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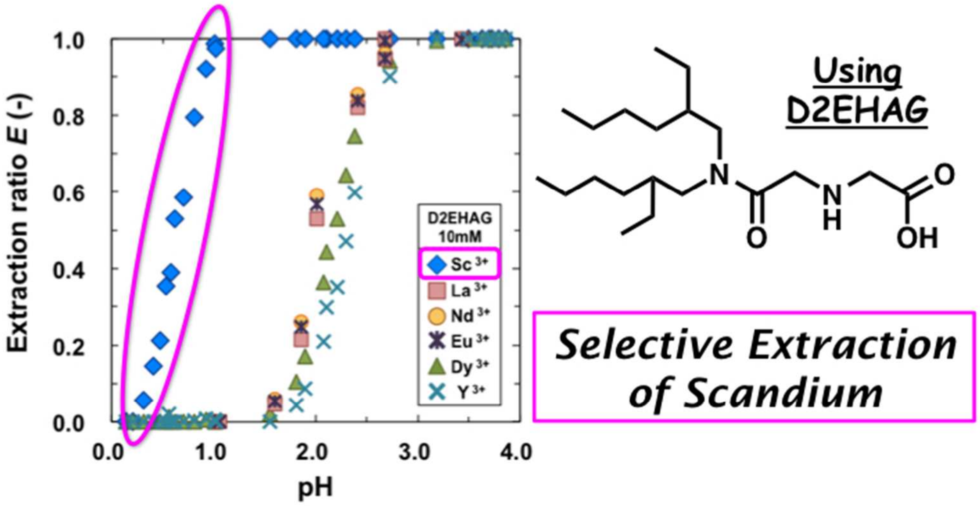

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# Selective extraction of scandium from yttrium and lanthanides with amic acid-type extractant containing alkylamide and glycine moieties

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**The liquid–liquid extraction of rare earth metal ions (scandium ($Sc^{3+}$), yttrium ($Y^{3+}$) and the lanthanides ($La^{3+}$, $Nd^{3+}$, $Eu^{3+}$ and $Dy^{3+}$)) was investigated using *N*-[*N,N*-di(2-ethylhexyl)aminocarbonylmethyl]glycine (D2EHAG). Scandium was extracted selectively from lanthanides under high acidic conditions ($0 < pH \leq 1.5$), and stripped easily using a mild acidic solution such as 1 mol $dm^{-3}$ $H_2SO_4$. By comparing the extraction behavior with *N,N*-dioctyldiglycol amic acid, which has a similar molecular structure to D2EHAG, or the commercial alkyl monocarboxylic acid extractant, Versatic 10, it was concluded that the affinity of D2EHAG to scandium was caused by a chelating effect and the size recognition ability of D2EHAG. The extraction mechanism was examined, and it was proven that the trivalent scandium ion is extracted by forming a stable metal complex with four D2EHAG molecules.**

## Introduction

Scandium is an important metal in high-technology industries because scandium and its compounds have been applied widely in the optical, electronic, aeronautical, automotive and transportation industries.[1] Demand for this metal has therefore increased in recent years. Scandium is classified as a rare earth element together with yttrium and lanthanides.[2–5] Among the rare earth elements, scandium is expensive because it is scarce and exists in low concentrations in known deposits. The metallurgical processes for its purification and recovery are complex and effective scandium separation techniques are strongly desired.

Liquid–liquid extraction (solvent extraction) is one of the most effective methods for the separation and purification of various metal ions.[6,7] In this method, the extractant used plays a key role and the selection of an appropriate extractant often determines the success of the extraction process.[7–10] A variety of extractants have been designed for the separation of critical metals including rare earth metals. Among them, industrially available organophosphorus extractants, such as di(2-ethyhexyl) phosphoric acid (D2EHPA) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A), have been used widely in commercial extraction processes.[7] However, certain disadvantages still remain in the process; a high acid concentration is required for the stripping of certain target metals, poor selectivity occurs when certain combinations of metals need to be separated from one another, and problematic phosphorous residue may result as a secondary waste.[11] Alkyl carboxylic acids such as Versatic 10 (neodecanoic acid) have also been used commercially; however, the extraction at a high pH range because of the high dissociation constant of carboxylic acid is disadvantageous in the effectiveness of the solvent extraction process.[1]

Many researchers have focused on developing novel extractants to solve these problems.[11-16] A recently developed extractant is *N,N*-dioctyldiglycol amic acid (DODGAA).[11,17]. DODGAA has a tridentate structure framed with an amide group and a carboxyl group connected by an ether chain, which results in its high affinity for rare earth metals over other common metals. More recently, we have developed another novel extractant, *N*-[*N,N*-di(2-ethylhexyl) aminocarbonylmethyl]glycine (D2EHAG)[18], which is also a tridentate ligand framed with an amide group and a carboxyl group and connected by a secondary amino group (-NH-). Like DODGAA, this compound is also free of phosphorus. Previously, we used D2EHAG to separate Co and Ni metal ions from Mn. These have been difficult to separate using conventional extractants such as D2EHPA, because of their high selectivity to Mn over Co and Ni. Thus, D2EHAG, which can change the selectivity in a combination of metal ions, would be effective for some metal ions including scandium.

