Mutual Separation Characteristics and Mechanism for Lanthanoid Elements via Gas Phase Complexes with Alkaline Metal and/or Aluminium Chlorides

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Mutual separations between mixed lanthanoid chlorides, $LnCl_3$ (Ln=Pr and Nd), were performed using a chemical-vapor transporting method via gaseous complexes with a series of alkaline metal chlorides (ACl). The resulting separation factor depended slightly on the alkaline metals, indicating a tendency for the factor to increase with the atomic number; good separation characteristics were observed for gaseous complexes with KCl and RbCl. For complexes in ternary systems, $LnCl_3$–ACl–$AlCl_3$, the codeposition of ACl with $LnCl_3$, which took place in the binary system, $LnCl_3$–ACl, was depressed and $LnCl_3$ was obtained in a form free from the used complex formers.

For the past three decades the chemistry of vapor complexes of metal halides has been well investigated for many systems.[1] Those vapor systems including lanthanoid (rare earth) halides have also been studied using many groups, e.g., $LnCl_3$–ACl,[2] $LnCl_3$–$AlCl_3$,[3] and LnI_3–AI[4] (Ln, lanthanoids; A, alkaline metals). The formation schemes are as follows:

$$LnCl_3\ (s,l) + n/2\ Al_2Cl_6\ (g) \rightleftarrows LnAl_nCl_{3+3n}\ (g) \qquad (1)$$

and

$$LnX_3\ (s,l) + AX\ (s,l) \rightleftarrows ALnX_4\ (g). \qquad (2)$$

In general, the vapor pressure of lanthanoid halides, LnX_3, themselves, is very low, even at elevated temperatures. However, the volatility is enhanced by complexation with other complex-forming metal halides; the partial pressure of $NdCl_3$ is increased by a factor of 10^{13} (at 600 K) or 10^7 (at 800 K) by complexation with $AlCl_3$.[3b] The resulting vapor complexes have been studied in terms of various application possibilities, viz., luminescent materials for high-intensity discharge lamps,[5] intermediate species for the selective crystallization to provide anhydrous lanthanoid chlorides in high purity,[6] and chemical transporting materials for the recovery of rare metals[7] or the mutual separation of lanthanoid elements.[8]

Among them, mutual separation among mixed lanthanoid chlorides on the basis of the mobility coefficients of individual $[LnAl_nCl_{3+3n}]$ complexes, has been performed on a gas-solid chromatograph system using $AlCl_3$ as a carrier gas.[8a] We have also recently briefly reported that the mutual separation between a lanthanoid chloride pair was successfully conducted by a chemical vapor transporting (CVT) method along a well-controlled temperature gradient using either $AlCl_3$ or ACl as the complex former,[8b,c] where the CVT method is based on differences in formation conditions of the vapor complexes between the lanthanoid chloride and the complex former.

In general, mutual separation among lanthanoid elements, particularly between neighboring element pairs in the periodic table, is quite difficult because of the similarity in their chemical properties. At present, solvent extraction and ion-exchange chromatography are mainly utilized to produce lanthanoids with sufficiently high purity for commercial use. However, these techniques require a series of complicated processes such as extraction, concentration, precipitation, filtration, drying, and calcining, each of which results in high production costs of lanthanoids in spite of their increasing demand in many fields of advanced materials industry.

On the other hand, the CVT method is free from the above-mentioned complicated processes. Furthermore, those lanthanoids purified by the CVT method are obtained as anhydrous chlorides, and can be directly used as raw materials for processing lanthanoid metals by metallothermic reduction with calcium metal, or by electrolytic reduction.

In the present work, the mutual separation characteristics between a mixture of $PrCl_3$ and $NdCl_3$, which is one of the neighboring lanthanoid pairs and the most difficult systems for mutual separation, were studied by the CVT method using alkaline metal chlorides as the complex former. They are discussed from the viewpoints of the transporting mechanism and industrial environment.

