Solvent Extraction Research and Development, Japan, **Vol. 30, No 2, 121 – 128 (2023)**

Extraction Behavior of Lanthanoids(III) with Bis(2-ethylhexyl)phosphoric Acid into Ionic Liquid 1-Butyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)imide

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(Received October 21, 2022; Accepted December 24, 2022)

The extraction behavior of 14 trivalent lanthanoids (Lns) with bis(2-ethylhexyl)phosphoric acid (HR) into a typical hydrophobic ionic liquid (IL), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, was investigated. The extraction is so slow that a shaking time of more than 36 hours is needed to reach extraction equilibrium. Compared to the extraction system using toluene as an extraction solvent, the IL extraction system has higher extraction ability for all Lns and higher selectivity for some couples of Lns (e.g., Ce/La and Tb/Gd). The dependences of the distribution ratio on the aqueous pH and the HR concentration suggest that the main extracted species are neutral $LnR_3(HR)_3$ for light and middle Lns and Tb, but anionic $LnR_4(HR)_2^-$ and $LnR_5(HR)^{2-}$ for heavy Lns (except for Tb). The addition of 1-octanol as a phase stabilizer decreases the extractability of Lns, which can be explained in terms of interaction between 1-octanol and HR dimer.

1. Introduction

Lanthanoids (Lns) have been used in a wide range of industries due to their unique magnetic, optical, and electrical properties [1,2]. The chemical properties of Lns are remarkably similar to each other, and their mutual separation is generally difficult. The solvent extraction systems using acidic organophosphorus compounds, such as bis(2-ethylhexyl)phosphoric acid (HR), are known to have a high separation selectivity for Lns and practically utilized for their mutual separation [3-5].

In recent years, ionic liquids (ILs) have been attracting attention as extraction solvents from their environmental-friendliness and unique extractability [6-8]. For example, unlike conventional organic molecular solvents, ILs have ability to extract charged chemical species through ion-exchange and ion-pair extraction with the constituent ions of IL [9-11]. The extraction of Lns using ILs has been studied by many workers [12-14], but the systems using acidic organophosphorus compounds as ligands have only be reported for limited Lns and ILs [15-18]. In this study, we investigated the extraction behavior of 14 kinds trivalent Lns (except for Pm) with HR into a typical hydrophobic IL, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide. The feature of the IL extraction system with HR is discussed by comparing with the toluene extraction system with HR.

2. Experimental

2.1 Reagents and Apparatus

1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide in water-saturated state was prepared according to the previous method [10,11]. HR (Tokyo Chemical Industry, ≥95.0%), 1-octanol (Wako Pure Chemical Industries, GR grade), nitric acid (Kanto Chemical, UGR grade), and sodium nitrate (Merck, ≥99.5%) were used as purchased. Aqueous solutions of trivalent Lns, except for Tb(III), were prepared by dissolving lanthanoid oxides or nitrate in aqueous nitric acid solutions; the oxides or nitrate used were La_2O_3 (≥99.99%), $Ce(NO_3)_3{\cdot}6H_2O$ (≥98.0%), Pr_6O_{11} (≥99.95%), Nd_2O_3 (≥99.95%), Sm_2O_3 (≥99.95%), Eu_2O_3 (≥99.95%), Gd_2O_3 (≥99.95%), Dy_2O_3 (≥99.95%), Ho_2O_3 (≥99.95%), Er_2O_3 (≥99.95%), Tm_2O_3 (≥99.95%), Yb_2O_3 (≥99.95%), and Lu_2O_3 (≥99.95%) from Kanto Chemical or Wako Pure Chemical Industries. Aqueous solutions of Tb(III) were prepared from commercial standard solutions (Wako Pure Chemical Industries). Water was deionized and further purified using a Simplicity Water Purification System (Millipore).

A Taitec SR-1N reciprocal shaker and a Kubota 2010 tabletop centrifuge with an RS-240 swing rotor were used for extraction experiments. The concentration of Lns in the aqueous phase after extraction was determined with a PerkinElmer Avio 500 ICP-OES instrument. The aqueous phase pH was measured with a Horiba F-23 or F-73 pH meter equipped with a Horiba 6261-10C glass electrode. An Anton Paar DMA35n oscillating U-tube density meter was used for density measurements.