In this study, we examine the extraction of rare earth metals by D2EHAG, and focus on the extraction properties of $Sc^{3+}$. The extraction behavior of $Sc^{3+}$ with D2EHAG was compared to that with other extractants, including DODGAA.

## Experimental

### *Chemicals*

The D2EHAG extractant (Fig. 1(a)) was synthesized by a two step $S_N2$ reaction as described previously.[18] Briefly, 2-chloro-*N,N*-di(2-ethylhexyl)acetamide (CDEHAA) was synthesized by adding chloroacetyl chloride to a dichloromethane solution of di-(2-ethylhexyl)amine and triethylamine followed by stirring for 3 h at room temperature. The resultant solution was washed with 0.1 M HCl and deionized water, and dried with anhydrous sodium sulfate. Yellow liquid CDEHAA was obtained after filtration and solvent removal *in vacuo*. CDEHAA (12.7 g, 0.04 mol) was added dropwise to a methanol solution of glycine (15.0 g, 0.2 mol) and sodium hydroxide (8.0 g, 0.2 mol), and the reactant was stirred for 15 h at 333 K. After removing the solvent *in vacuo,* the residue was dissolved in dichloromethane and washed with 1 mol dm$^{-3}$ $H_2SO_4$. The organic phase was washed with deionized water several times. Through the same purification step as that described for CDEHAA, a yellow viscous liquid was obtained (12.5 g, yield 87%). D2EHAG: $^1$H NMR (300 MHz, $CDCl_3$) δ 8.83 (br, 1H), 4.04 (s, 2H), 3.74–2.80 (m, 6H), 1.60 (m, 2H), 1.25 (m, 16H), 0.88 (m, 12H). $^{13}$C NMR (75.5 MHz, $CDCl_3$) δ 170.4, 165.9, 50.1, 48.2, 47.6, 37.7, 36.6, 30.5, 28.8, 23.8, 33.4, 14.1, 11.0, 10.9. Anal. calcd for $C_{20}H_{40}N_2O_3 \cdot 0.2H_2O$ C, 66.70; H, 11.31; N, 7.78. Found: C, 66.71; H, 11.30; N, 7.49.

For the comparison with D2EHAG, DODGAA (Fig. 1(b)) was synthesized as described previously.[11,17] Versatic 10 (Fig. 1(c)) was supplied by Mitsubishi Chemical Co., (Tokyo, Japan).

Scandium(III) nitrate tetrahydrate was from Nacalai Tesque Inc. (Kyoto, Japan). Dysprosium(III) nitrate pentahydrate, and yttrium(III), lanthanum(III), europium(III) and neodymium(III) nitrate hexahydrates were from Kishida Chemical Co., Ltd. (Osaka, Japan). Special grade *n*-dodecane was used as an organic solvent.

The deionized water used in the experiments was purified with a Millipore Milli-Q system. All other reagents and solvents were of analytical grade and were used as received.

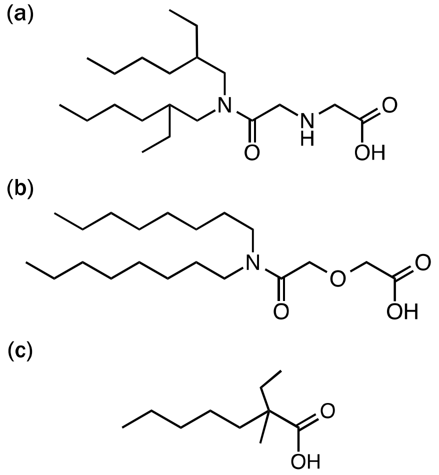

**Fig. 1** Molecular structures of extractants: (a) D2EHAG, (b) DODGAA, (c) Versatic 10

*Extraction procedure*

The extracting organic solution was prepared by dissolving the D2EHAG in *n*-dodecane, which is similar to industrial solvent kerosene. When DODGAA was used as an extractant, 1-octanol (5 vol.%) was added to the *n*-dodecane phase as a solubilizer. An aqueous solution containing 0.1 mmol dm$^{-3}$ rare earth metal ions was prepared by dissolving their nitrates in 0.1 mol dm$^{-3}$ $HNO_3$ or $NH_4NO_3$. The pH of the aqueous feed solution was adjusted by mixing these aqueous solutions and/or by adding 28 wt.% ammonia solution.

