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Comparisons of the Masking Effect of Carboxylic, Amic-Acidic, and Amidic Compounds on Lanthanides and Am Complexation

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Magnitude of the masking effect of carboxylic, amic-acidic, and amidic compounds through Ln and Am extractions by tetraoctyl diglycolamide (TODGA) is compared, and their properties are studied in this paper. The compounds used are diglycol, ethylenediamine, diethylenetriamine-type, and two other amides (dioxaoctane diamide and nitrylotriacetamide). The results show that below pH 1.2, where carboxylic acids are less dissociated, amide O atoms have higher reactivity with lanthanides than O atoms in carboxyl groups. Seeing the Ln patterns (*D*(Ln) vs. their atomic number), the compounds primarily show high reactivity, with middle and heavy Ln having a higher charge density than light Ln. Four amide compounds are employed in this work. Those with tertiary amine N atoms have pH dependence on *D*(Ln) due to protonation and dissociation from amine N atoms. However, amides with no amine N atoms have no pH dependence.

1. Introduction

In reprocessing research of atomic energy fields, lanthanides (Ln), U, Pu, Am, and Cm in high-level radioactive waste should be isolated and subject to subsequent treatments (disposal, interim storage, and fuel production). The mutual separation of Ln and An [1-5] for many extractants, i.e., malonamide, carbamoylmethyl phosphine oxide tetraoctyl diglycolamide (TODGA), and alkyldiamideamine (ADDAM), have been developed and studied. Apart from the atomic energy field, the general industry has requested to study the recovery of valuable Sc, Y, Ln, and some Ln-extraction are encouraged [6-8]. The novel masking agents are less developed than the extractant studies, although they perform well on the mutual separation between two metals [9,10]. Many masking agents are commercially available; their reagents belong primarily to the carboxylic acid type. Water-soluble and amide-type reagents can be developed from extractants with a short alkyl chain but with the same central frame. Through solvent extraction experiments, the water-soluble compound works independently in the aqueous phase; there is no steric hindrance or competition with extractants in the organic phase, which might lead to significant separation factors (SFs) between the two phases. Previous papers support enlarging the SF of Ln and actinides (An) through solvent extraction by adding water-soluble compounds [9,11,12]. However, less information exists for basic research on the masking effects obtained from analogous compounds.

In this work, we took eight water-miscible compounds categorized in carboxylic acids, amic acids, and amides in diglycol, ethylenediamine, diethylenetriamine frames, and two other references of dioxaoctanediamide (DOODA) and nitrilotriacetamide (NTAamide). Figures 1 and 2 illustrate the compound structures and a rough sketch of the complexation with La. These compounds are taken into the solvent extraction of Ln and Am with TODGA, and the distribution ratio (D) variation is investigated. Comparing the D values, the magnitude of the masking effect and the complexing reactions are discussed.

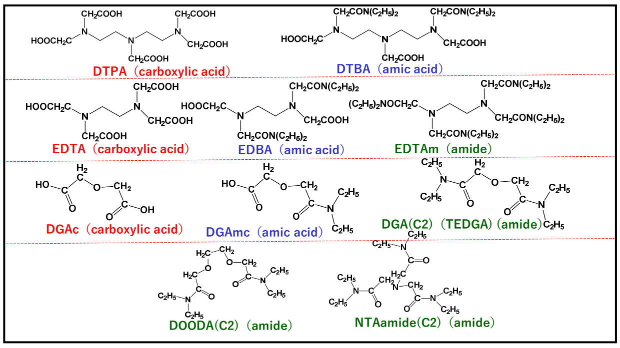

Figure 1. Masking agents used in this work (10 kinds).

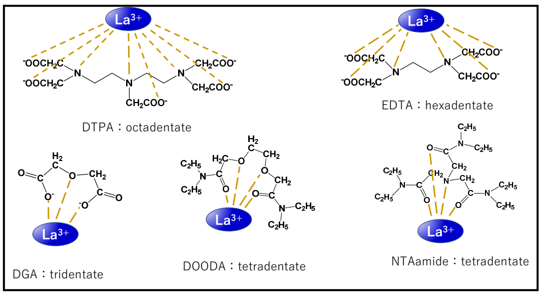

Figure 2. Complex formations presumed for La-complexants.

