Environmental friendly separation of dysprosium and neodymium by fractional precipitation of coordination polymers†

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Against a backdrop of increasing demand, the recovery of neodymium (Nd) and especially dysprosium (Dy) from manufacturing scraps and used magnets has necessitated the development of Nd/Dy separation technologies. To this end, we suggest a simple and environmentally friendly separation method by fractional precipitation of coordination polymers (CP)—extended complexes of metal ions and organic ligands. With the di(2-ethylhexyl) phosphoric acid ligand functioning as a precipitant, Dy was exclusively precipitated as a CP due to its precipitation equilibrium that is considerably different from that for Nd.

Dysprosium (Dy)-doped neodymium (Nd) magnets are small, lightweight, and incredibly powerful. As the demand for Nd magnets increases, it has become more difficult to secure supplies of both Nd and Dy worldwide. The recovery of these elements from manufacturing scraps and used magnets has the potential to solve the problem of their limited supply. Because of their similar chemical properties, one of the most difficult processes is Nd/Dy separation. The solvent extraction method that is conventionally used to separate lanthanide elements from manufacturing scraps and used magnets has necessitated the development of Nd/Dy separation technologies. To this end, we suggest a simple and environmentally friendly separation method by fractional precipitation of coordination polymers (CP)—extended complexes of metal ions and organic ligands. With the di(2-ethylhexyl) phosphoric acid ligand functioning as a precipitant, Dy was exclusively precipitated as a CP due to its precipitation equilibrium that is considerably different from that for Nd.

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Our research,†‡‡ has focused on coordination polymers (CPs) formed with di(2-ethylhexyl) phosphoric acid (PO(OH)(OCH2CH(CH3)2)2, Hdehp), hereinafter described as [Ln(dehp)3]. CPs are solid-state extended complexes formed with organic ligands and metal ions. We previously revealed that [Ln(dehp)3] could be formed simply by mixing LnCl3 and Hdehp in a binary ethanol-water mixture. Powder X-ray diffraction analysis indicated that [Ln(dehp)3] has monoclinic structure and its lattice parameters vary only slightly with a kind of Ln3+. The stability of complex between Hdehp and Ln3+ is governed by charge density of ions. Hdehp prefers to form a mononuclear complex with Dy3+ rather than Nd3+ in solvent extraction systems. Thus, it was expected that CPs based on Hdehp would impart different precipitation properties in Nd and Dy as well. In this communication, we examine the difference in the precipitation behaviors of [Nd(dehp)3] and [Dy(dehp)3] in a binary ethanol-water mixture and its potential to separate Nd and Dy by fractional precipitation.

Precipitation equilibrium of [Ln(dehp)3] and Ksp are given by the following equations:

\[
\text{Ln}^{3+} + 3\text{dehp}^- \rightleftharpoons [\text{Ln(dehp)}_3] \quad (1)
\]

\[
\text{K}_{\text{sp}} = a(\text{Ln}^{3+}) \cdot a(\text{dehp}^-)^3 = \left[\gamma(\text{Ln}^{3+}) \cdot c(\text{Ln}^{3+})\right] \cdot \left[\gamma(\text{dehp}^-) \cdot c(\text{dehp}^-)\right]^3 \quad (2)
\]

where \(a\), \(\gamma\), and \(c\) represent the activity, activity coefficient, and concentration of the species, respectively. The concentration of H+ in the solution (c(H+)) will affect the precipitation reaction, because dehp‐ is generated by the dissociation of Hdehp as follows:

\[
\text{Hdehp} \rightleftharpoons \text{H}^+ + \text{dehp}^- \quad (3)
\]

In order to assess the difference in the formation of [Nd(dehp)3] and [Dy(dehp)3], their precipitation equilibria

