable in the mixtures with larger averaged cationic radius, *i.e.*, smaller P . The slope of the stability on P for ternary mixtures was similar to that for binary mixtures. The change in the oscillator strength of the ${}^4G_{5/2}, {}^2G_{7/2} \leftarrow {}^4I_{9/2}$ transition and the degree of the energy splitting in electronic energy levels suggested that the octahedral symmetry of the NdCl_6^{3-} complex is more distorted in the melts with higher P . It was concluded from these results that the interaction of surrounding alkali cations to the Nd(III) complex can be averaged to determine the octahedral symmetry of NdCl_6^{3-} to make it the most stable thermodynamically. From the engineering point of view, it was confirmed in Chapter 3 that the operating temperature of electrorefining process

can be decreased to 673 K by using ternary molten salt media, 100 K lower than that assumed for general pyroprocess.

In Chapter 4, the thermodynamic stability of Nd(III) complex for the melts containing alkaline earth cations also showed linear dependence on P . The slope was similar to that for alkali chloride systems. P is a parameter based on the simple assumption that the coordination environments further from second neighbor are homogeneous as bulk. This assumption would be rational since the dependence of the thermodynamic stability on P for alkali chlorides is kept for alkaline earth chlorides whose matrix of component ions is not as simple as alkali chlorides due to higher electron density in alkaline earth cations. On the other hand, changes in spectrophotometric characteristics of the oscillator strength and the energy splittings on P were not explained simply by the distortion of the octahedral structure of NdCl_6^{3-} . The result indicated that the coordination environments further from second coordination sphere could have considerable effect on the electromagnetic structure in ligand field of Nd(III) complex for the mixtures including alkaline earth chloride.

In Chapter 5, differences in the P dependence of the thermodynamic stability of Ln(III) and U(III) complexes were clarified. The thermodynamic stability of smaller Ln(III) complexes like Tb and Er linearly decreased with the increase of P due to the distortion from octahedral symmetry of LnCl_6^{3-} as the case of Nd. The linearity was not kept for larger Ln(III) complexes such as La and Ce in the mixtures with higher P , where the number of Cl^- around Ln^{3+} is possibly more than six. The potential difference between depositions of light and heavy Lns increased in chloride mixtures with higher P . The U(III) complex was more stabilized with respect to the Ln(III) complexes. This implies that the covalent character in the bonding of 5f orbital, which is well-known for aqueous system, is also considerable for molten salt system in the electrostatic bonding between lighter An^{3+} and surrounding chloride ions. It was suggested that the solvation characteristic of Am and Cm is comparable to that of Lns with similar ionic radius due to weakened covalent character. The values of the activity coefficient of Ln(III) and U(III) complexes decreased systematically with ionic radius of Ln^{3+} or U^{3+} in LiCl-KCl eutectic melt. The solvation effect was more significant for smaller Ln(III) and An(III) solutes in alkali chloride mixtures with higher P .

The knowledge accumulated in this thesis is helpful to craft a separation strategy for the advanced Am/Cm/Ln separation. Molten chloride mixtures with P around 1.8 are preferable for the following separation procedure:

- (1) Am separation using its divalent state: Am^{2+} efficiently produced in the melt should be collected by reaction with solid oxide like SiO_2 .
- (2) Cm separation by its electrodeposition: Deposition potential of Cm would be more positive than that of Lns enough for selective collection of Cm metal on an inert electrode.
- (3) Lns collection: Residual Ln ions are collected by electrolysis using liquid Cd electrode or by feeding oxygen gas into the melt to make Ln oxide precipitations.

Lns are a kind of rare metal, and development of their recycling system is desirable. Furthermore, they are often contained in ores together with Th. This is one of the recent motivations for Th utilization in nuclear reactors. The present study has focused on the similarities and the differences in chemical properties of Lns and Ans for various molten chloride mixtures. Similar characteristics are prospective for other molten halide systems such as molten fluoride fuel with Th of molten salt reactor. The author will be happy if achieves in this thesis contribute to the establishment of advanced pyroprocesses for An and Ln separation for sustainable growth in both nuclear and high-tech industries.

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List of Publications

- Chapter 2 **K. Fukasawa**, A. Uehara, T. Nagai, T. Fujii, H. Yamana,
“Electrochemical and Spectrophotometric Study on Neodymium Ions in Molten Chloride Mixtures”, Journal of Alloys and Compounds, Elsevier, Vol.509, 16 (2011) 5112-5118.
- K. Fukasawa**, A. Uehara, T. Nagai, T. Fujii, H. Yamana,
“Electrochemical Study of Neodymium Ions in Molten Chlorides”, Proceedings of the 1st International Symposium of Global COE Program “Zero-Carbon Energy Kyoto 2009”, Springer, 2009, pp. 330-333.
- Chapter 3 **K. Fukasawa**, A. Uehara, T. Nagai, T. Fujii, H. Yamana,
“Thermodynamic Stability of Nd(III) Complex in Ternary Mixtures of Molten Alkali Chlorides”, Proceedings of the 3rd International Symposium of Global COE Program “Zero-Carbon Energy Kyoto 2011”, Springer, 2011, in press.
- Chapter 4 **K. Fukasawa**, A. Uehara, T. Nagai, T. Fujii, H. Yamana,
“Electrochemical and Spectrophotometric Study on Trivalent Neodymium Ion in Molten Binary Mixtures of LiCl and Alkali Earth Chlorides”, Journal of Nuclear Materials, Elsevier, Vol.414 (2010) 265-269.
- Chapter 5 **K. Fukasawa**, A. Uehara, T. Nagai, N. Sato, T. Fujii, H. Yamana,
“Thermodynamic Properties of Trivalent Lanthanide and Actinide Ions in Molten Mixtures of LiCl and KCl”, Journal of Nuclear Materials, Elsevier, in press.

Others

H. Yamana, A. Uehara, T. Nagai, **K. Fukasawa**, T. Fujii,
“Am/Cm Separation in Molten Chloride Melt Utilizing the Divalency of Am”,
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H. Uehara, **K. Fukasawa**, T. Nagai, T. Fujii, H. Yamana,
“Separation of Nd metal by using disproportionation reaction of Nd(II) in
molten chlorides”, Journal of Nuclear Materials, Elsevier, Vol.414 (2010)
336-339.