2. Experimental

2.1 Reagents

The hydrophilic compounds, such as tetraethyl-diglycolamide (DGA(C2), TEDGA), *N,N′,N″*-hexaethyl-nitrilotriacetamide (NTAamide (C_2)), diethylenetriamine-*N,N′,N″*-triacetic acid-*N,N″*-bis (diethylacetamide) (DTBA), *N*-diethyl-diglycolamicacid (DGAmc), *N,N′*-tetraethyl-dioxaoctanediamide (DOODA(C2)), ethylenediamine-*N,N′*-diacetic acid-*N″,N‴*-bis (diethylacetamide) (EDBA), and ethylenediamine-*N,N,N′,N′*-octaethyl-tetramide (EDTAm), and the extractant, TODGA, were purchased from Wako Pure Chemical Industries. Other reagents of analytical grade, such as HNO_3, *n*-dodecane, diglycolic acid(DGAc), ethylenediamine-*N,N,N′,N′*-tetraacetic acid (EDTA), diethylenetriamine-*N,N,N′,N″,N″*-pentaacetic acid (DTPA), the Ln solutions used for the atomic absorption spectrometry (1000 ppm, Wako Pure Chemical Industries), and ^{241}Am obtained from Isotope Products Laboratories (USA), were used as received to prepare the aqueous phase.

2.2 Solvent Extraction

An organic phase was prepared by dissolving TODGA in *n*-dodecane. A solution to dissolve a masking agent with distilled water and HNO_3 was used for the aqueous phase. A previous paper reported that ethylenediamine (en) could neutralize the acidity because N atoms in en can scavenge protons in the acid [13]. Therefore, en was used instead of NaOH to adjust the pH to maintain the salt-free principle. The pH values in the experiments are limited in the range of 1 – 2 and without compensation because of the same ionic strength (1 M (= mol/dm^3) HNO_3 or 1 M $NaNO_3$). The corresponding pairs of organic and aqueous phases with metal (1:1 volume ratio of organic and aqueous phases) were mixed and mechanically shaken at 1500 – 2000 rpm (SI-300C, As-one) or 160 rpm (FS-003, Fine) for 20 min at 25 ± 0.1 °C. After the phase separation, an aliquot of the organic sample that included Ln metals was decomposed by $HClO_4$ fuming at 200 °C for 2 h using $HClO_4$-HNO_3, and the residue was dissolved in 0.5 M HNO_3. The aqueous samples were diluted in HNO_3 before being measured using inductively coupled plasma (ICP) optical emission spectrometry (SPS3100, Seiko Instruments Inc) and ICP-mass spectrometry (SPQ 9000, Seiko-EG&G). We confirmed the complete decomposition of the organic sample by mass balance of the analytical results. The organic and aqueous samples of radioactive Am solutions were mixed in a liquid scintillation cocktail (Ultima gold, 3 mL [= dm^3]), and a liquid scintillation counter (PerkinElmer, Tri-Carb 4910TR) was used to measure their alpha activities. D was the metal concentration or radioactivity ratio between the organic ($[M]_{org}$) and aqueous phases ($[M]_{aq}$), $D = [M]_{org}/[M]_{aq}$.

3. Results and Discussion

3.1 Solubility of masking agents in water

The solubilities of 10 masking agents into the aqueous phase were confirmed by observation. DTBA, EDTAm, DGAc, DGA(C2)(TEDGA), DOODA(C2), and NTAamide(C2) are well-soluble in water. DGAmc can be soluble but maximal concentration to be 0.25 M. DTPA is well-soluble in acid, against EDTA and EDBA can be soluble in aqueous phase with high pH.