2.2 Procedure

The aqueous solutions containing some trivalent Lns, each concentration of which ($[\mathrm{Ln}]_{\mathrm{init}}$) was 1.0×10^{-5} mol dm^{-3}, was prepared; the pH (1.0 – 3.0) and the ionic strength (1.2 mol dm^{-3}) were adjusted with nitric acid and sodium nitrate. The IL solution containing $(0.67 - 1.8) \times 10^{-2}$ mol dm^{-3} HR and 5.0%(w/w) 1-octanol were also prepared. Here, 1-octanol was added as a phase stabilizer, without which a white precipitate-like third phase formed at the interface after extraction. The aqueous and IL solutions were placed in a centrifuge tube, where the volume ratio of the aqueous phase to the IL phase ($V_{\mathrm{aq}}/V_{\mathrm{IL}}$) was adjusted to 5; the volume of the IL phase was calculated from the mass using the density of the water-saturated IL phase (1.38 g cm^{-3}). The tube was mechanically shaken at 220 strokes min^{-1} for 0.5 – 48 hours at 25.0 °C. After phase separation by centrifugation, the aqueous phase pH and Ln concentration ($[\mathrm{Ln}]_{\mathrm{aq}}$) were measured. The distribution ratio of each Ln was determined by the following equation:

$$D = ([\mathrm{Ln}]_{\mathrm{init}} - [\mathrm{Ln}]_{\mathrm{aq}}) \cdot (V_{\mathrm{aq}} / V_{\mathrm{IL}}) / [\mathrm{Ln}]_{\mathrm{aq}} \tag{1}$$

3. Results and Discussion

3.1 Dependence on shaking time

First, the effect of the shaking time on the extractability of Lns was investigated, where the concentration of HR in the IL phase was fixed to 1.0×10^{-2} mol dm^{-3}. Figure 1(a), 1(b), and 1(c) show the log D vs. shaking time plots for the IL extraction system of light Lns (La, Ce, Pr, Nd) at pH 2.4, middle Lns (Sm, Eu, Gd) at pH 1.8, and heavy Lns (Tb, Dy, Ho, Er, Tm, Yb, Lu) at pH 1.2, respectively. The D values of light Lns become constant by shaking for 1 – 12 hours, whereas shaking for more than 36 hours is required until the D values of middle and heavy Lns become constant. Although the results that the extraction is slower for heavy and middle Lns than for light Lns is consistent with the knowledge that the water substitution rate is slower for heavier Lns [19-23], the extraction of middle and heavy Lns seems very slow. For comparison,

