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Environmentally 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.[1,2] 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 ions (Ln^{3+}), including Nd^{3+} and Dy^{3+}, requires large amounts of organic solvent and energy. Thus, a precipitation method can be a powerful technique when the solubilities of the resulting solids are low and the solubility products (K_{sp}) are sufficiently different for partitioning. For example, the selective precipitation of lanthanide sulfates from Ln^{3+}–transition metal ion mixtures (*e.g.*, Sm^{3+} from a Sm^{3+} and Co^{2+} mixture, or Nd^{3+} from a Nd^{3+} and Fe^{3+} mixture) was suggested to recover Ln from magnet scraps.[3] In the case of Nd/Dy separation by the formation of inorganic salts such as phosphate,[4]

hydroxides,[5] and oxalate,[6] quite similar K_{sp} values between Nd and Dy do not offer the efficient separation.

   Our research[7–10] has focused on coordination polymers (CPs) formed with di(2-ethylhexyl) phosphoric acid ($PO(OH)(OCH_2CHC_2H_5C_4H_9)_2$, 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 $LnCl_3$ and Hdehp in a binary ethanol-water mixture.[7] Powder X-ray diffraction analysis indicated that [$Ln(dehp)_3$] has monoclinic structure and its lattice parameters vary only slightly with a kind of Ln^{3+}.[10] Because the stability of complex between Hdehp and Ln^{3+} is governed by charge density of ions, Hdehp prefers to form a mononuclear complex with Dy^{3+} rather than Nd^{3+} in solvent extravtion systems.[11] 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 K_{sp} are given by the following equations:

$$Ln^{3+} + 3dehp^- \rightleftharpoons [Ln(dehp)_3] \qquad (1)$$
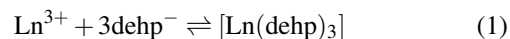
$$
\begin{aligned}
K_{sp} &= a(Ln^{3+}) \cdot a(dehp^-)^3 \\
&= \left[\gamma(Ln^{3+}) \cdot c(Ln^{3+})\right] \cdot \left[\gamma(dehp^-) \cdot c(dehp^-)\right]^3 \quad (2)
\end{aligned}
$$

where a, γ, 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:

$$Hdehp \rightleftharpoons H^+ + dehp^- \qquad (3)$$
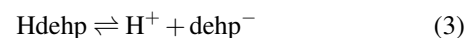
In order to assess the difference in the formation of [$Nd(dehp)_3$] and [$Dy(dehp)_3$], their precipitation equilibria

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 concentration 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 addition. 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,[12] 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 precipitates were decomposed in a HNO$_3$ solution under microwave irradiation (see ESI† for more details). Ln and P concentrations in each phase were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Shimadzu ICPE9000).

The Ln (= Nd or Dy) and P contents of the solids were consistent with the calculated values based on the chemical formulas of [Ln(dehp)$_3$], indicating that Ln precipitates as a coordination polymer from binary ethanol-water solutions (Tables S2 and S3, ESI†). From the Ln^{3+} concentrations in the solutions ($c(Ln^{3+})$), the precipitation yields ($Y/\%$) were calculated according to the following equation,

$$Y = \frac{c^i(Ln^{3+}) - c(Ln^{3+})}{c^i(Ln^{3+})} \times 100 \qquad (4)$$

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 different 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 ligand concentration (entries d and f–h in Table 1. The horizontal axes represent the values measured after equilibrium had been attained. As expected, Hdehp preferentially forms precipitates 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
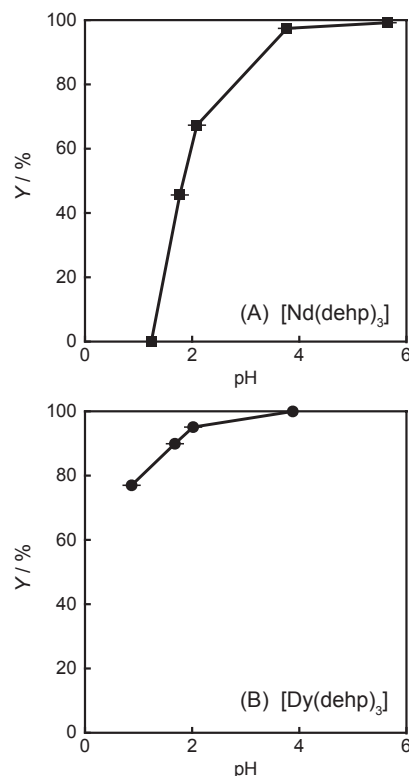