Equal volumes (5 cm$^3$) of aqueous and organic solutions were mixed in a sealed tube using a vortex mixer and shaken gently for more than 1 hour to attain extraction equilibrium at 298 K. (We experimentally confirmed that rare earth metal ions were not soluble in *n*-dodecane at all without an extractant.)

After phase separation, the metal ions in the organic phase were stripped using an acidic solution. Stripping test was performed using equal volumes (3 cm$^3$) of acidic aqueous and metal loaded organic solutions, and shaken intensely for 30 minutes after mixing solutions. The metal concentrations in the aqueous phase for the extraction and stripping tests were measured using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Optima 5300, Perkin Elmer Co, Waltham, Ma, USA). The pH was measured using a pH meter (HM-30R, DKK-TOA Co, Tokyo, Japan).

The extent of extraction and stripping of the metal ions, *E* [-] and *S* [-], respectively, were calculated using Eqs (1) and (2):

$$E = \frac{C_{\mathrm{M},org}}{C_{\mathrm{M},aq,init}} = \frac{C_{\mathrm{M},aq,init} - C_{\mathrm{M},aq}}{C_{\mathrm{M},aq,init}} \quad (1)$$

$$S = \frac{C_{\mathrm{M},aq,strip}}{C_{\mathrm{M},org,init}} \quad (2)$$

where $C_{\mathrm{M}}$ represents the total concentration of metal ion; the subscripts *aq*, *org* and *strip* denote the aqueous, organic and stripping phases, respectively, and the subscripts *init* is the initial state.

The distribution ratio *D*[-] was calculated from Eq. (3):

$$D = \frac{C_{\mathrm{M},org}}{C_{\mathrm{M},aq}} = \frac{C_{\mathrm{M},aq,init} - C_{\mathrm{M},aq}}{C_{\mathrm{M},aq}} \quad (3)$$

In a loading test, an organic phase containing 0.6 mmol dm$^{-3}$ D2EHAG and aqueous phases with varying $Sc^{3+}$ concentrations were equilibrated at a constant pH. In Job's continuous variation method, the total concentration of $Sc^{3+}$ and D2EHAG was maintained at 100 mmol dm$^{-3}$ and the extraction equilibrium was measured at various molar ratios of D2EHAG to the total concentration.

## Results and discussion

*Extraction behavior of metal ions*

The extraction behavior of the rare earth metal ions ($Sc^{3+}$, yttrium ($Y^{3+}$) and the lanthanides ($La^{3+}$, $Nd^{3+}$, $Eu^{3+}$ and $Dy^{3+}$)), by D2EHAG in *n*-dodecane is shown in Fig. 2(a) as a function of equilibrium pH in the feed aqueous phase. Metal ion extraction was promoted with increasing pH, and quantitative extraction was achieved around pH 1 for $Sc^{3+}$. The other rare earth metal ions were extracted at a pH from 1.5 to 3.0 to reach quantitative extraction. D2EHAG extracts $Sc^{3+}$

selectively and permits its efficient separation from other rare earth metal ions. The extraction behavior of the metal ions was compared with that of DODGAA, which has a similar structure to D2EHAG except that a nitrogen atom in the center of D2EHAG is replaced by an oxygen atom.