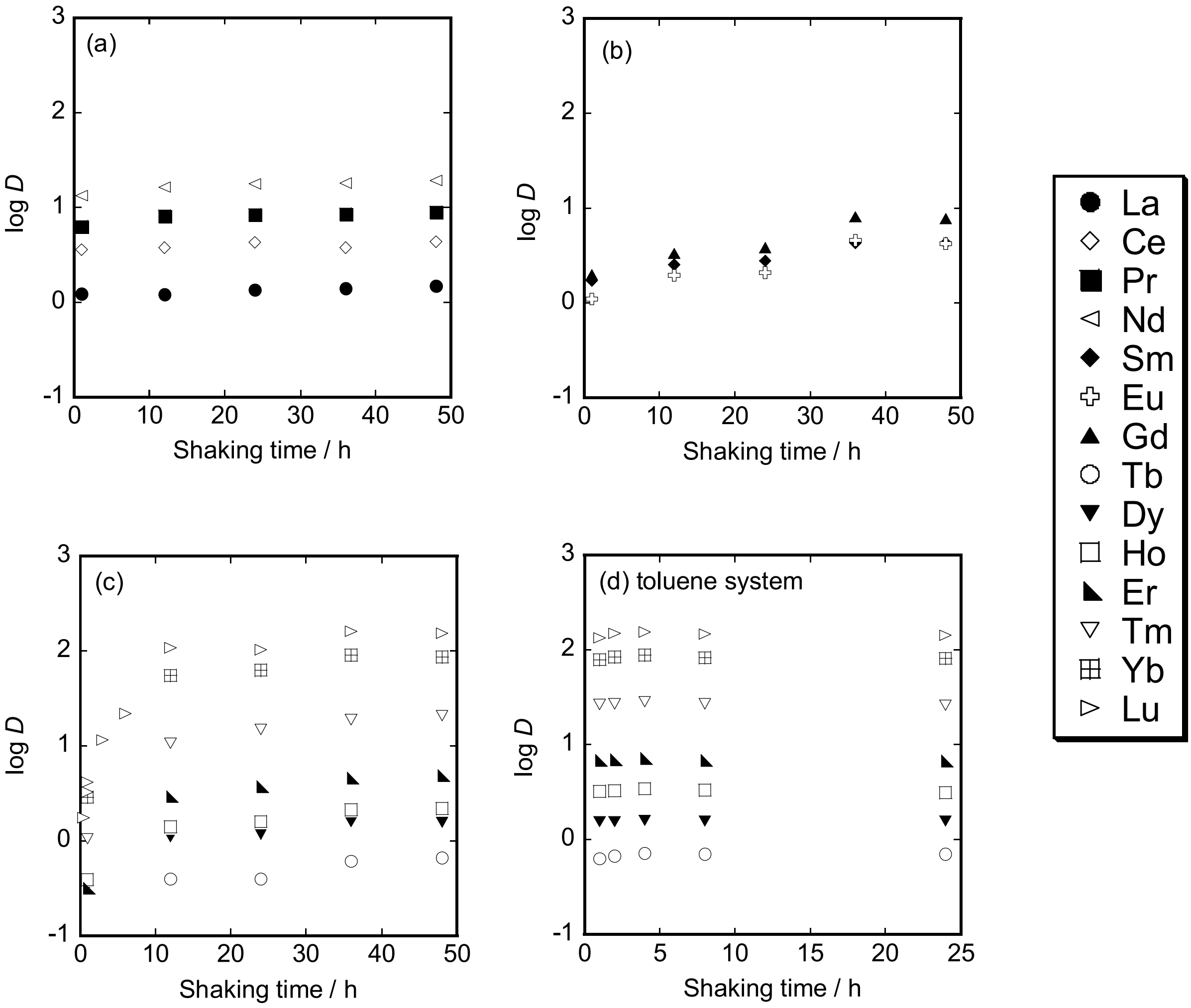

Figure 1. Dependence of distribution ratio of Ln^{3+} on shaking time. IL extraction systems: (a) light lanthanoids at pH 2.4, (b) middle lanthanoids at pH 1.8, (c) heavy lanthanoids at pH 1.2. Toluene extraction system: (d) heavy lanthanoids at pH 2.0.

similar extraction experiments were conducted for heavy Lns by using toluene as an extraction solvent in place of IL, and the results are shown in Figure 1(d). The *D* value becomes constant by shaking for about 4 hours, showing that the extraction in the toluene system is much faster than that in the IL system. The reason is not clear at this stage, but the high distribution ratio of HR between the IL phase and the aqueous phase might be the cause. We tried to determine the concentration of H in the aqueous phase after the extraction of Lns by phosphorus measurements with ICP-OES, but the phosphorous in the aqueous phase was below the limit of quantification (< 10^{-6} mol dm^{-3}).

3.2 Dependence on HR concentration and pH

In the following experiments, shaking time was fixed at 48 hours. The effect of HR concentration in the IL phase on the extraction of Lns was investigated at a constant pH. The log *D* vs log $[HR]_{IL}$ plots are

