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Mutual Separation Characteristics for Lanthanoid Elements via Gas Phase Complexes with Alkaline Chlorides

Gin-ya ADACHI,* Kuniaki MURASE, Kiyoshi SHINOZAKI, and Ken-ichi MACHIDA
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Yamadaoka, Suita, Osaka 565

Mutual separation characteristics of lanthanoid chlorides $LnCl_3$ (Ln = Pr, Nd) using a chemical vapor transporting method via gaseous complexes were investigated. Compared with $AlCl_3$ as the transporting agent, alkaline chlorides can transport more amounts of $LnCl_3$, and enhance the separation efficiency between $PrCl_3$ and $NdCl_3$.

Metal halides are volatile at high temperature in greater or less degree as gaseous complexes,[1a-c] and some of them (e.g. $AlCl_3$, $FeCl_3$, and so on) give gas phase complexes with other metal halides.[1a,b] It was reported that several lanthanoid chlorides ($LnCl_3$) also form such complexes with $AlCl_3$[2a-d] or ACl[3] (A = alkaline metal elements) at elevated temperatures according to following equations:

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

$$LnCl_3\ (s,l) + ACl\ (s,l) \rightleftharpoons ALnCl_4\ (g). \qquad (2)$$

They have been mainly studied as gas phase materials for discharge lamps.[4] The lanthanoid elements possess closely similar and common chemical properties, but the complexation conditions are slightly different from one another. This indicates that a mutual separation among the lanthanoid elements is valid by precisely controlling the formation conditions of them, and two research groups have already found that mixed lanthanoid elements are mutually separated by a gas-solid chromatographic technique[5] or a chemical vapor transport method,[6] using $AlCl_3$ as a complexing agent (complex former).

The present work conducts the mutual separation between neighboring lanthanoid elements, Pr and Nd, which is very difficult because of their very close similarity in chemical properties, by using the complex former of alkaline chlorides.

The lanthanoid chlorides $LnCl_3$ were prepared by heating of the corresponding oxides, Pr_6O_{11} and Nd_2O_3 (purity 99.9%), with a large excess of NH_4Cl in dry N_2 at 300 °C. The other chlorides, ACl (A = Li, Na, K, Rb, and Cs) and $AlCl_3$ were used as received. The equimolar amount of $PrCl_3$ and $NdCl_3$ were weighed and further the appropriate amount of ACl was added to them. Then, these chlorides were intimately mixed with one another in a glove box.

An assembly of the electric furnaces employed for the mutual separation of lanthanoid chlorides was shown elsewhere.[6] A quartz tube (outer diameter, 28 mm; length, 1000 mm) was used as a reactor, in which twelve pieces of alumina tubing (outer diameter, 21 mm; length, 30 mm) were put side by side along the inner wall in order to avoid a reaction of the aluminium chlorides with the quartz tube and to enable us to collect the sample transported via the gas phase complex along the temperature gradient. The sample was collected every portion deposited on the alumina tubes. The reactor was heated by two electric furnaces (A and B) which were independently controlled. The raw material mixture of $PrCl_3$, $NdCl_3$, and ACl was introduced at the upper end of the temperature gradient (see Fig.1) in the furnace B, while the furnace A was employed when $AlCl_3$ was used as the complex former and its usual charged amount was 10 g. The furnace B was composed of several divided heaters which can produce various temperature gradients.