3.2 Dependence of *D* on the concentration of the masking agent and pH

Figures 3 and 4 show the dependencies of D(Ln) on the concentration of the masking agent and pH. In these figures, Ln represents the light (La, Ce), middle (Eu, Gd), and heavy (Yb, Lu) ones. All D values decrease gradually with the concentration of the masking agent and pH, indicating that Ln ions are masked in the aqueous phase at high complexant concentrations and pH conditions. Figure 5 summarizes all positive slope values, and Figures 5(a) and (b) are received from the information in Figures 3 and 4, respectively. The numbers in Figure 5 were rounded off to obtain the nearest integer. DTPA and DTBA have a constant slope of 1 in Figure 5(a), and the slope values of EDTA, EDBA, and NTAamide change from 0 (light Ln) to 1 (heavy Ln). These reagents form the maximal one-to-one (Ln-ligand) complex due to the many coordination sites (6 – 8). Four compounds (EDTAm, DGAc, DGAmc, and DGA) have a slope of 1 (light Ln) to 2 (heavy Ln). However, the slope values in DOODA vary between 0 (heavy Ln) and 1 (light Ln).

The slopes in Figure 5(b) are relatively high due to the data from the pH dependence. DTPA, DTBA, and EDTA comprise five, three, and four carboxylic acid groups, respectively, in their structures. Thus, the slope values, 3 to 5, are conceivable in Figure 5. EDBA is characterized by di-amic acids, and the slope of 2 in the pH dependence is reasonable. EDTAm is a neutral amide compound with two tertiary amino N atoms, and the slope of two comes from the dissociation of H^+ from amino N atoms protonated. DGAc shows the maximal slope of 4 because of the complexation of Ln with two DGAc molecules having two carboxylic acids. DGAmc shows a slope of 2 for heavy Ln by complexation with two DGAmc with one carboxylic acid. NTAamide has a maximal slope of 3; however, the data are unreasonable. DGA and DOODA are neutral diamides without tertiary amino N atoms. Thus, these compounds might have no pH dependence.

3.3 Comparison of *D*(M) using different complexants

Figure 6 summarizes the pH dependence on D(Am) in TODGA-masking agent extraction systems. Lowering D(Am) means the high complexing ability in this figure. We can decide the trend of the masking effect on each reagent using these D values, namely TEDGA > EDTAamide > DOODA > NTAamide–EDBA–DGAmc > DTBA–EDTA–DGAc–DTPA at pH 1.2. This result indicates that the masking effect is influenced significantly by the central frame and the functional group in the complexants. The central frames of DGA and EDTA show high complexing ability. In this pH condition, the series of masking effects concerning the functional groups is amide > amic acid > carboxylic acid. Comparing the D(Am) values with