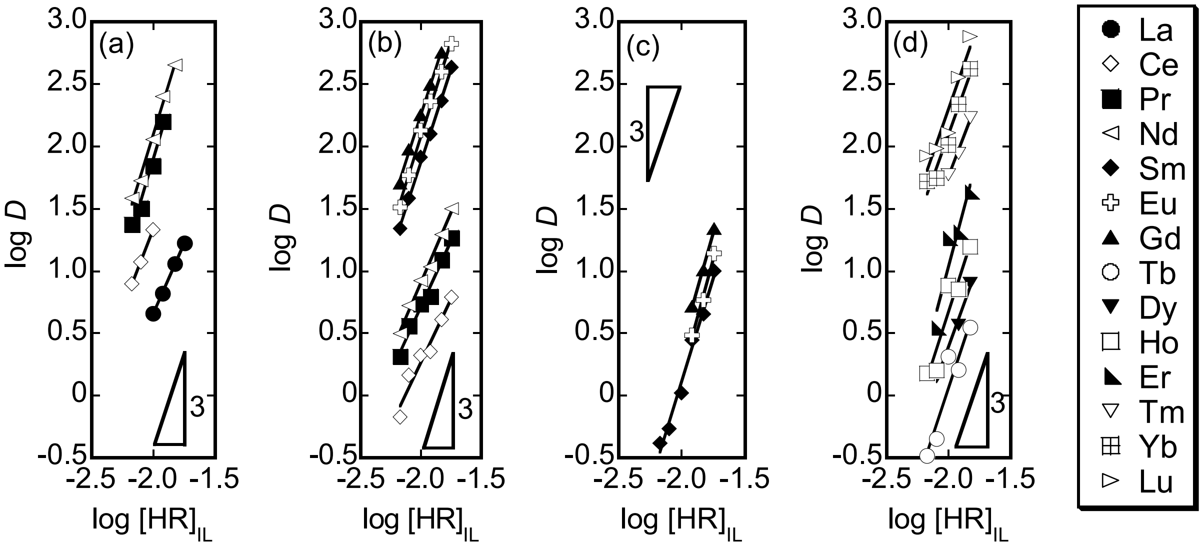

Figure 2. Dependence of distribution ratio of Ln^{3+} on HR concentration in IL phase: (a) pH 2.7, (b) pH 2.3, (c) pH 1.7, (d) pH 1.3.

shown in Figure 2, where $[HR]_{IL}$ is the initial concentration of HR in the IL phase. As shown in Figure 2, the slope of the log D vs. log $[HR]_{IL}$ plot was +3 for each Ln^{3+}. This means that the total number of HR and R^- molecules bound to Ln^{3+} is 3 when most HR molecules exist as monomers in the IL phase or that the number is 6 when HR molecules are fully dimerized in the IL phase. Considering the coordination number of trivalent Lns, the latter seems more probable as is the case in the extraction systems using nonpolar organic solvents such as toluene and heptane [3-5]. It is known that dialkylphosphoric acids form dimers even in polar organic solvents such as nitrobenzene [24].

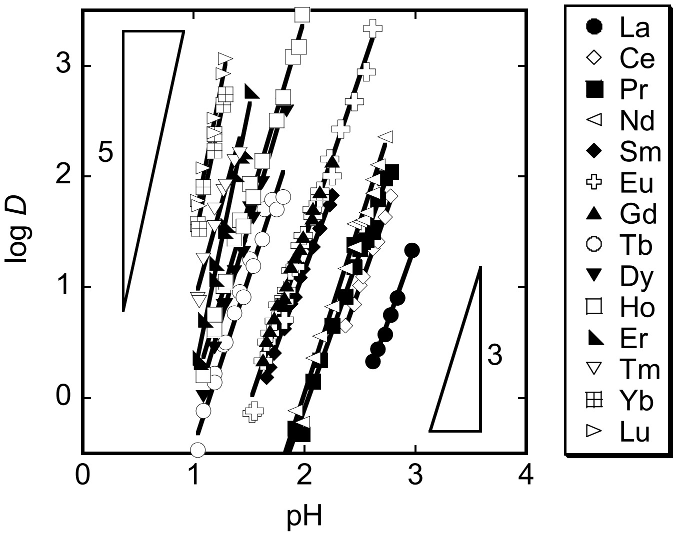

Figure 3. Dependence of distribution ratio of Ln^{3+} on aqueous pH.

The effect of aqueous phase pH at equilibrium on the distribution ratio of Lns was investigated under a constant $[HR]_{IL}$ condition (1.0×10^{-2} mol dm^{-3}). The results are shown in Figure 3. The slope of the log D vs. pH plot indicates the number of anionic ligands (R^-) bound to Ln^{3+}. According to previous reports using toluene and heptane as extraction solvents [4,5], the slope of the log D vs. pH plot is always +3. However, in this IL system, the slope of the log D vs. pH plot increased from +3 (light and middle Lns, Tb) to +4 or +5 (heavy Lns except for Tb), suggesting that the number of R^- molecules bound to Ln^{3+} is 3 - 5. Taken together with the aforementioned founding from the HR-concentration dependence of log D, it is likely that HR exists as a dimer in the IL phase and that the total number of HR and R^- bound to Ln^{3+} is 6. This suggests that light and middle Lns and Tb are extracted mainly as neutral $LnR_3(HR)_3$, and heavy Lns (except for Tb) as anionic $LnR_4(HR)_2^-$ or $LnR_5(HR)^{2-}$.