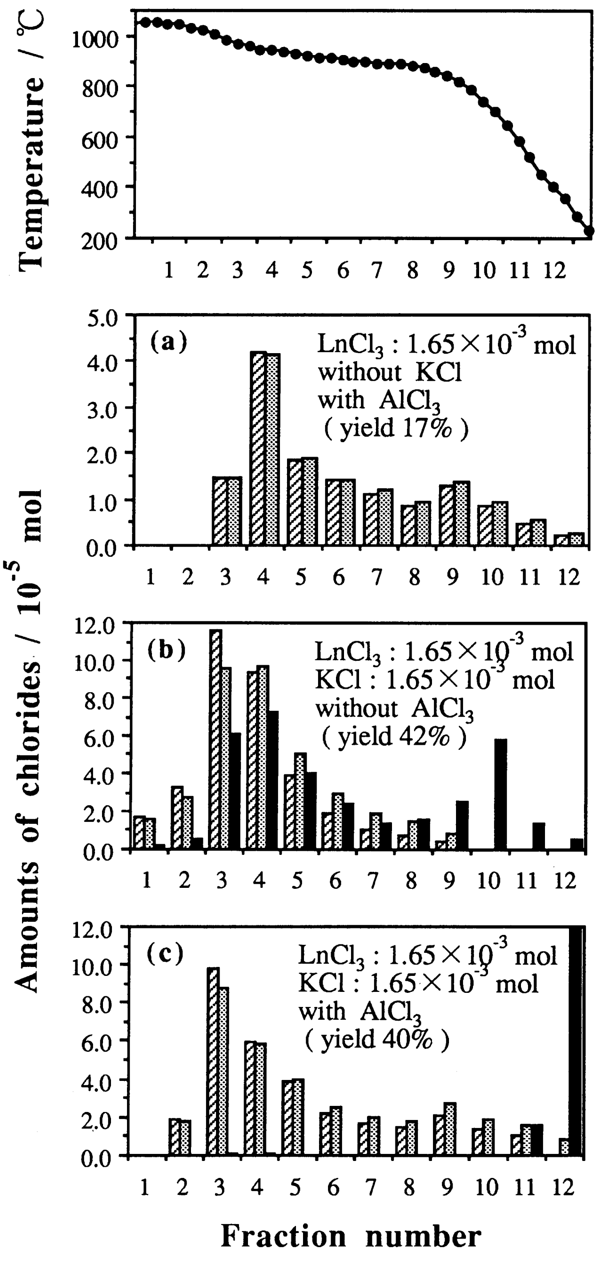

Fig.1. Temperature dependence curve, and lanthanoid and complex former distributions for a mixture of $PrCl_3$ and $NdCl_3$. Complex former is $AlCl_3$ (a), KCl (b), and KCl-$AlCl_3$ (c).

▨ $PrCl_3$ ▒ $NdCl_3$ ■ KCl

The chemical vapor transport for the mutual separation between Pr and Nd was carried out by the same operations as described in the previous paper.[6] A mixed gas of Cl_2 and N_2 was introduced in the reactor at respective flow rates of 5 and 30 ml/min as a carrier gas. At first, the lanthanoid chloride mixture containing the alkaline metal chloride was heated to 1000 °C, and then, if need be, the $AlCl_3$ placed in furnace A was heated in a range of 80 to 200 °C to generate the gas phase aluminum chloride Al_2Cl_6 for 6 h. The resulting gas phase complexes $ALnCl_4$ were driven with the carrier gas and decomposed along the temperature gradient according to the reverse process as leaving $LnCl_3$. The portions collected were dissolved in water and the molar ratio of Pr : Nd was determined from the peak intensities of visible absorption spectra. The contents of ACl (except for LiCl) and $AlCl_3$ in each portion were checked by means of X-ray fluorometry.

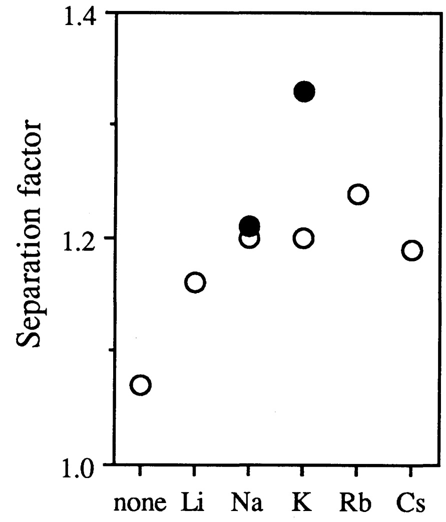

Fig.2. Alkaline metal dependencies of the separation factor for $NdCl_3$; $SF(Nd)_{LT}$. The separation factor were calculated from the amount of $NdCl_3$ deposited at the lower temperature fractions. ○: with $AlCl_3$, ●: without $AlCl_3$

