Separation and Recovery of Scandium from Sulfate Media by Solvent Extraction and Polymer Inclusion Membranes with Amic Acid Extractants

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ABSTRACT: We report on the separation and recovery of scandium(III) from sulfate solutions using solvent extraction and a membrane transport system utilizing newly synthesized amic acid extractants. Scandium(III) was quantitatively extracted with 50 mmol dm−3 N-[N,N-di(2-ethylhexyl)aminocarbonylmethyl]-glycine (D2EHAG) or N-[N,N-di(2-ethylhexyl)-aminocarbonylmethyl]-phenylalanine (D2EHAF) in n-dodecane at pH 2 and easily stripped using a 0.5 mol dm−3 sulfuric acid solution. The extraction mechanisms of scandium(III) extraction with D2EHAG and D2EHAF were examined, and it was established that scandium(III) formed a 1:3 complex with both extractants (HR), that is, $\text{Sc(SO}_4)_2\text{R(HR)}_2\text{aq} + \text{H}^+ = \text{Sc(SO}_4)_2\text{R(HR)}_2\text{org} + \text{H}_2\text{SO}_4\text{aq}$ (Equation 1). The equilibrium constants of extraction were evaluated to be 4.87 and 9.99 (mol dm−3)0.65 for D2EHAG and D2EHAF, respectively. D2EHAG and D2EHAF preferentially extracted scandium(III) with a high selectivity compared to common transition metal ions under high acidic conditions (0 < pH ≤ 3). In addition, scandium(III) was quantitatively transported from a feed solution into a 0.5 mol dm−3 sulfuric acid receiving solution through a polymer inclusion membrane (PIM) containing D2EHAG as a carrier. Scandium(III) was completely separated thermodynamically from nickel(II), aluminum(III), cobalt(II), manganese(II), chromium(III), calcium(II), and magnesium(II), and partially separated from iron(III) kinetically using a PIM containing D2EHAF as a carrier. The initial flux value for scandium(III) ($J_{\text{Fe,Sc}} = 1.9 \times 10^{-7}$ mol m−2 s−1) was two times higher than that of iron(III) ($J_{\text{Fe,Fe}} = 9.3 \times 10^{-8}$ mol m−2 s−1).

1. INTRODUCTION

Recently, scandium (Sc) has been widely used in optical, electronic, and chemical industries, aerospace, nuclear technology, and other fields and its demand has continued to grow.1,2,5 Demand for Sc has been expected to increase in the future because it is also used in fuel cells.4,6 Nevertheless, Sc-rich ores are rare and the average abundance of Sc in the Earth’s crust is not high, with an average of only 22 mg kg−1.1 Therefore, efficient recovery methods for Sc are required to sustain the rapidly growing demand for this metal in the global market. Sc can be mainly recovered as a byproduct from leachates in the manufacture of other metals such as rare earths, nickel, and aluminum.1,4 However, in many cases, large amounts of undesired base metals such as iron and aluminum are codissolved along with scandium.1 Therefore, purification steps for the manufacturing of Sc are generally required.4,8

Solvent extraction (SX) has been widely used for the recovery of Sc from leachates with traditional extractants such as organophosphorus and carboxylic acids or neutral organophosphorus compounds.4 However, organophosphorus acids, carboxylic acids, and neutral organophosphorus extractants have the following drawbacks: difficulty of stripping of Sc(III),5,10 weak affinity to Sc(III),11,12 and lack of selectivity for Sc(III).13 Therefore, extractants offering high affinity and selectivity for Sc, and allowing easy stripping with acids are important for the efficient recovery of Sc.14–16 In recent years, three new amic acid extractants $\text{N-[N,N-di(2-ethylhexyl)-aminocarbonylmethyl]glycine (D2EHAG), N-[N,N-di(2-ethylhexyl)aminocarbonylmethyl]phenylalanine (D2EHAF), and N-[N,N-di(2-ethylhexyl)aminocarbonylmethyl]sarcosine (D2EHAS), and}$ have been synthesized in our laboratory and applied to the extraction of critical metals such as nickel and cobalt,17 indium and gallium,18 platinum group metals,19 and gold.20 In addition, it was found that D2EHAG can selectively extract Sc(III) from nitrate solutions containing other rare metals.
earth metals.21 In this study, we investigate the extraction of Sc(III) from sulfate solutions with amic acid extractants and compare it with the extraction of Sc(III) involving commercial extractants (i.e., D2EHPA, Versatic 10, and TOPO).