Experimental

Reagents. Anhydrous lanthanoid chlorides, $LnCl_3$ (Ln=Pr and Nd), were prepared by heating the corresponding oxides, Pr_6O_{11} and Nd_2O_3 (purity 99.9%), with a large excess of NH_4Cl (99.0%) at 623 K for 2 h in a stream of the N_2 gas dried by passing through a P_2O_5 column; further, the NH_4Cl residue was removed by sublimation at 673 K. The resulting $LnCl_3$ was identified by the powder X-ray diffraction pattern.[9]

A series of chlorides, viz. anhydrous $AlCl_3$ (98.0%), LiCl (99.0%), NaCl (99.9%), KCl (99.5%), RbCl (99.0%), and CsCl (99.0%) was used as complex formers without any pretreat-

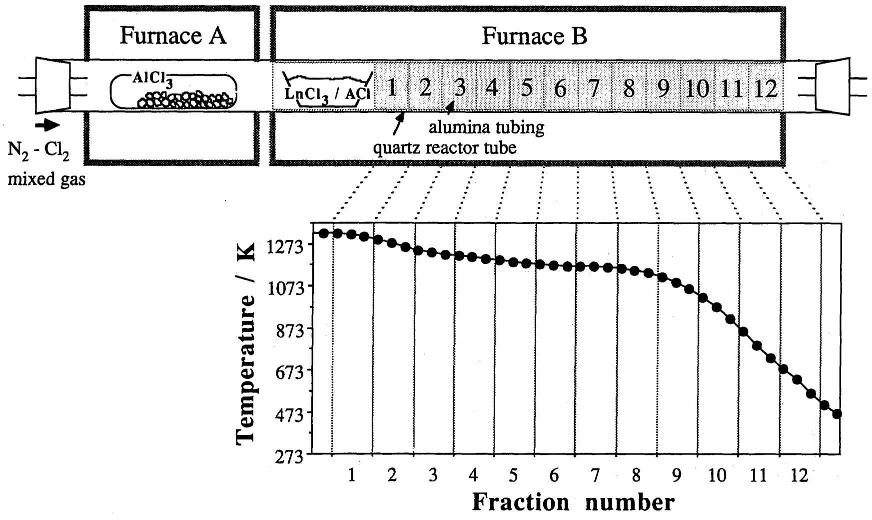

Fig. 1. Assembly of electric furnaces A and B for the chemical vapor transporting reaction and temperature gradient in furnace B. The figures concerning furnace B denote the fraction numbers (*FN*).

ment for the CVT reaction.

Apparatus. The apparatus employed for the CVT reaction comprises two furnaces (A and B). Furnace B (length, 500 mm) comprises eight divided heaters which are independently controlled by thermoregulators so as to produce various temperature gradients. The gradient used for this work is shown in Fig. 1. A quartz tube (outer diameter, 28 mm; inner diameter, 25 mm; length, 1000 mm) was used as a reactor. Twelve pieces of alumina tubing (outer diameter, 21 mm; inner diameter, 16 mm; length, 30 mm) were put side by side along the inner wall of the reactor in order to avoid any reaction of aluminium chloride vapor with the quartz tube,[3b)] such as

$$2\ Al_2Cl_6\,(g) + 3\ SiO_2\,(s) \longrightarrow 2\ Al_2O_3\,(s) + 3\ SiCl_4\,(g). \quad (3)$$

In addition, the sample transported via gas-phase complexes along the temperature gradient was collected and divided every alumina tubing.

Operation. An equimolar mixed chloride of $PrCl_3$ and $NdCl_3$ was weighed and then put on a alumina boat (length, 90 mm). The boat was placed in an alumina tube (outer diameter, 21 mm; inner diameter, 16 mm; length, 140 mm) and set at the upper end of the temperature gradient (see Fig. 1). The complex former (ACl) was added directly to $LnCl_3$. Since $AlCl_3$ is very volatile compared to ACl, however, it was charged into a glass ampule with a small hole with a diameter of about 0.5 mm. The ampule was then loaded into furnace A (length, 180 mm) and mildly heated in order to control its evaporation rate.