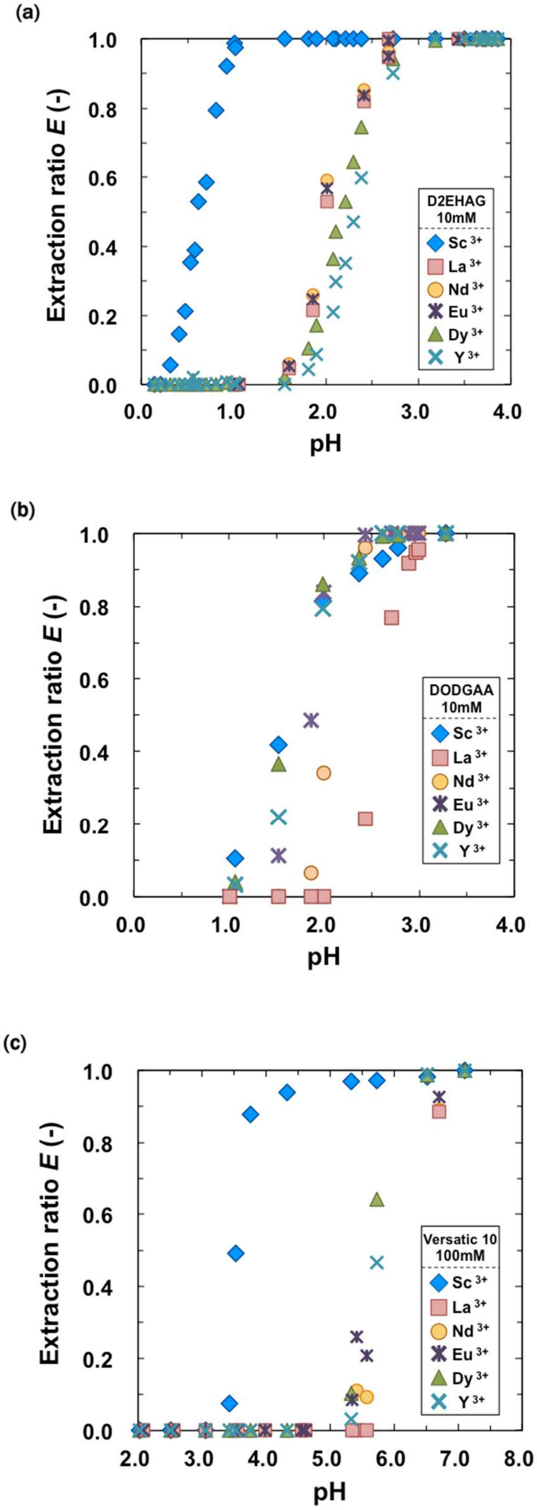

**Fig. 2** Extraction behavior of rare earth metals using (a) D2EHAG, (b) DODGAA, (c) Versatic 10

As shown in Fig. 2(b), $Sc^{3+}$ was extracted together with other rare earth metal ions such as $Y^{3+}$ and other lanthanide ions in almost the same pH range. Figure 2(c) shows the extraction behavior of rare earth metal ions by a commercial extractant, Versatic 10, which is a typical alkyl monocarboxylic acid. $Sc^{3+}$ was extracted at higher pH conditions, but its separation from other rare earth metal ions was possible. The higher extraction ability of D2EHAG or DODGAA for rare earth metal ions than that of Versatic 10 occurs because of the chelate effect created by the tridentate coordination structure with an amide and a carboxylic acid moiety. As described above, D2EHAG has a secondary amine at the center of the molecule instead of the ether oxygen of DODGAA, and this leads to its remarkably higher selectivity for $Sc^{3+}$ compared with DODGAA. DODGAA appears to recognize a metal ion with a planar structure framed by the three oxygen atoms, while D2EHAG can capture the ion with a more flexible O, N, O frame in three dimensions. Therefore D2EHAG, which can recognize ion size more closely, is considered to be advantageous in that it can form a stable complex with $Sc^{3+}$, for which the ionic radius is smaller than other rare earth metal ions.

Stripping of the rare earth metal ions from the extracting phase was also performed. Fig. 3 shows the stripping ratio, *S*, for the metal ions from the extracting phase prepared by extraction at $pH_{eq} = 3.5$. As shown in Fig. 3, quantitative recovery could almost be attained using 1 mol $dm^{-3}$ $H_2SO_4$, even for $Sc^{3+}$, which was extracted under highly acidic conditions ($0 < pH \leq 1.5$). Thus, it was demonstrated that D2EHAG can extract $Sc^{3+}$ selectively from other rare earth metal ions.

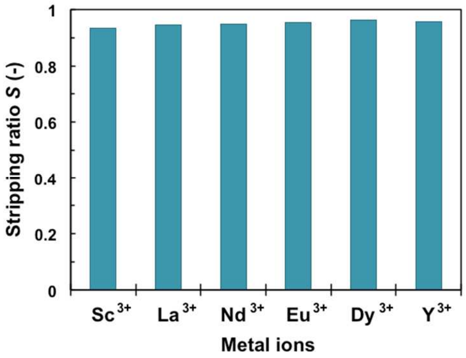

**Fig. 3** Stripping of rare earth metals using 1 mol $dm^{-3}$ $H_2SO_4$

*Extraction mechanism*

Slope analysis was conducted to investigate the extraction mechanism of $Sc^{3+}$with D2EHAG. Fig. 4(a) shows the relationship between the logarithmic distribution ratio of $Sc^{3+}$, log *D* and pH. A linear correlation with a slope of 3 was obtained, indicating that three protons are released into the aqueous phase during the extraction of a trivalent scandium ion as described later.