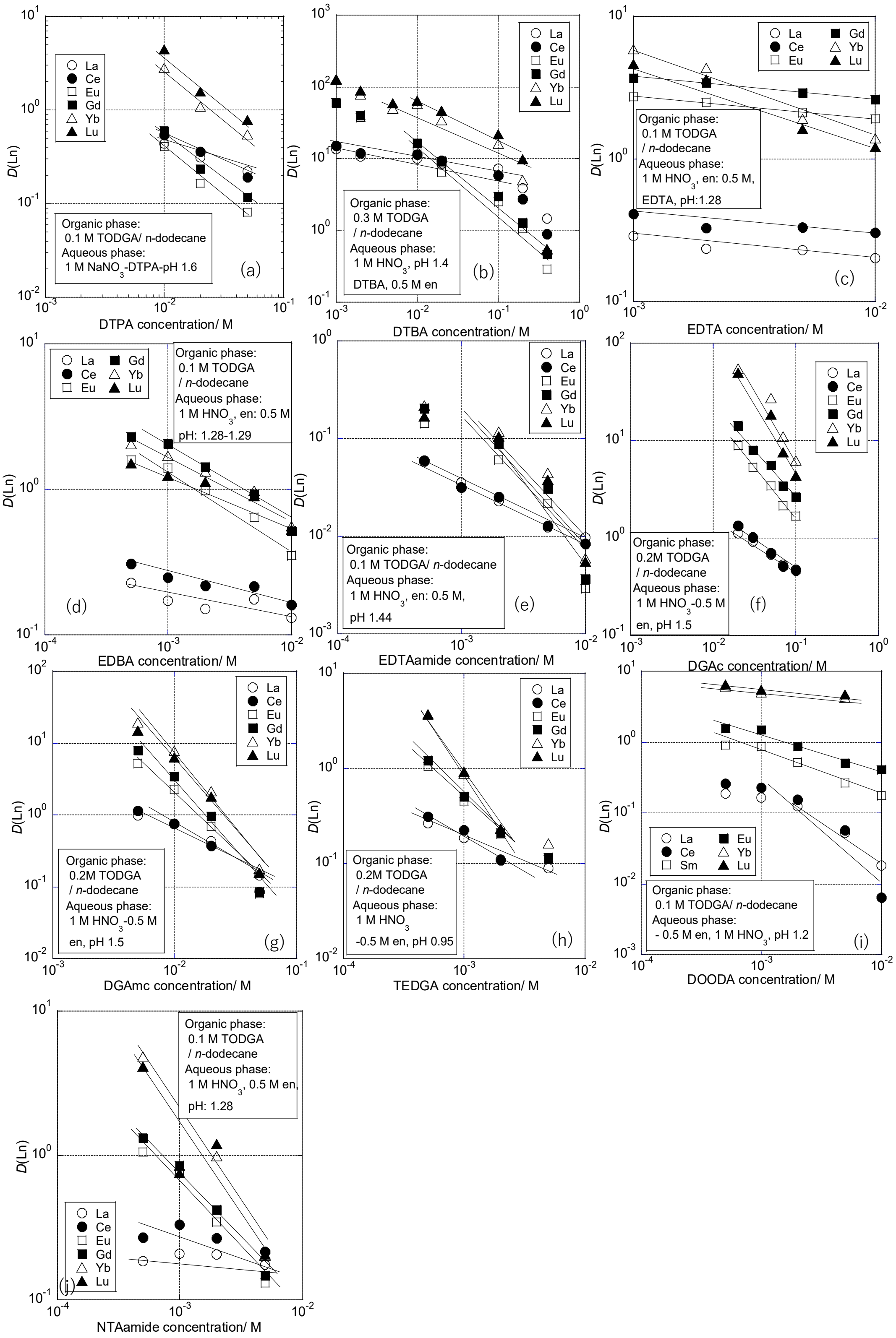

Figure 3. Dependence of *D*(Ln) on the concentration of masking agents. (a): DTPA, (b): DTBA, (c): EDTA, (d): EDBA, (e): EDTAamide, (f): DGAc, (g): DGAmc, (h): TEDGA, (i): DOODA, (j): NTAamide.