The CVT reaction was performed in a stream of mixed Cl_2 and N_2 gas with flow rates of 5 and 30 ml min^{-1}, respectively. By operating furnace B, the desired temperature gradient was attained. The raw material of $LnCl_3$, or its mixture with ACl, was heated to 1273 K. Further, if need be, furnace A was heated over the temperature range 353 to 573 K at a rate of 20 K h^{-1} in order to generate gas-phase aluminium chloride, Al_2Cl_6. The lanthanoid chlorides reacted with ACl or Al_2Cl_6 to form gas-phase complexes: [$ALnCl_4$] or [$LnAl_nCl_{3+3n}$] (n=3, 4). The resulting complexes were driven with the carrier gas and decomposed along the temperature gradient according to the reverse process of Eqs. 1 and 2 to regenerate $LnCl_3$. The transporting reaction lasted for 6 h.

The deposits were collected by removing the twelve pieces of alumina tubing; they were then dissolved individually in deionized water, and the compositions of $PrCl_3$ and $NdCl_3$ were determined for every portion from the peak intensity values of the visible absorption spectra at 444.2 nm for the Pr^{3+} ion and 794.0 nm for the Nd^{3+} ion. The content of ACl (except for LiCl) in each portion was checked by means of an X-ray fluorescence analysis using $ZnCl_2$ as an internal standard.

Results and Discussion

Binary System. Three metal chlorides ($AlCl_3$, NaCl, and KCl) were used as complex formers. Figure 2 shows a series of deposition profiles for the CVT reaction over the divided twelve portions, numbered as fraction numbers (*FN*). The charged amounts of $LnCl_3$, $AlCl_3$, and ACl were as follows: $LnCl_3$, 1.65×10^{-3}; $AlCl_3$, 7.5×10^{-2}; ACl, 1.65×10^{-3} mol.

For $AlCl_3$ (see Fig. 2a), the deposition profile of $PrCl_3$ was almost same as that of $NdCl_3$, peaking at *FN*=4. This means that the formation and decomposition conditions of vapor complexes [$PrAl_nCl_{3+3n}$] and [$NdAl_nCl_{3+3n}$] are closely similar to each other. Under this condition tailing up to the end of the temperature gradient (*FN*=12) and the second small peak at *FN*=9 were also observed on their profiles. The latter is probably due to a steep decline in the temperature gradient.

The deposition profiles of $LnCl_3$ observed for the CVT reactions upon using NaCl and KCl were greatly sharpened, and their gravity centers were shifted to the higher-temperature side compared with the case of $AlCl_3$. This means that the temperature region for the formation of vapor complex [$ALnCl_4$] is higher than that for $AlCl_3$. Furthermore, some differences between the deposition profiles for $PrCl_3$ and $NdCl_3$ were