Although SX is an effective separation technique, the use of large amounts of organic diluents, which can adversely affect the environment, is required.22 In recent years, a separation technique involving the use of polymer inclusion membranes (PIMs) has attracted much attention as a green alternative to SX because organic diluents are not required.23,24 Also, much smaller amounts of extractants (often referred to as carriers) are required, thus allowing the utilization of relatively advanced extractants without significant impact on the cost of the separation process.25,26 In this technique, the extractant is anchored between the entangled chains of the base polymer and the corresponding PIMs have shown excellent transport properties and high stability.23,25 Although PIMs have already been applied to the transport of many metal ions,27–35 only a few studies on the separation of Sc(III) using PIMs have been reported so far.46–48 Successful transport of Sc(III) was reported using a PIM containing 2-thienyltrifluoroacetone (HTTA) as a carrier.46 In a previous study we have reported on the selective transport of Sc(III) from solutions of rare earth metal ions across a PIM containing a mixture of 2-ethylhexyl hydrogen (2-ethylhexyl)phosphonate (PC-88A) and Versatic 10 as the membrane carriers.47 Recently, we have also reported on the separation of Sc(III) from Y(III) and lanthanides using a PIM incorporating D2EHAG and D2EHAH.48 However, these studies have only focused on the separation of Sc(III) from rare earth metal ions, and there are no reports on the PIM-based separation of Sc(III) from other metal ions present in ore leachates such as iron and aluminum ions.

This paper reports on the performance of amic acid extractants in the selective SX and PIM-based separation and recovery of Sc(III) from sulfate solutions containing various common metal ions [i.e., Fe(III), Ni(II), Al(III), Co(II), Mn(II), Cr(III), Ca(II), and Mg(II)]. The potential of amic acid derivatives as industrial extractants and PIM carriers for Sc(III) and their mechanism of Sc(III) extraction are also discussed.

2. RESULTS AND DISCUSSION

2.1. Solvent Extraction and Stripping of Sc(III). Three amic acids (D2EHAG, D2EHAS, and D2EHAH), an organophosphorus acid (D2EHPA), a carboxylic acid (Versatic 10), and a solvating extractant (TOPO) were tested to identify suitable scandium extraction systems. The chemical structure of these extractants is shown in Figure 1. Figure 2a shows the plots of the degree of extraction for Sc(III) from its sulfate solutions with these extractants in n-dodecane as a function of the equilibrium pH in the feed aqueous solution. Extraction of Sc(III) by D2EHAG was promoted by increasing the pH, and Sc(III) was found to be quantitatively extracted around pH 2. D2EHAH, where a phenyl group was introduced in the molecular structure, showed a similar extraction behavior and the efficiency of Sc(III) extraction was improved. The pKₐ values of the carboxyl group of D2EHAG and D2EHAH are 2.89 and 2.74, respectively,48 and it is considered that this decrease in the pKₐ value as a result of the introduction of the phenyl group contributes to the improvement of the Sc(III) extraction efficiency of D2EHAH. On the other hand, quantitative extraction was not achieved by D2EHAS below pH 3. Similarly, lower extraction efficiency of D2EHAS compared to D2EHAH has been observed with respect to In(III) and Ga(III).18 These observations can be explained by the fact that the N donor atom in the center of the amic acid extractants studied plays a crucial role in the extraction of the metal ions, and it should be pointed out that the secondary amine group in D2EHAG and D2EHAH has a higher affinity to Sc(III) than the tertiary amine group in D2EHAS. D2EHPA quantitatively extracted Sc(III) even under very high acidic conditions (<pH 0.5), thus indicating a possible difficulty in stripping Sc(III). On the other hand, Versatic 10 and TOPO were found to show poor extraction ability below pH 3 where only 6–23% of Sc(III) could be extracted.