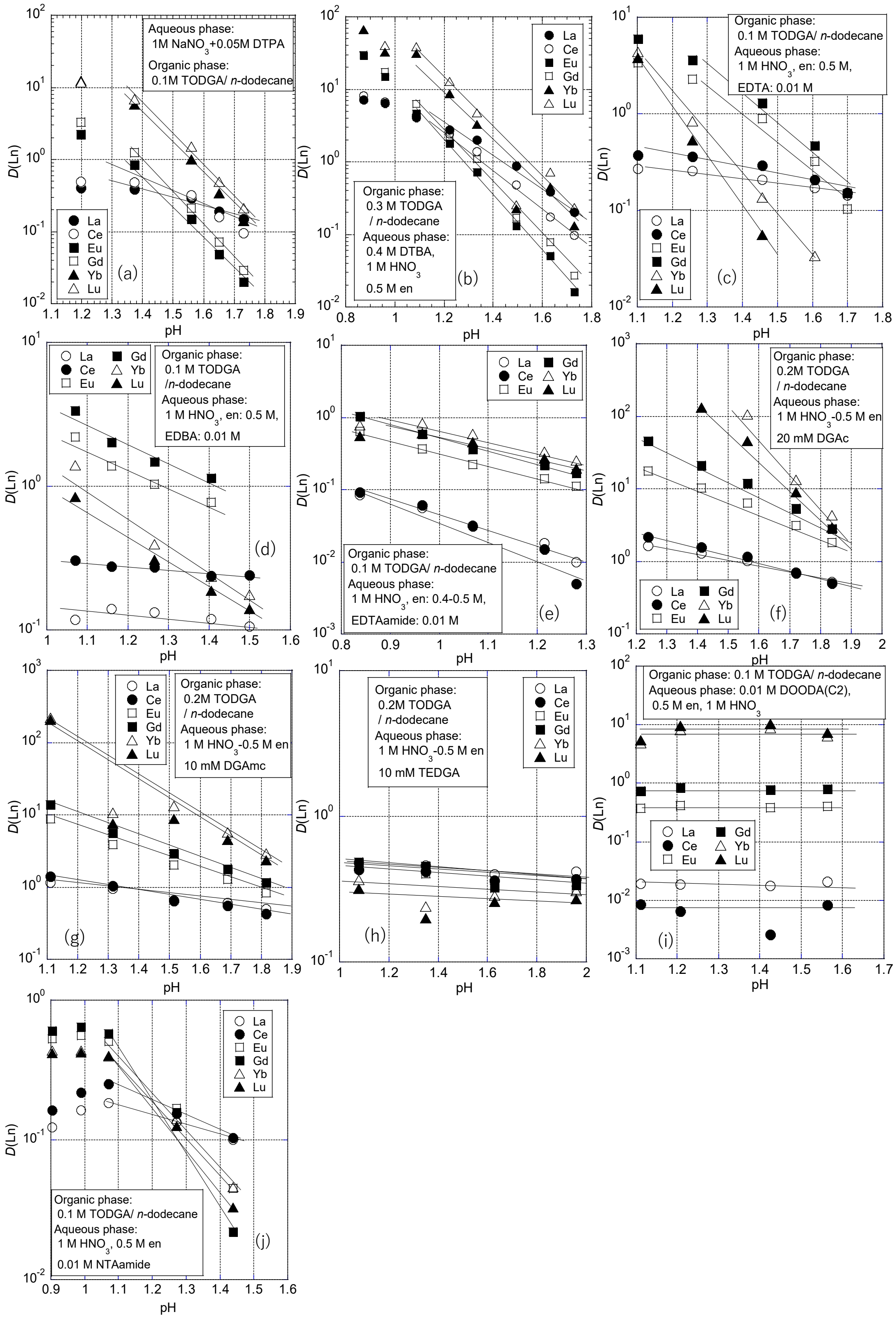

Figure 4. Dependence of *D*(Ln) on pH. (a): DTPA, (b): DTBA, (c): EDTA, (d): EDBA, (e): EDTAamide, (f): DGAc, (g): DGAmc, (h): TEDGA, (i): DOODA, (j): NTAamide.

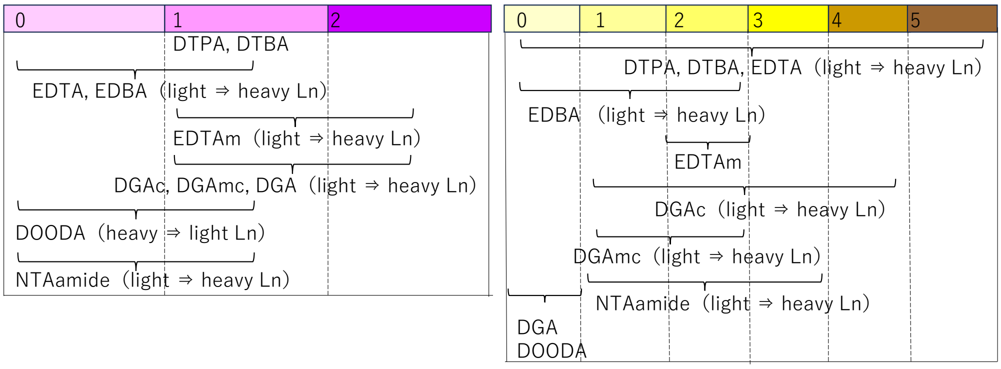

Figure 5. Slope values summarized. (a): From Figure 3, (b): From Figure 4.