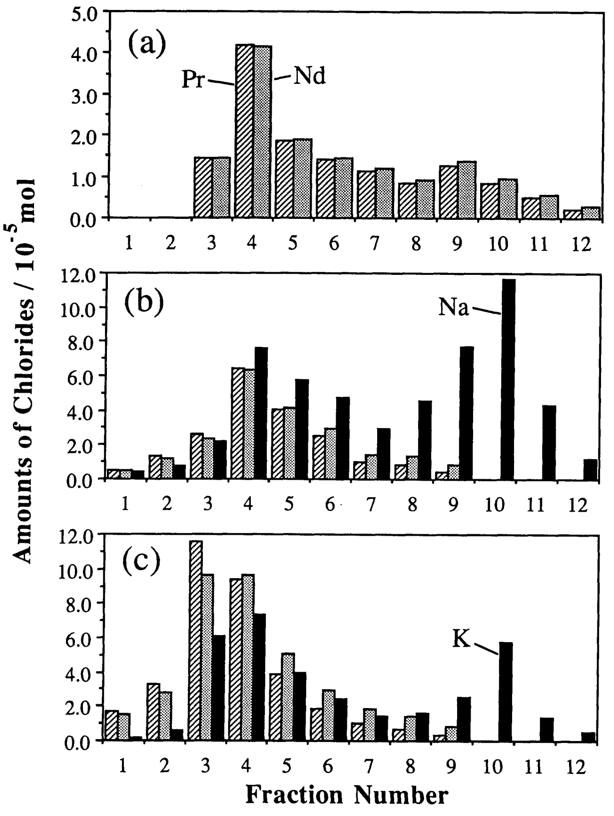

Fig. 2. Distribution profiles of lanthanoid chlorides and complex formers in the transported deposits. The complex formers were (a) $AlCl_3$, (b) NaCl, and (c) KCl.

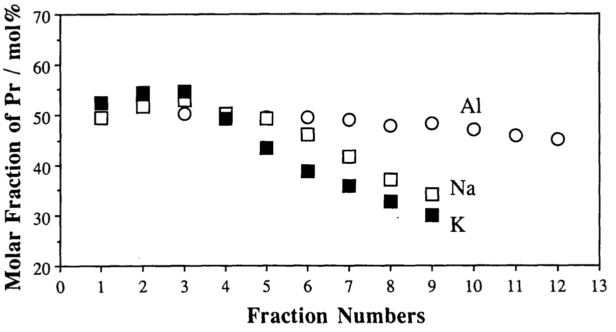

Fig. 3. Molar fraction profiles of $PrCl_3$ per $PrCl_3$ and $NdCl_3$ contents for the deposits shown in Fig. 2. The complex formers were $AlCl_3$, NaCl, and KCl.

emphasized by using them as complex formers. Generally, the amount of the lighter lanthanoid chloride is greater than that of the heavier one at higher temperature fractions, while the situation is inverted at the lower-temperature side. This tendency was more or less observed in each case of $AlCl_3$, NaCl, and KCl. Particularly, when KCl was used, $PrCl_3$ peaked at *FN*=3, while $NdCl_3$ peaked at *FN*=4.

The total amount of the $LnCl_3$ deposited, that is, the yield of $LnCl_3$, was low (17%) when $AlCl_3$ was employed as the complex former. However, by using ACl in place of $AlCl_3$, the yield was improved: NaCl, 25%; KCl, 42% (see Table 1). This indicates that the formation of vapor complex $[LnAl_nCl_{3+3n}]$ is limited and, hence, is too slow to equilibrate,[3b] since in this case complexation takes place only on the surface of the $LnCl_3$ melt, compared with the bulk reaction in the melt of $LnCl_3$ and ACl.

Figure 3 shows the molar fraction profiles of $PrCl_3$ for deposits transported by $AlCl_3$, NaCl, and KCl. Transport with $AlCl_3$ gave a flat relation against *FN*, and the separation efficiency between $PrCl_3$ and $NdCl_3$ was very poor. The molar fraction value of $PrCl_3$ slightly decreased with an increase in *FN*. The above-mentioned tendency, that the deposition profile of $LnCl_3$ schematically shifts to the lower temperature side with an increase in the atomic number of Ln, was also observed under this condition. This feature is in accord with the previous results obtained regarding the $PrCl_3$–$ErCl_3$ system.[8b]

On the other hand, the use of ACl as a complex former makes the molar fraction profiles sharpen and allows an improved separation efficiency. The molar-fraction profiles of $PrCl_3$ were maximized at around *FN*=3 and steeply declined with an increase in *FN* compared with the values for $AlCl_3$ (see Fig. 3). This results in a selective concentration of $PrCl_3$ or $NdCl_3$ onto every fraction along the temperature gradient, and realizes mutual separation between $PrCl_3$ and $NdCl_3$ in high efficiency.