† Electronic Supplementary Information (ESI) available: [Changes in precipitation yield of Nd and Dy with ethanol concentration, changes in Ln and P contents in precipitates with pH, estimation of apparent solubility product (Ksp), XAFS measurement, and acid dissociation constant (Ka) of Hdehp].
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were investigated in various acidic solutions. Water or 0.06–
3.0 M aq. HCl solution (1.6 mL), 1 M LnCl$_3$ (Ln = Nd or Dy)
in 0.25 M aq. HCl solution (0.4 mL), ethanol (14 mL), and
0.3 M Nadehp in an 80:20 ethanol-water mixture (4 mL) were
mixed in the order shown. The Nadehp solution was prepared
by mixing 14.5 M aq. NaOH and ethanolic Hdehp solutions
in equimolar amounts. We had found that a lower concentra-
tion of water would result in better separation (see Electronic
Supplementary Information, ESI†); thus, an 86 vol% ethanol
concentration, obtained after mixing in the aqueous LnCl$_3$
and HCl solutions, was used. The c(H$^+$) varied with the HCl ad-
dition. Whitish precipitates obtained were filtered after ca. 20
h, washed several times with 80:20 vol% ethanol-water, and
dried. The pH values of the filtrates were measured by a pH
meter (Metrohm pH meter 744) equipped with an electrode for
ethanol solutions (Metrohm EtOH-trode). According to the
literature, the true pH values should be larger than the pH
measured by 0.04–0.3 due to the difference in standard states
between aqueous and binary ethanol-water solutions, thus we
consider the pH in this range. The filtrates and the precipi-
tations (Y) of [Nd(dehp)$_3$] (A) and [Dy(dehp)$_3$] (B) from NdCl$_3$
and DyCl$_3$ solutions, respectively, as a function of pH. The initial
concentrations (c$_i$) of Ln$^{3+}$ (Ln = Nd or Dy$^{3+}$), Nadehp, and H$^+$
are 0.02, 0.06, and 0.05–0.24 M, respectively.

Fig. 1 Y (%) of [Nd(dehp)$_3$] (A) and [Dy(dehp)$_3$] (B) from NdCl$_3$
and DyCl$_3$ solutions, respectively, as a function of pH. The initial
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The Ln (= Nd or Dy) and P contents of the solids were con-
sistent with the calculated values based on the chemical for-
mulas of [Ln(dehp)$_3$], indicating that Ln precipitates as a co-
ordination polymer from binary ethanol-water solutions (Tables
S2 and S3, ESI†). From the Ln$^{3+}$ concentrations in the solu-
tions (c(Ln$^{3+}$)), the precipitation yields (Y/%) were calculated
according to the following equation,

$$
Y = \frac{c_i(Ln^{3+}) - c(Ln^{3+})}{c_i(Ln^{3+})} \times 100
$$

(4)

The Ys for [Nd(dehp)$_3$] and [Dy(dehp)$_3$] (Figures 1(A) and
(B), respectively) increase with pH, and Dy shows a more
gradual change than Nd: the Ys for Dy exceed 75% within
the pH range 0.7–4.0, whereas the Ys for Nd vary from 0 to
100% over the similar pH range. It seems that such differ-
tent precipitation equilibria between the two CPs would enable
Nd/Dy separation by fractional precipitation.

Separations of Nd and Dy were investigated under various
conditions in the same manner described above: the initial
concentrations of the species are listed in Table 1. Figures
2(A) and 2(B) show the Y values for Nd and Dy from Nd/Dy
mixtures as a function of pH (entries a–e in Table 1, and lig-
and concentration (entries d and f–h in Table 1. The horizont-
al axes represent the values measured after equilibrium had
been attained. As expected, Hdehp preferentially forms pre-
cipitates with Dy rather than Nd under any conditions except
at pH 3.7. As shown in Figure 2(A), the Y of Nd at a pH
lower than 1.0 is small enough to be separated from Dy, while
both Nd and Dy give relatively high Y values when the pH
is higher than 1. Since the cube of c(dehp$^-$) is involved in
determining $K_{sp}$ (Eq. 2), the term c(dehp$^-$) is crucial to sepa-
ration efficiency. Figure 2(B), which compares the Ys at pH =
~0.8 as a function of c$^{tot}$(P) = c(dehp$^-$) + c(Hdehp), as mea-
sured by ICP-OES analysis, indicates that Dy is exclusively
precipitated regardless of c$^{tot}$(P) under conditions in which
the pH is in the range 1–2 equivalents per c$^i$(Dy$^{3+}$)
(entries e–g in Table 1). In practice, the Nd$^{3+}$ concentration
is higher than Dy$^{3+}$ in Nd magnets, i.e., in their leached solu-
tions. The Ys at c$^i$(Nd$^{3+}$)/c$^i$(Dy$^{3+}$) = 5 (h) show no substantial
differences from those at c$^i$(Nd$^{3+}$)/c$^i$(Dy$^{3+}$) = 1 (g), offering
a useful example.