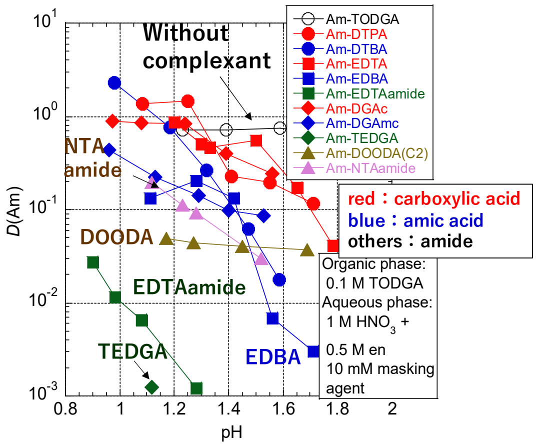

Figure 6. *D*(Am) dependence on pH.

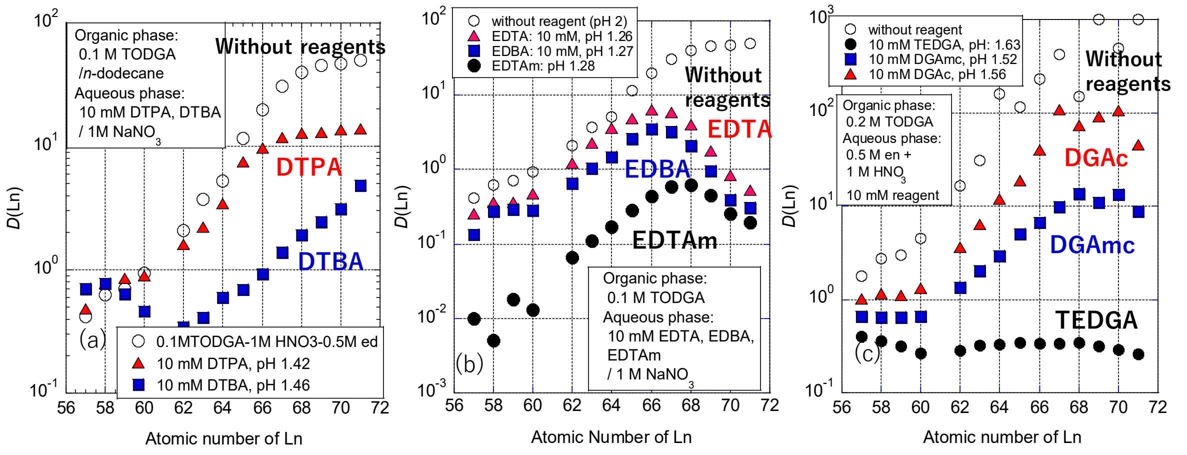

Figure 7. *D*(Ln) compared with amide, amic acid, and carboxylic acid at the same central frame. (a): DTPA, (b): EDTA, (c): DGA frames.

and without the masking agent (white circle in this figure) shows no effect for the carboxylic acids (DTPA, EDTA, and DGAc) or an amic acid (DTBA) on Am extraction below pH 1.2 due to less dissociation. Such complexants would be exposed to the strong masking effect at high pH conditions. We collect the *D*(Ln) value to observe the variations using different functional groups (carboxylic acid, amic acid, and amide) at the same central frames (DTPA, EDTA, and DGA) in Figure 7. The trends of *D*(Ln) using the different functional groups shown in Figures 7(a)–(c) are carboxylic acid > amic acid > amide, especially in heavy Ln. This result indicates that the amide group has a higher affinity to Ln than carboxylic acid at these pH regions (1.2 – 1.6). This result correlates with that in Figure 6.

3.4 Comparison of D(M) of light and heavy Ln at each complexant

We compare the complexing ability of light and heavy Ln using these reagents. Light Ln has large ionic radii with small charge density compared to middle and heavy Ln, lowering the affinity by the masking agents. Figure 8 shows the variations of Ln patterns using each masking agent with different concentrations at the same pH. A higher reagent concentration gives a lower *D*(Ln), and its decreasing rate shows the difference in light and heavy Ln. Most reagents significantly decrease in middle and heavy *D*(Ln) with their concentration—only DOODA has an opposite trend; namely, light *D*(Ln) shows a significant variation in the DOODA concentration range of 0.5 – 10 mM. This work shows that middle and heavy Ln have more affinity with organic materials than light Ln.