The difference between the sharpnesses of the molar-fraction curves for NaCl and KCl indicates that the formation equilibria of $[KLnCl_4]$ and $[KNdCl_4]$ cause an apparent difference from each other compared with that of $[NaPrCl_4]$ and $[NaNdCl_4]$; further, deposition is more selective when using KCl. Novikov et al. have determined that though the formation enthalpies and entropies of these complexes are equal to each other ($\Delta H_{1350K}=59.3\pm4$ kcal mol^{-1}; $\Delta S_{1350K}=32.3\pm3$ e.u. (e.u.=cal °C^{-1})), the compositions of the vapor complexes over a 50 mol% melt of the $LnCl_3$–KCl system (Ln=Pr, Nd) are quite different at 1273 K: $[KPrCl_4]$, 13.0 mol%; $[KNdCl_4]$, 23.0 mol%.[2a] Unfortunately, thermodynamic data with respect to the sodium-

Table 1. Separation Factors and Yields for the Chemical Vapor Transportation Using Various Complex Formers

Complex former	Separation factor[a]		Yield/%
	SF(Pr)$_{HT}$	*SF*(Nd)$_{LT}$	
$AlCl_3$	1.00	1.07	17
NaCl	1.04	1.21	25
KCl	1.07	1.33	42
LiCl/$AlCl_3$	1.04	1.16	19
NaCl/$AlCl_3$	1.08	1.20	33
KCl/$AlCl_3$	1.07	1.20	40
RbCl/$AlCl_3$	1.08	1.24	26
CsCl/$AlCl_3$	1.11	1.19	38

a) See the text.

containing complex have been obtained only for [$NaNdCl_4$].2c) Therefore, one can not argue for a difference between the formation conditions of [$NaPrCl_4$] and [$NaNdCl_4$] as well as the reason for the improved separation efficiency (NaCl<KCl) from the viewpoint of thermodynamics.

To compare the separation efficiency for each complex former, the value separation factor (*SF*) was evaluated. The *SF* values at the high- and low-temperature sides, at which each amount of $LnCl_3$ deposited is equal to half the total, are defined as follows:

$$SF(\mathrm{Pr})_{\mathrm{HT}}=\frac{[\mathrm{Pr}]_{\mathrm{dep,\ HT}}}{[\mathrm{Nd}]_{\mathrm{dep,\ HT}}}\bigg/\frac{[\mathrm{Pr}]_{\mathrm{raw}}}{[\mathrm{Nd}]_{\mathrm{raw}}}=\frac{[\mathrm{Pr}]_{\mathrm{dep,\ HT}}}{[\mathrm{Nd}]_{\mathrm{dep,\ HT}}}$$

and

$$SF(\mathrm{Nd})_{\mathrm{LT}}=\frac{[\mathrm{Nd}]_{\mathrm{dep,\ LT}}}{[\mathrm{Pr}]_{\mathrm{dep,\ LT}}}\bigg/\frac{[\mathrm{Nd}]_{\mathrm{raw}}}{[\mathrm{Pr}]_{\mathrm{raw}}}=\frac{[\mathrm{Nd}]_{\mathrm{dep,\ LT}}}{[\mathrm{Pr}]_{\mathrm{dep,\ LT}}}$$

Here, $[\mathrm{Ln}]_{\mathrm{raw}}$ and $[\mathrm{Ln}]_{\mathrm{dep}}$ are the molar concentrations of the raw mixture charged and the deposits transported, respectively. In this work, $[\mathrm{Pr}]_{\mathrm{raw}}$ and $[\mathrm{Nd}]_{\mathrm{raw}}$ are equal to each other and, hence, the *SF* values can be simply expressed as the right-hand sides of the equations.