3.3 Extractability and selectivity

The extraction ability and selectivity of the IL system were compared with those of the toluene system [5] by half-extraction pH ($pH_{1/2}$) with 1.0×10^{-2} mol dm^{-3} HR. The $pH_{1/2}$ values were calculated as the pH values when $D = 1$ and are summarized in Table 1. For all Lns, the $pH_{1/2}$ value in the IL system is lower than that in the toluene system; the difference in $pH_{1/2}$ ranges from 0.54 (La) to 0.95 (Tb). This indicates that the extraction ability of this IL system is remarkably higher than that of the toluene system. In the IL system, the $pH_{1/2}$ value is smaller for Ln with higher atomic number, indicating that heavier Ln is more extractable. This is the same tendency as in the toluene system. The difference in $pH_{1/2}$ between adjacent Lns is also generally comparable in both systems. However, the $pH_{1/2}$ difference between La and Ce in the IL system (0.37) is clearly greater than that in the toluene system (0.16), indicating that the extraction selectivity for Ce over La is higher in the IL system than in the toluene system. The same is true for the selectivity for Tb over Gd; the $pH_{1/2}$ difference between Gd and Tb is 0.34 in the IL system and 0.23 in the toluene system. Additionally, in the IL system, the separation factor between the heavy Ln group and the middle or light Ln group increases with an increase of the aqueous phase pH because the slope of the log D vs. pH plots is generally higher for the former Ln group.

Table 1. $pH_{1/2}$ values of Ln^{3+} with 1.0×10^{-2} mol dm^{-3} HR.

Ln	$pH_{1/2}$ *	
	IL system	Toluene system [#]
La	2.51	3.05
Ce	2.14	2.89
Pr	2.03	2.79
Nd	1.99	2.74
Sm	1.57	2.47
Eu	1.52	2.37
Gd	1.48	2.32
Tb	1.14	2.09
Dy	1.04	1.98
Ho	0.98	1.89
Er	0.96	1.77
Tm	0.76	1.64
Yb	0.71	1.47
Lu	0.70	1.38

* pH value when $D = 1$; the values for La, Ce, Sm, Gd, Ho, Er, Tm, Yb, and Lu in the IL system are estimated by extrapolation.

[#] Calculated from the extraction equilibrium constants [5].

3.4 Effect of 1-octanol addition

In this study, 5.0%(w/w) 1-octanol (OcOH) was added in the IL phase to prevent the formation of a third phase at the liquid-liquid interface. Here, the effect of OcOH on extraction was investigated by varying the concentration in the IL phase from 2.5%(w/w) to 6.3%(w/w). In Figure 4, the log D values of Lns are shown as a function of log $[\mathrm{OcOH}]_{\mathrm{IL}}$, where $[\mathrm{OcOH}]_{\mathrm{IL}}$ is the initial concentration (molarity) of OcOH in the IL phase. The distribution ratio of each Ln decreases with an increase of the OcOH concentration, suggesting that OcOH is not involved in the extraction complex but interacts with HR. The slope of the log D vs. log $[\mathrm{OcOH}]_{\mathrm{IL}}$ plot is all about –3. From this, we propose a model in which OcOH associates with HR dimer in the IL phase:

$$\mathrm{(HR)_{2\,IL} + OcOH_{IL} \rightleftharpoons (HR)_2{\cdot}OcOH_{IL}}$$

$$K_{\mathrm{ass,21}} = [\mathrm{(HR)_2{\cdot}OcOH}]_{\mathrm{IL}} / ([\mathrm{(HR)_2}]_{\mathrm{IL}}[\mathrm{OcOH}]_{\mathrm{IL}}) \qquad (2)$$