Fig. 1 Y (%) of [Nd(dehp)$_3$] (A) and [Dy(dehp)$_3$] (B) from NdCl$_3$ and DyCl$_3$ solutions, respectively, as a function of pH. The initial concentrations (c^i) of Ln^{3+} (Ln^{3+}=Nd^{3+} or Dy^{3+}), Nadehp, and H$^+$ are 0.02, 0.06, and 0.05–0.24 M, respectively.

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 separation efficiency. Figure 2(B), which compares the Ys at pH = ~0.8 as a function of $c^{tot}(P) = c(dehp^-) + c(Hdehp)$, as measured by ICP-OES analysis, indicates that Dy is exclusively precipitated regardless of $c^{tot}(P)$ under conditions in which $c^i(Nadehp)$ is in the range from 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 solutions. 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 $\gamma(Ln^{3+})$, $\gamma(dehp^-)$, and $\gamma(Hdehp)$ are unity, the apparent solubility product, hereinafter described as K_{sp}^a, is given by;

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

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

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

From the $c^{tot}(P)$ and $c(Ln^{3+})$ values (shown in Figure S2, ESI†), K_{sp}^a(Nd)= $2.9 \times 10^{-12}(\pm 0.8 \times 10^{-12})$ mol$^4 \cdot$ L^{-4} and K_{sp}^a(Dy)= $1.2 \times 10^{-15}(\pm 0.8 \times 10^{-15})$ mol$^4 \cdot$ L^{-4} (see ESI† for more details). Their ratio is ~2400, meaning that their concentration ratio in an equilibrated mixture of Nd^{3+} and Dy^{3+} should be ~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 1.1×10^{-26} mol$^2 \cdot$ L^{-2} and 7.1×10^{-26} mol$^2 \cdot$ L^{-2} , respectively.[4] By comparison, it is obvious that such a large difference in the K_{sp}^as 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 an 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.
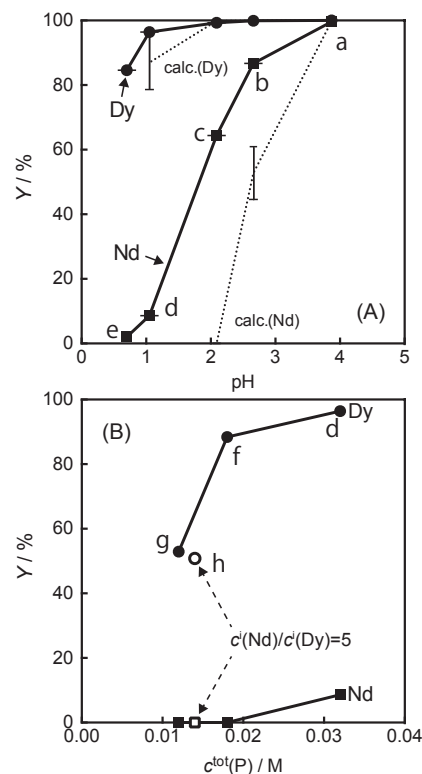

Fig. 2 Ys (%) of [Nd(dehp)$_3$] and [Dy(dehp)$_3$] from a NdCl$_3$ or DyCl$_3$ mixture as a function of pH (A) and $c^{tot}(P)$ (B). Both maximum and minimum K_{sp}^a values (Table S2, ESI†) were employed to calculate Y (dotted lines in (A)).

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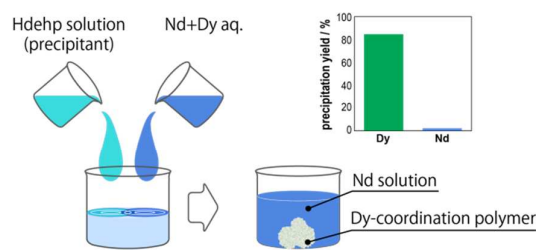
Dy is exclusively precipitated as a coordination polymer from Nd-and-Dy mixture.