The obtained separation factors are summarized in Table 1 together with the yields. The $SF(\mathrm{Pr})_{\mathrm{HT}}$ and $SF(\mathrm{Nd})_{\mathrm{LT}}$ values show a tendency to increase in the order $AlCl_3$<NaCl<KCl, as well as the yields. In general, the $SF(\mathrm{Pr})_{\mathrm{HT}}$ value is smaller than that of $SF(\mathrm{Nd})_{\mathrm{LT}}$, since the vapor complex comprising $NdCl_3$, [$NdAl_nCl_{3+3n}$] and [$ANdCl_4$] are easy to form, compared with those of $PrCl_3$. $NdCl_3$ thus tends to be transported more than $PrCl_3$. If the amounts of $PrCl_3$ and $NdCl_3$ deposits were similar to each other, the two above-mentioned *SF* values should be equal.

It is noteworthy that the $SF(\mathrm{Nd})_{\mathrm{LT}}$ value for KCl (1.33) is not inferior to those of the complexing agents for conventional solvent extractions, e.g., 1.38 for bis(2-methylhexyl)phosphoric acid "D2EHPA"10a) and 1.50 for tributyl phosphate "TBP".10b)

When $AlCl_3$ was used as the complex former, the $AlCl_3$ residue reproduced by the reverse process of Eq. 1 was passed through the lower temperature region and condensed at the right-hand corner of furnace B (see Fig. 1), due to the relatively low sublimation temperature of $AlCl_3$ (below 473 K). Consequently, the $LnCl_3$ deposits transported by $AlCl_3$ are obtained in pure form without any contamination of the used complex former. In other words, it is possible that complex former $AlCl_3$ can be recovered and recycled for further processing.

In contrast, the volatility of ACl is low in the temperature region studied in this work; these are widely spread over furnace B, showing two deposition peaks at *FN*=4 and *FN*=10. The peak at *FN*=4 is assigned to the ACl deposit related to the CVT reaction, since it almost coincides with the deposition peak position of $LnCl_3$. The peak at *FN*=10 seems to be responsible for the residue which results from the free ACl vapor after migrating via the gas phase, since the deposition profile of the ACl deposit usually has a single peak at *FN*=6 in furnace B when only ACl is loaded. Consequently, the $LnCl_3$ deposits transported by ACl contain a significant amount of ACl as an impurity and, thus, they need to be removed from the $LnCl_3$ deposits.

Ternary System. To remove the ACl residue from the $LnCl_3$ deposit, both ACl and $AlCl_3$ were simultaneously used as complex formers. That is to say, 1.65×10^{-3} mol of ACl (A=Li, Na, K, Rb, and Cs) was mixed with an equimolar amount of raw $LnCl_3$ (Pr : Nd=1 : 1); furthermore, gaseous Al_2Cl_6 (total 7.5×10^{-2} mol) was introduced from furnaces A to B as a second complex former.

Figure 4 shows the deposition profiles for $LnCl_3$ and ACl. The profile of ACl was remarkably changed upon the addition of $AlCl_3$. The greatest amount of ACl was carried to fraction *FN*=12 and, hence, the transported $LnCl_3$ deposit scarcely contained any ACl residue as an impurity. Furthermore, the separation factors and yields of $LnCl_3$ (see Table 1) were maintained at similar levels to that obtained in the binary $LnCl_3$–ACl system. It has been found that complexation between ACl and $AlCl_3$,

$$\mathrm{ACl\ (s)} + 1/2\ \mathrm{Al_2Cl_6\ (g)} \rightleftarrows \mathrm{AAlCl_4\ (g)}, \qquad (4)$$

takes place.11) It is concluded that any ACl residue codeposited according to the reverse process of Eq. 1 is removed by the regeneration of much more volatile complexes, i.e., [$NaAlCl_4$] and [$KAlCl_4$].11)

All of the alkaline metal chlorides had a positive effect on the separation factor. Among them, RbCl gave the best result under the condition of simultaneously using ACl with $AlCl_3$ as the complex formers. However,