where $K_{\mathrm{ass,21}}$ is the association constant between $\mathrm{(HR)_2}$ and OcOH in the IL phase. The extraction reaction of Ln and the equilibrium constant (K_{ex}) are expressed as follows when the slope of the log D vs. pH plot is x:

$$\mathrm{Ln^{3+}_{aq} + 3\,(HR)_{2\,IL} \rightleftharpoons LnR_{\mathit{x}}(HR)_{6-\mathit{x}}{}^{(\mathit{x}-3)-}{}_{IL} + \mathit{x}\,H^{+}{}_{aq}}$$

$$K_{\mathrm{ex}} = [\mathrm{LnR}_x\mathrm{(HR)}_{6-x}{}^{(x-3)-}]_{\mathrm{IL}}[\mathrm{H^+}]_{\mathrm{aq}}{}^{x} / ([\mathrm{Ln^{3+}}]_{\mathrm{aq}}[\mathrm{(HR)_2}]_{\mathrm{IL}}{}^{3}) \qquad (3)$$

When the D value is nearly equal to $[\mathrm{LnR}_x\mathrm{(HR)}_{6-x}{}^{(x-3)-}]_{\mathrm{IL}} / [\mathrm{Ln^{3+}}]$,

$$\log D \approx \log K_{\mathrm{ex}} + 3 \log [\mathrm{(HR)_2}]_{\mathrm{IL}} + x\,\mathrm{pH} \qquad (4)$$

From eqs. (2) and (4), the following equation is derived:

$$\log D \approx \log K_{\mathrm{ex}} + 3\,(-\log K_{\mathrm{ass,21}} - \log [\mathrm{OcOH}]_{\mathrm{IL}} + \log [\mathrm{(HR)_2{\cdot}OcOH}]_{\mathrm{IL}}) + x\,\mathrm{pH}$$

$$= -3 \log [\mathrm{OcOH}]_{\mathrm{IL}} + (\log K_{\mathrm{ex}} - 3 \log K_{\mathrm{ass,21}} + 3 \log [\mathrm{(HR)_2{\cdot}OcOH}]_{\mathrm{IL}} + x\,\mathrm{pH}) \qquad (5)$$

Since OcOH is present in large excess compared to HDEHP, if the value of $K_{\mathrm{ass,21}}$ is sufficiently large, most of the HDEHP molecules in the IL phase will be associated with OcOH; in this case, $[\mathrm{(HR)_2{\cdot}OcOH}]\mathrm{IL}$ in eq. (5) can be regarded as constant. Therefore, at a constant pH, the slope of the log D vs. log $[\mathrm{OcOH}]_{\mathrm{IL}}$ plot should be –3. This is consistent with the results in this study (Figure 4).

However, another possibility is that OcOH forms a 1:1 associate with HR monomer in IL phase as supposed:

$$\mathrm{HR_{IL} + OcOH_{IL} \rightleftharpoons HR{\cdot}OcOH_{IL}}$$

$$K_{\mathrm{ass,11}} = [\mathrm{HR{\cdot}OcOH}]_{\mathrm{IL}} / ([\mathrm{HR}]_{\mathrm{IL}}[\mathrm{OcOH}]_{\mathrm{IL}}) \qquad (6)$$

where $K_{\mathrm{ass,11}}$ is the association constant between HR and OcOH in the IL phase. From eqs. (4) and (6), the following equation is derived:

$$\log D \approx -6 \log [\mathrm{OcOH}]_{\mathrm{IL}} + (\log K_{\mathrm{ex}} + 6 \log K_{\mathrm{dim}} - 6 \log K_{\mathrm{ass,11}} + 3 \log [\mathrm{HR{\cdot}OcOH}]_{\mathrm{IL}} + x\,\mathrm{pH}) \qquad (7)$$

where K_{dim} denotes the dimerization constant of HR in the IL phase. When $[\mathrm{HR{\cdot}OcOH}]_{\mathrm{IL}}$ and pH in eq. (7) are nearly constant, the slope of the log D vs. log $[\mathrm{OcOH}]_{\mathrm{IL}}$ plot should be –6. This is inconsistent with the experimental results. The same is true if we assume that OcOH and HR form a 2:2 associate $\mathrm{(HR)_2{\cdot}(OcOH)_2}$ in the IL phase. Therefore, it is supported that HR exists as dimers in the IL phase and forms an aggregate $\mathrm{(HR)_2{\cdot}OcOH}$. As a result, the addition of OcOH has a negative effect on the IL extraction of Lns with HR.