3.5 Reactions of water-soluble amide compounds with Nd

Four amide compounds, EDTAm, TEDGA, DOODA(C2), and NTAamide(C2), are selected to determine the pH dependence of *D*(Nd) through TODGA extraction. Figure 9 shows the results. This figure shows that although *D*(Nd) using DGA and DOODA stay constant, those for EDTAm and NTAamide have pH dependence. Since tertiary amine N atoms might be protonated under acidic conditions [14], EDTAm and NTAamide have pH dependence by the release of protons. After that, these reagents show high complexing ability without steric hindrance or positive charge. However, DGA and DOODA have no pH dependence on *D*(Nd), indicating that amide N atoms hardly protonate. The extraction and complexing reactions might be in the following equations:

$$\mathrm{Nd(TODGA)_3(NO_3)_{3org}} + \mathrm{2TEDGA_{aq}} \rightleftarrows \mathrm{Nd(TEDGA)_2{}^{3+}{}_{aq}} + \mathrm{3TODGA_{org}} + \mathrm{3NO_3{}^{-}{}_{aq}}$$

$$\mathrm{Nd(TODGA)_3(NO_3)_{3org}} + \mathrm{2DOODA_{aq}} \rightleftarrows \mathrm{Nd(DOODA)_2{}^{3+}{}_{aq}} + \mathrm{3TODGA_{org}} + \mathrm{3NO_3{}^{-}{}_{aq}}$$

$$\mathrm{Nd(TODGA)_3(NO_3)_{3org}} + \mathrm{H_2EDTAamide^{2+}{}_{aq}} \rightleftarrows \mathrm{Nd(EDTAamide)^{3+}{}_{aq}} + \mathrm{2H^{+}{}_{aq}} + \mathrm{3TODGA_{org}} + \mathrm{3NO_3{}^{-}{}_{aq}}$$

$$\mathrm{Nd(TODGA)_3(NO_3)_{3org}} + \mathrm{HNTAamide^{+}{}_{aq}} \rightleftarrows \mathrm{Nd(NTAamide)^{3+}{}_{aq}} + \mathrm{H^{+}{}_{aq}} + \mathrm{3TODGA_{org}} + \mathrm{3NO_3{}^{-}{}_{aq}}$$

4. Conclusion

Using 10 water-soluble complexants through Ln and An extraction by TODGA, the masking effects for the central frames and the functional groups in their structures are studied. The results confirmed that reagents with DGA and EDTA frames show high complexing ability. Under low pH regions (<1.2), amide has stronger complexation than acid, and most reagents have a high affinity with middle and heavy Ln with high charge density. Amide compounds with tertiary amine N atoms have pH dependence on *D* values due to protonation and dissociation.