The stripping of Sc(III) from the extracting phase containing D2EHAG, D2EHAH, or D2EHPA was carried out using H₂SO₄ solutions with varying concentrations (0.5–5 mol
Figure 2b shows the plots of the degree of stripping of Sc(III) as a function of the sulfuric acid concentration. These results indicate that over 90% of Sc(III) can be stripped into a 0.5 mol dm$^{-3}$ of H$_2$SO$_4$ solution from the extraction phases containing D$_2$EHAG and D$_2$EHAF and loaded with 0.1 mmol dm$^{-3}$ of Sc(III), whereas in the case of D$_2$EHPA, stripping of Sc(III) with the same sulfuric acid concentration was unsuccessful. It can be concluded that D$_2$EHAG and D$_2$EHAF are more suitable for the recovery of Sc(III) than conventional extractants because of the high efficiency of the corresponding extraction and stripping processes.

2.2. Extraction Equilibrium of Sc(III). In order to elucidate the extraction mechanism of Sc(III) with D$_2$EHAG and D$_2$EHAF, slope analysis was performed. In the cases of 10 mmol dm$^{-3}$ D$_2$EHAG or D$_2$EHAF organic phases, the corresponding plots of log $D$ of Sc(III) versus equilibrium pH were both linear with slopes of 0.98 and 1.04, respectively (Figure 3a). These values indicated that one hydrogen ion was released into the aqueous solution during the extraction of Sc(III) with D$_2$EHAG and D$_2$EHAF.

Figure 3b shows the plots of the distribution ratio of Sc(III) as a function of the concentration of the sulfate ion in the cases of 10 mmol dm$^{-3}$ D$_2$EHAG or D$_2$EHAF in n-dodecane. The plots of log $D$ versus log $[\text{SO}_4^{2-}]$ were linear with slopes of 1.36 and 1.39 for D$_2$EHAG and D$_2$EHAF, respectively, indicating that 1.5 mol of the dimer (i.e., three extractant molecules) were involved in the formation of the Sc(III)-extractant complex.

The extraction stoichiometry of Sc(III) to D$_2$EHAG or D$_2$EHAF in the corresponding metal complexes was determined to be 1:3.

Based on the results outlined above, the extraction equilibrium of Sc(III) with D$_2$EHAG or D$_2$EHAF, relevant to high aqueous SO$_4^{2-}$ concentrations (e.g., $>0.1$ mol dm$^{-3}$) such as those typical for Sc(III) sulfate leachates, can be described by the following equation

$$\text{Sc(SO}_4\text{)}_2^- + 1.5\text{[HR]_2} \rightleftharpoons \text{Sc(SO}_4\text{)}_2\text{R(HR)}_2 + \text{H}^+ + \text{SO}_4^{2-}$$

(1)

where the bars denote the species in the organic phase.

The extraction equilibrium constant $K_{\text{ex}}$ can be expressed as follows

\[ K_{\text{ex}} = \frac{[\text{Sc(SO}_4\text{)}_2\text{R(HR)}_2][\text{H}^+][\text{SO}_4^{2-}]}{[\text{Sc(SO}_4\text{)}_2^-][1.5\text{[HR]_2}]} \]
\[ K_{ex} = \frac{[\text{ScSO}_4^2](\text{HR})_3[\text{H}^+][\text{SO}_4^{2-}]}{[\text{ScSO}_4^2][\text{HR}^2_2]} (2) \]

The distribution ratio of Sc(III) between the organic and the aqueous solutions is defined as
\[ D = \frac{[\text{ScSO}_4^2](\text{HR})_3}{[\text{Sc}(\text{III})][\text{ScSO}_4^2]} \times \alpha_2 \]

where \( \alpha_2 = \beta_2[\text{SO}_4^{2-}]^2/(1 + \sum_{i=1}^{2} \beta_i[\text{SO}_4^{2-}]^i) \) (i = 1–2), log \( \beta_1 = 4.04 \) [mol dm\(^{-3}\)]\(^{-1}\) and log \( \beta_2 = 5.70 \) [mol dm\(^{-3}\)]\(^{-2}\).\(^{50}\)