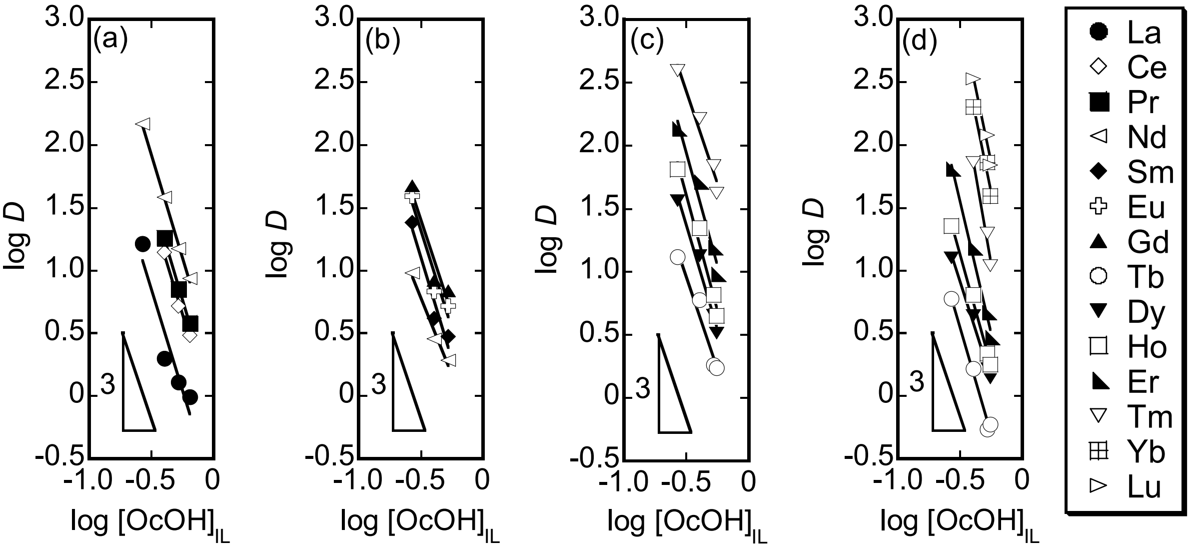

Figure 4. Dependence of distribution ratio of Ln^{3+} on initial concentration (molarity) of 1-octanol (OcOH) in IL phase: (a): pH 2.4, (b): pH 1.8, (c): pH 1.3, (d): pH 1.2.

4. Conclusion

This study showed the following characteristics for the IL extraction system of 14 trivalent lanthanoids (Lns) using 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide solution containing bis(2-ethylhexyl)phosphoric acid (HR) as an extractant:

(1) The extraction of middle Lns (Sm, Eu, and Gd) and heavy ones (Tb, Dy, Ho, Er, Tm, Yb, and Lu) is so slow and the shaking time of more than 36 hours is necessary to establish the extraction equilibrium.

(2) The extractability is sufficiently high compared to that in the toluene extraction system. The selectivity for some couples of Lns (e.g., Ce/La and Tb/Gd) is also high.

(3) The slope of the log D vs. log $[HR]_{IL}$ plot showed +3 for each Ln. On the other hand, the log D vs. pH slope is nearly +3 for light and middle Lns and Tb but about +4 to +5 for heavy Lns (except Tb). These results suggest that the extracted species are mainly neutral $LnR_3(HR)_3$ for the former Lns, but anionic $LnR_4(HR)_2^-$ and $LnR_5(HR)^{2-}$ for the latter ones. This is partially different from that in the extraction systems using nonpolar organic solvent where the extracted species are always neutral $LnR_3(HR)_3$.

(4) The addition of 1-octanol as a phase stabilizer decreases the extraction of Lns. The effect can be explained in terms of interaction between 1-octanol and HR dimer.

Acknowledgments

The ICP-OES measurements were performed at Chiba Iodine Resource Innovation Center (CIRIC), Chiba University. This work was supported by JSPS KAKENHI Grant Number 18K05165.

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