A series of deposition profiles for the chlorides over the divided portions (in the figure, each portion is numbered as a fraction number) is shown in Fig.1. The mixture of $PrCl_3$ and $NdCl_3$ transported by $AlCl_3$ (ACl free) provided almost the same profile as each other and the mutual separation hardly took place (see Fig.1a), although the previous result of $PrCl_3$ and $ErCl_3$ demonstrated the good mutual separation characteristics.$^{6)}$ This means that the mutual separation between the neighboring lanthanoid elements such as Pr and Nd is much more difficult than that of other combinations (e.g. Pr-Er), since their chemical properties become very similar between neighboring lanthanoid elements, as mentioned above, or the complexing reaction (1) is very slow to equilibrate.$^{2b)}$

On the other hand, the use of ACl in place of $AlCl_3$ as the complex former does enhance the total yield of lanthanoid chlorides transported and make a large difference in the deposition profile of $PrCl_3$ and $NdCl_3$. For KCl (see Fig.1b), the distribution of $PrCl_3$ deposit relatively shifted to the high temperature side compared with that of $NdCl_3$: The relative amount of $PrCl_3$ deposit increased in the high temperature region of the gradient, whereas $NdCl_3$ was concentrated in low temperature region. The separation factors (SF) at high and low temperature sides, at which each amount of $LnCl_3$ deposit was equal to half of the total one, were evaluated by the following equations:

$$SF(Pr)_{HT} = \frac{\text{concentration ratio of deposited } LnCl_3 \text{ (Pr/Nd)}}{\text{concentration ratio of raw mixed } LnCl_3 \text{ (Pr/Nd)}},$$

$$SF(Nd)_{LT} = \frac{\text{concentration ratio of deposited } LnCl_3 \text{ (Nd/Pr)}}{\text{concentration ratio of raw mixed } LnCl_3 \text{ (Nd/Pr)}}.$$

The values of $SF(Pr)_{HT}$ and $SF(Nd)_{LT}$ were 1.13 and 1.33, respectively, while the values were 1.00 and 1.07 when $AlCl_3$ was used as the complex former. It is noteworthy that the value (1.33) is not low compared with that of conventional solvent extractions (e.g. 1.38 for D2EHPA$^{7a)}$ and 1.50 for TBP$^{7b)}$). Therefore, this method has a great advantage because the separation process is all dry and much simpler than those of conventional ones which need the complicated operations of extraction, concentration, precipitation, filtration, drying, calcining, and so on.

The resulting deposits of $LnCl_3$ contain a significant amount of KCl, and thus one needs to remove the KCl impurity from the $LnCl_3$ deposits. On the contrary, no KCl residue was detected in the $LnCl_3$ deposits transported by using $AlCl_3$ as the second complex former in addition to KCl. Furthermore, the separation factor was kept at the similar level to that observed in the system using the complex former of only KCl (Fig.1c). This means that very volatile complex between KCl and $AlCl_3$$^{8)}$ is formed by following the decomposition of $KLnCl_3$, and plays a role to move away the KCl deposits.

In Fig.2, the $SF(Nd)_{LT}$ values are plotted against a series of ACl. All the alkaline chlorides possessed the positive effect for improving the SF value and, among of them, RbCl gave a best result. However, KCl may be better in view of economical efficiency.

Concluding the above, a series of the alkaline metal chlorides produces the gas phase complexes with the lanthanoid chlorides of which the formation conditions realize the good mutual separation characteristics even between the neighboring lanthanoid elements. In addition, the simultaneous use of alkaline metal chlorides with aluminium chloride as the complex former allows us to get the lanthanoid chlorides in high purity.

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