To evaluate these results, we consider the $K_{sp}$ values, and
compare the calculated and experimental precipitation data.
On the assumption that the values of γ(Ln$^{3+}$), γ(dehp$^-$), and
γ(Hdehp) are unity, the apparent solubility product, hereinafter
described as $K_{sp}^a$, is given by:

$$
K_{sp}^a = \frac{c_i(Ln^{3+})}{c_i(P)}
$$

(5)
Table 1 $c^i$ (Ln$^{3+}$), $c^i$ (Nadehp), and $c^i$ (H$^+$) (cf. Fig. 2)

<table>
<thead>
<tr>
<th></th>
<th>$c^i$ (Nd$^{3+}$) / M</th>
<th>$c^i$ (Dy$^{3+}$) / M</th>
<th>$c^i$ (Nadehp) / M</th>
<th>$c^i$ (H$^+$) / M</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.010</td>
<td>0.010</td>
<td>0.060</td>
<td>0.0050</td>
</tr>
<tr>
<td>b</td>
<td>0.010</td>
<td>0.010</td>
<td>0.060</td>
<td>0.020</td>
</tr>
<tr>
<td>c</td>
<td>0.010</td>
<td>0.010</td>
<td>0.060</td>
<td>0.040</td>
</tr>
<tr>
<td>d</td>
<td>0.010</td>
<td>0.010</td>
<td>0.060</td>
<td>0.20</td>
</tr>
<tr>
<td>e</td>
<td>0.010</td>
<td>0.010</td>
<td>0.060</td>
<td>0.40</td>
</tr>
<tr>
<td>f</td>
<td>0.010</td>
<td>0.010</td>
<td>0.045</td>
<td>0.20</td>
</tr>
<tr>
<td>g</td>
<td>0.010</td>
<td>0.010</td>
<td>0.030</td>
<td>0.020</td>
</tr>
<tr>
<td>h</td>
<td>0.050</td>
<td>0.010</td>
<td>0.030</td>
<td>0.020</td>
</tr>
</tbody>
</table>

$$K_{sp}^a = \left( \frac{c^{tot}(P)}{1 + a(H^+)/K_a} \right)^3 \cdot c^i(Ln^{3+})$$ \hspace{1cm} (5)

From the $c^{tot}(P)$ and $c(Ln^{3+})$ values (shown in Figure S2, ESI†), $K_{sp}^a$(Nd)= $2.9 \times 10^{-12}$ (±0.8 $\times 10^{-12}$) mol$^{-3}$. L$^{-1}$ and $K_{sp}^a$(Dy)= $1.2 \times 10^{-15}$ (±0.8 $\times 10^{-15}$) mol$^{-3}$. L$^{-1}$ (see ESI† for more details). Their ratio is $\sim 2400$, meaning that their concentration ratio in an equilibrated mixture of Nd$^{3+}$ and Dy$^{3+}$ should be $\sim 2400$. The ratio of $K_{sp}$ for the phosphate salts, for instance, is only about 6.5; the $K_{sp}$ values of NdPO$_4$ and DyPO$_4$ are $1.1 \times 10^{-26}$ mol$^{-2}$. L$^{-2}$ and $7.1 \times 10^{-26}$ mol$^{-2}$. L$^{-2}$, respectively.\(^4\) By comparison, it is obvious that such a large difference in the $K_{sp}$s of [Nd(dehp)$_3$] and [Dy(dehp)$_3$] is adequate for fractional precipitation. According to Eq. 5, $K_{sp}^a$, $c^{tot}(P)$, and the pH allow us to calculate $c(Ln^{3+})$, and thus, Y in Nd–and–Dy mixtures. The calculated Ys are shown in Figure 2(A) (dotted lines). For Dy, there are small differences between the experimental and calculated values, whereas the calculated Ys for Nd are much smaller than the experimental values. The $c(Nd^{3+})/c(Dy^{3+})$ ratio at equilibrium is as much as 100 unlike the calculation. Hdehp may incorporate a small amount of Nd$^{3+}$ when it forms coordination polymer with Dy$^{3+}$, i.e. coprecipitation results in their smaller separation performance than the calculation. Because coprecipitation reaction is kinetically controlled, the separation efficiency can be enhanced by changing mixing rate and concentrations of metal ion and ligand. We will discuss ways to achieve a higher performance in more detail in the near future.

The precipitation behaviors of [Nd(dehp)$_3$] and [Dy(dehp)$_3$] in a binary ethanol-water solution considerably differ from each other. This offers a simple and environmentally friendly separation of Dy and Nd from their mixture by fractional precipitation. The comparison between calculated and experimental data suggests that an optimization of the conditions will enhance the separation efficiency.

References

Dy is exclusively precipitated as a coordination polymer from Nd-and-Dy mixture.