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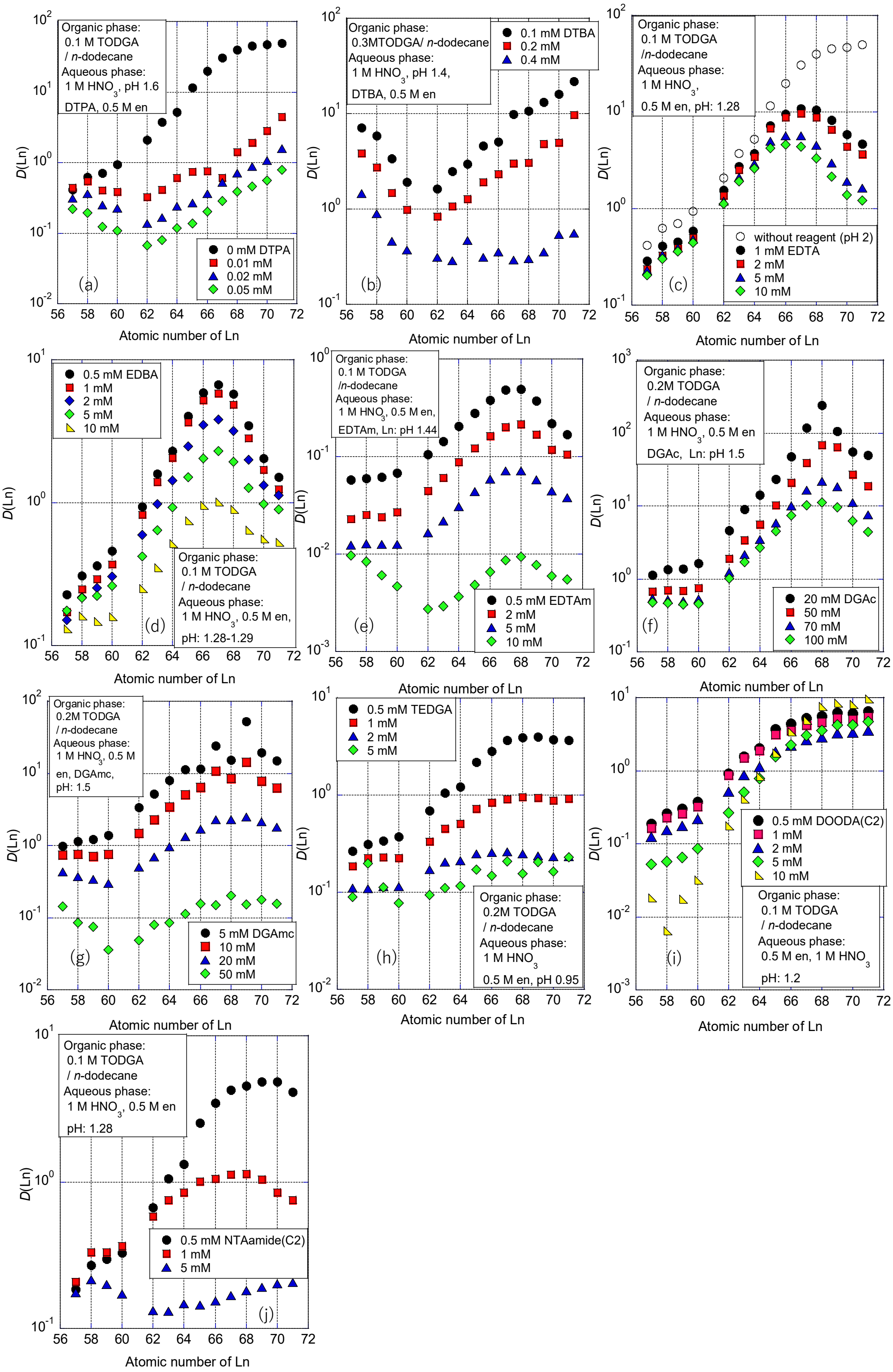

Figure 8. Variations of Ln patterns obtained in each masking agent with different concentrations. (a): DTPA, (b): DTBA, (c): EDTA, (d): EDBA, (e): EDTAm, (f): DGAc, (g): DGAmc, (h): TEDGA, (i): DOODA(C2), (j): NTAamide(C2).

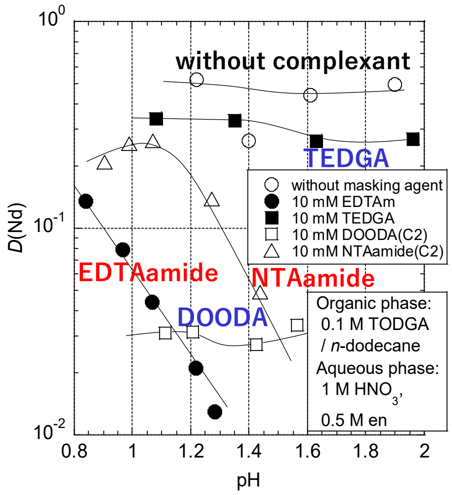

Figure 9. pH dependence on *D*(Nd) using amides through extraction by TODGA.

Declaration

The authors declare that they have no conflict of interest.

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