The mass balance for the extractant and the sulfate ion under the experimental conditions in this study is represented by the following equations
\[ ([\text{HR}]_2)_0 = ([\text{HR}]_2) + \frac{3}{2}\text{ScSO}_4^2(\text{HR})_3([\text{HR}]_2) \approx ([\text{HR}]_2) \]

\[ ([\text{SO}_4^{2-}]_0 = [\text{SO}_4^{2-}] + [\text{HSO}_4^-] + [\text{ScSO}_4^2] + 2[\text{ScSO}_4^2] + [\text{ScSO}_4^2][\text{HR}]_2 \]

\[ [\text{SO}_4^{2-}] \approx \frac{[\text{SO}_4^{2-}]_0}{K_a + [\text{H}^+]} \]

where \( K_a = [\text{H}^+][\text{SO}_4^{2-}] / [\text{HSO}_4^-] = 1.02 \times 10^{2} \) [mol dm\(^{-3}\)].\(^{51}\} ([\text{HR}]_2)_0 and \([\text{SO}_4^{2-}]_0\) refer to the initial concentrations of the extractant and the sulfate ion in the organic and aqueous phases, respectively.

By combining eqs 1–6, the following expression for log \( D \) can be derived
\[ \log D = \log \left( \frac{([\text{HR}]_2)_0^{1.5} \alpha_2 (K_a + [\text{H}^+])}{K_a [\text{H}^+][\text{SO}_4^{2-}]_0} \right) + \log K_{ex} \]

(7)

The experimental results for both D2EHAG and D2EHAF were plotted according to eq 7 (Figure 4) and fitted by a linear equation. A correlation coefficient of 0.95 and 1.02 was obtained for D2EHAG and D2EHAF, respectively, indicating that the extraction equilibria of Sc(III) with the two extractants can be described by eq 1. The extraction equilibrium constants (\( K_a \)) for Sc(III) with D2EHAG or D2EHAF (i.e., 4.87 and 9.99 [mol dm\(^{-3}\)]\(^{0.3}\), respectively) were obtained as the intercepts of the corresponding lines with the ordinate (Figure 4).

It should be pointed out that at low sulfate concentrations (i.e., <0.1 mol dm\(^{-3}\)) the dominant Sc–sulfate complex is \( \text{ScSO}_4^2^- \) (Figure 3d). Under such conditions, which are not relevant to sulfate Sc(III) leachates, log \( D \) is independent of the sulfate concentration as observed in Figure 3c. This result suggests the following extraction stoichiometry at low sulfate concentrations
\[ (\text{ScSO}_4^2^- + 1.5[\text{HR}]_2 + \text{ScSO}_4^2(\text{HR})_2 + \text{H}^+ \]

(8)

2.3. Extraction Selectivity of D2EHAG and D2EHAF for Sc(III) and Common Metal Ions. Solvent extraction of various metal ions [i.e., Sc(III), Fe(III), Ni(II), Al(III), Co(II), Mn(II), Cr(III), Ca(II), and Mg(II)] was performed using D2EHAG and D2EHAF. The interference of Si(IV) was not studied because it is generally not present in the sulfuric acid leachate of Sc(III).\(^{7,15,52,53}\) Figure 5 shows the plots of the degree of extraction of the metal ions listed above from a 0.1 mol dm\(^{-3}\) \( \text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{SO}_4 \) solution with 50 mmol dm\(^{-3}\) D2EHAG or D2EHAF as a function of equilibrium aqueous pH. The initial concentration of each metal ion in the aqueous phase was 0.1 mmol dm\(^{-3}\).

The degree of extraction in the case of D2EHAG followed the order: Sc(III) > Fe(III) > Ni(II) > Cr(III) > Co(II) > Al(III) > Mn(II) > Ca(II) > Mg(II), while in the case of D2EHAF the order was: Sc(III) > Fe(III) > Ni(II) > Co(II) > Al(III) > Cr(III) > Mn(II) > Ca(II) > Mg(II). For both extractants Al(III), Co(II), Mn(II), Cr(III), Ca(II), and Mg(II) were extracted less than 10% at equilibrium at pH 2 while Sc(III) was extracted quantitatively. Ni(II) was extracted less than 10% at equilibrium at pH 1.5, while over 80% Sc(III) was extracted at the same time using each extractant. The extraction of Fe(III), abundantly contained in ores, showed a similar degree of extraction as Sc(III) and up to 99% of Fe(III) was extracted at equilibrium at pH 2. These extraction results indicate that Sc(III) can be separated from the other metal ions except for Fe(III) using D2EHAG or D2EHAF.