The effect of extractant concentration on the extraction of $Sc^{3+}$ was examined. Some alkyl monocarboxylic acids such as Versatic 10 exist as dimers in aliphatic solvents.[19,20] Therefore D2EHAG is considered to be in dimer form, $(HR)_{2,org}$, in *n*-dodecane. As shown in Fig. 4(b), plots of log *D versus* $\log(HR)_{2,org}$ yield a linear correlation with a slope of 2, suggesting that one $Sc^{3+}$ is extracted as a complex with four D2EHAG molecules into the organic phase.

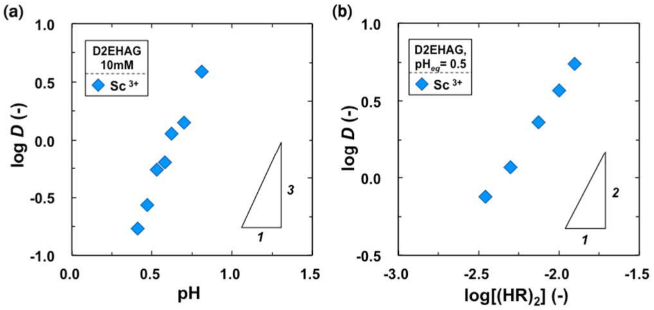

**Fig. 4** Extraction dependencies of $Sc^{3+}$ on (a) pH with 10 mmol $dm^{-3}$ D2EHAG, and (b) concentration of extractant dimer at $pH_{eq}$ = 0.5

A loading test was conducted to confirm the extraction stoichiometry. Figure 5(a) shows plots of the molar ratio of initial D2EHAG concentration to loaded $Sc^{3+}$ concentration in the organic phase as a function of the initial $Sc^{3+}$ concentration. The plots decrease with increase in initial $Sc^{3+}$ concentration to approach a constant value of 4. This result supports the idea that one trivalent scandium ion is extracted to the organic phase with four D2EHAG molecules, that is, two D2EHAG dimers. Job's continuous variation method for the extraction of $Sc^{3+}$ was examined as shown in Fig. 5(b). The extracted $Sc^{3+}$ density reached a maximum when the molar ratio of D2EHAG concentration to total concentration of $Sc^{3+}$ and D2EHAG was approximately 0.78. Therefore, the ratio of $Sc^{3+}$ to D2EHAG in the metal complex was estimated to be 1:4.

Based on the analyses, the extraction of trivalent scandium by D2EHAG can be expressed by Eq. (4):

$$\mathrm{Sc}^{3+}_{org} + 2(\mathrm{HR})_{2,org} \leftrightarrow \left(\mathrm{ScR}_3 \cdot (\mathrm{HR})\right)_{org} + 3\mathrm{H}^+ \qquad (4)$$

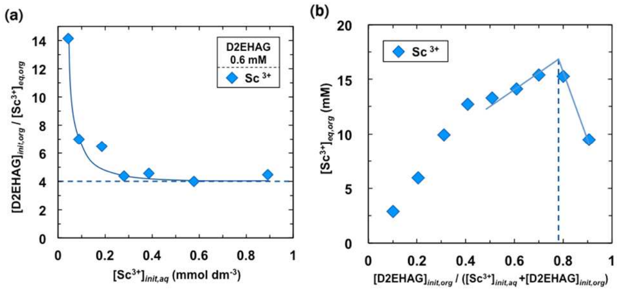

**Fig. 5** Binding-stoichiometry estimation of D2EHAG with $Sc^{3+}$ (a) loading test ($pH_{eq}$ = 3.7), (b) Job's continuous variation method ($pH_{eq}$ = 3.0)

## Conclusions

The extraction behavior of rare earth metals with a novel extractant, D2EHAG, was investigated. D2EHAG showed a significantly higher selectivity to $Sc^{3+}$ than the other rare earth metal ions. DODGAA, which has a similar molecular structure to D2EHAG, exhibited little selectivity for Sc against heavy rare earth metal ions. The high affinity of D2EHAG for $Sc^{3+}$, which has a smaller ionic radius than the other rare earth metal ions, was considered to be because of the size-recognition ability of D2EHAG with a flexible O, N, O tridentate extractant structure. Scandium was stripped easily using 1 mol $dm^{-3}$ $H_2SO_4$. D2EHAG is therefore useful for the separation and recovery of scandium.

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## Notes and references

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