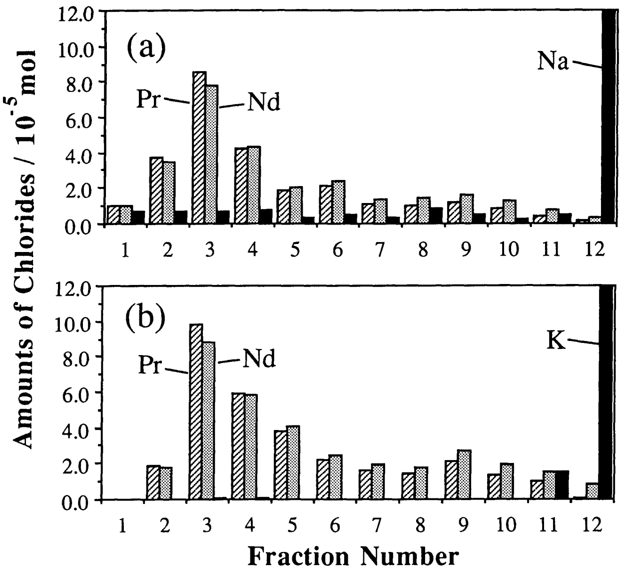

Fig. 4. Distribution profiles of lanthanoid chlorides and complex formers in the deposits transported under the simultaneous uses of two complex formers. The complex formers were (a) NaCl and $AlCl_3$; (b) KCl and $AlCl_3$.

Table 2. Separation Factors, Amounts, and Yields of the $LnCl_3$[a] Deposits Transported with Various Amounts of NaCl

NaCl	Separation factor		Amounts of $LnCl_3$	Yield
10^{-3} mol	$SF(Pr)_{HT}$	$SF(Nd)_{LT}$	deposits/ 10^{-4}mol	%
0	1.00	1.07	2.79	17
0.55	1.04	1.17	4.11	25
0.65	1.08	1.20	5.40	33
4.95	1.08	1.18	4.97	30

a) The loaded amount of $LnCl_3$ for all runs was 1.65×10^{-3} mol.

KCl may be better from the viewpoint of economical efficiency.

Amount Dependence of ACl. The CVT reaction was carried out by using a variable amount of ACl. In order to compare the $LnCl_3$ contents of the transported deposits, the amount of $LnCl_3$ (Pr : Nd=1 : 1) initially loaded was kept constant at 1.65×10^{-3} mol. The chloride (NaCl) was mixed at two amounts: 5.50×10^{-4} mol (Na : Ln=1 : 3) and 4.95×10^{-3} mol (Na : Ln=3 : 1). As the second complex former, a total of 7.5×10^{-2} mol of $AlCl_3$ was also used.

The amounts $LnCl_3$ in the deposits transported for a series of runs are summarized in Table 2, together with the separation factors and yields. As mentioned above, each $SF(Nd)_{LT}$ value is generally larger than the corresponding $SF(Pr)_{HT}$ value, due to the difference in the complexation rates between $LnCl_3$ and the complex formers. The highest $SF(Nd)_{LT}$ value and yield were 1.20 and 33% upon the addition of 1.65×10^{-3} mol of NaCl (Na : Ln=1 : 1). The fact that those values are maximized when the raw mixture comprises an equimolar composition of NaCl and $LnCl_3$ explains the increase in the amounts of $LnCl_3$ deposits transported, since $LnCl_3$ and ACl are known to form 1 : 1 vapor complexes, such as [$NaPrCl_4$] and [$NaNdCl_4$].[2)] Moreover, the result that the *SF* values varied in a similar manner as the yield indicates that NaCl plays a key role in the CVT reaction for $LnCl_3$, even when $AlCl_3$ and NaCl are simultaneously used as complex formers.

Conclusions

The effective mutual separation between neighboring Pr and Nd was realized by the CVT method while using alkaline metal chloride as complex formers. The separation factor evaluated in the system ($LnCl_3$–KCl) is 1.33. It is comparable to the value observed by the conventional solvent-extraction method. Furthermore, the lanthanoid chlorides separated via the gas-phase complexes were obtained in pure form upon removing the codeposited alkaline metal chloride by using aluminium chloride as the second complex former.

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