Co-extraction of Fe(III) along with Sc(III) is often reported\(^{7,15,16}\) and separation of these metal ions is challenging because of the same charge and closer values of hydration enthalpies.\(^{54}\) Masking Fe(III) with orthophosphate\(^{51}\)
or reducing it to Fe(II) can eliminate co-extraction of Fe(III). Fe(II) is easier to separate from Sc(III) by solvent extraction with acidic extractants because it has a lower charge density than Fe(III). However, addition of a masking or reducing agent could contaminate the aqueous feed solution because they are difficult to recover after the completion of the masking/redox reaction. Furthermore, these steps make the process more costly.

2.4. Membrane Transport through a PIM Containing D2EHAF. The results from the SX selectivity experiments, outlined above, indicated that it was not possible to completely separate Sc(III) and Fe(III) thermodynamically. However, extraction and stripping kinetics of Sc(III) and Fe(III) using D2EHAF are significantly different (Figure S1). Several researchers have reported on the slow extraction rate for Fe(III), and on separation of yttrium(III), which has similar properties to Sc(III), from Fe(III) based on extraction kinetics. Kinetic PIM-based separation of UO$_2^{2+}$ from Fe(III) has also been reported. Results suggest the possibility of kinetic separation of Sc(III) from Fe(III) using a PIM containing D2EHAF. In addition, the potential of the PIMs containing D2EHAF for the separation of Sc(III) from other rare earth metal ions was already demonstrated in our previous study, where it was shown that D2EHAF was more suitable as a carrier of PIMs compared to D2EHAG in terms of selectivity for Sc(III) and membrane stability.

PIM transport experiments, therefore, were performed to investigate the possibility of separating Sc(III) from the other common metal ions [i.e., Fe(III), Ni(II), Al(III), Co(II), Mn(II), Cr(III), Ca(II), and Mg(II)] using PIMs containing D2EHAF.

Figure 6a shows the competitive transport of the metal ions mentioned above across a PIM consisting of 30 wt % CTA, 40 wt % D2EHAF, and 30 wt % 2NPOE. It was found that Sc(III) was quantitively transported from the feed to the receiving solution and was partially separated from Fe(III) kinetically. Only a small amount of the other metal ions [i.e., Ni(II), Al(III), Co(II), Mn(II), Cr(III), Ca(II), and Mg(II)] were transported through the PIM during the same period. After 96 h, the recovery factors for Sc(III) and Fe(III) were calculated as 94% and 32%, respectively.

The numerical value of first order rate constant $k$ was evaluated as the slope of ln($C_{M,0}/C_{M,t}$) versus time for the feed solution (Figure 6b). The initial flux $J_0$ and the ratio of initial flux values of Sc(III) on one hand and the other metal ions on the other, and the corresponding recovery factors were calculated (Table 1). These results demonstrated the potential of the D2EHAF-based PIM for the selective separation of Sc(III) from aqueous solutions containing other common metal ions.

Based on other PIM studies indicating the similarity between solvent extraction and membrane transport mechanisms using the same extractants and feed solutions, eq 7 was assumed to be able to explain the extraction and stripping of Sc(III) at the corresponding membrane/solution interfaces. Figure 7 shows the proposed mechanism for the transport of Sc(III) through the PIM containing D2EHAF as the carrier. It should be noted that based on results obtained by us in a previous study, the rate determining step in the overall PIM transport process is the diffusion of the Sc(III)-carrier adduct within the membrane.

![Figure 6. Transport of various common metal ions through a PIM containing 40 wt % D2EHAF, 30 wt % CTA, and 30 wt % 2NPOE. (a) Normalized metal concentrations in the feed and receiving solutions as a function of time. (b) Kinetic plots of the transport of metal ions. Experimental conditions: feed solution volume and composition—50 mL, 0.1 mmol L$^{-1}$ each of Sc(III), Fe(III), Ni(II), Al(III), Co(II), Mn(II), Cr(III), Ca(II), and Mg(II) in 0.1 mol L$^{-1}$ sulfuric acid/ammonium sulfate buffer solution adjusted to pH 3.0; receiving solution volume and composition—50 mL, 0.5 mol L$^{-1}$ H$_2$SO$_4$; membrane thickness: 54 ± 4 μm.]

![Table 1. First Order Rate Constant ($k$), Initial Flux ($J_0$), Ratios of the Initial Flux Values of Sc(III) on One Hand and Each One of Other Metal Ions Studied on the Other, and Recovery Factors (RF) for Transport Across a PIM Containing D2EHAF of the Metal Ions Studied]

| Metal   | $k$ [h$^{-1}$] | $J_0$ [mol m$^{-2}$ s$^{-1}$] | $J_{Sc(III)}/J_{Fe(III)}$ | RF $^a$ [%] |
|---------|---------------|------------------------------|---------------------------|-------------|
| Sc(III) | 6.67 × 10$^{-2}$ | 1.9 × 10$^{-7}$               | 94                        |             |
| Fe(III) | 3.57 × 10$^{-2}$ | 2.3 × 10$^{-8}$               | 32                        |             |
| Ni(II)  | 1.40 × 10$^{-3}$ | 4.8 × 10$^{-9}$               | 39.3                      | <0.1        |
| Al(III) | 9.40 × 10$^{-8}$ | 2.6 × 10$^{-8}$               | 74.1                      | <0.1        |
| Co(II)  | 4.50 × 10$^{-2}$ | 1.2 × 10$^{-8}$               | 16.1                      | <0.1        |
| Mn(II)  | 2.90 × 10$^{-3}$ | 8.5 × 10$^{-9}$               | 23.0                      | <0.1        |
| Cr(III) | 4.90 × 10$^{-3}$ | 1.7 × 10$^{-8}$               | 11.2                      | <0.1        |
| Ca(II)  | 2.00 × 10$^{-3}$ | 5.7 × 10$^{-9}$               | 33.3                      | <0.1        |
| Mg(II)  | 1.30 × 10$^{-3}$ | 3.7 × 10$^{-9}$               | 51.2                      | <0.1        |

$^a$Recovery factors after 96 h of transport.

![Figure 7. Proposed mechanism for the transport of Sc(III) through the PIM containing D2EHAF.]

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3. CONCLUSIONS

The results obtained in this study demonstrate that the recently synthesized two amic acid extractants D2EHAG and D2EHAF allow easier extraction and stripping of Sc(III) in comparison with frequently used industrial extractants such as Versatic 10, TOPO and D2EHPA. Sc(III) was quantitatively extracted with D2EHAG or D2EHAF from 0.1 mol dm\(^{-3}\) sulfate solutions (pH > 2) and stripped from the extracting phases quantitatively using a 0.5 mol dm\(^{-3}\) H\(_2\)SO\(_4\) solution. The extraction of Sc(III) with D2EHAG and D2EHAF (HR) can be described by the following stoichiometric equation: 

\[
\text{Sc(SO}_4\text{)}_{2n}\overset{\text{aq.}}{\rightleftharpoons} \text{Sc(SO}_4\text{)}_{2n}\overset{\text{org.}}{\rightleftharpoons} + \text{H}^{+} + \text{SO}_4^{2-}\overset{\text{aq.}}{\rightleftharpoons}. \quad \text{D2EHAG and D2EHAF also allowed the efficient separation of Sc(III) from sulfate solutions containing a variety of common base metal ions. Although Sc(III) could not be thermodynamically separated from Fe(III) by solvent extraction, it was successfully separated kinetically using a D2EHAF-based PIM. The PIM composed of 30% CTA, 40% D2EHAF, and 30% 2NPOE allowed quantitative and selective transport of Sc(III) from 0.1 mol dm\(^{-3}\) sulfate feed solution at pH 3 and containing Fe(III), Ni(II), Al(III), Co(II), Mn(II), Cr(III), Ca(II), and Mg(II) ions to a receiving solution containing 0.5 mol dm\(^{-3}\) H\(_2\)SO\(_4\) solution. This result indicates that the PIM containing D2EHAF is promising for applications such as hydrometallurgical processing of ore leachates containing Sc(III) and other base metal ions. Studies aiming at improving the separation efficiency of Sc(III) from Fe(III) using actual Sc leachates will be conducted to facilitate the industrial implementation of the newly synthesized extractants and the associated PIM-based separation technology.

4. EXPERIMENTAL

4.1. Reagents. Three amic acid extractants were synthesized using the procedure described previously.\(^{17,19}\) TOPO and D2EHPA were purchased from Kanto Chemical Co., Inc. and Tokyo Chemical Industry Co., Ltd., respectively. Versatic 10 was supplied by Japan poxy resin and used as received. Scandium(III) sulfate n-hydrate was purchased from Mitsuwa Chemicals. Iron(III) sulfate n-hydrate, aluminum(III) sulfate, calcium(II) sulfate dihydrate, and magnesium(II) sulfate were purchased from Wako Pure Chemical Industries. Cobalt(II) sulfate heptahydrate, chromium(III) ammonium sulfate dodecahydrate, manganese(II) sulfate pentahydrate, nickel(II) sulfate hexahydrate, sulfuric acid, ammonium sulfate, and a special grade n-dodecane were purchased from Kishida Chemical. Cellulose triacetate (CTA) and 2-nitrophenyloctyl ether (2NPOE) were purchased from Sigma-Aldrich and Dojindo Laboratories, respectively. All of the aqueous solutions in this study were prepared in deionized water (resistivity > 18.2 \(\Omega\) cm, Millipore, Milli-Q Integral 3, Merck).

4.2. Solvent Extraction Experiments (Equilibrium Separation). The extracting organic phase containing D2EHAG, D2EHAS, D2EHAF, D2EHPA, Versatic 10, or TOPO was prepared by dissolving the corresponding extractant in \(n\)-dodecane. The aqueous solution containing 0.1 mmol dm\(^{-3}\) of each metal ion was prepared by dissolving their metal salts in 0.1 mol dm\(^{-3}\) sulfuric acid/ammonium sulfate solution. Sulfate solutions were selected because sulfuric acid is widely used in the hydrometallurgical process of Sc leaching because of its high leaching efficiency from ores and minerals\(^{5,6,9}\) and its relatively low cost. The pH was adjusted by using 0.1 mol dm\(^{-3}\) sulfuric acid and ammonium sulfate solution. Equal volumes (2.5 cm\(^3\)) of the aqueous metal solution and the organic solution containing an extractant were added in a glass centrifuge tube, mixed with a vortex mixer, and shaken (160 rpm) on a shaker for 3 h to attain extraction equilibrium at 25.0 \(\pm\) 0.5 °C. After phase separation, the organic phase was contacted with 0.1–5 mol dm\(^{-3}\) sulfuric acid solution to strip the extracted metal ions. In a loading test, equal volumes of the organic phase containing 10 mmol dm\(^{-3}\) D2EHAG or D2EHAF and aqueous phases with varying Sc(III) concentrations were equilibrated. In Job’s continuous variation method, the extraction of Sc(III) was performed at various molar ratios of the extractant to the total Sc(III) concentration. The pH in the aqueous solution was measured using a pH meter (HM-30R, DKK-TOA). The concentrations of the metal ions in the aqueous solutions were determined using an inductively coupled plasma optical emission spectrometer (Optima 8300, PerkinElmer).

The degree of extraction (\(E\)) (\%), the distribution ratio (\(D\)) (\(-\)), and the degree of stripping (\(S\)) (\%) were calculated by using eqs 9–11:

\[
E = \frac{C_{\text{M,aq,eq}} - C_{\text{M,aq,init}}}{C_{\text{M,aq,init}}} \times 100
\]

\[
D = \frac{C_{\text{M,org,eq}}}{C_{\text{M,aq,eq}}} = \frac{C_{\text{M,aq,init}} - C_{\text{M,aq,eq}}}{C_{\text{M,aq,eq}}} \times 100
\]

\[
S = \frac{C_{\text{M,aq,strip}}}{C_{\text{M,aq,init}}} - \frac{C_{\text{M,aq,eq}}}{C_{\text{M,aq,eq}}} \times 100
\]

where \(C_{\text{M}}\) represents the concentration of a metal ion and aq, org, init, eq, and strip denote the aqueous phase, organic phase, initial state, equilibrium state, and the stripping phase at equilibrium, respectively.

4.3. Membrane Transport Experiments (Dynamic Separation). PIMs were prepared by a casting method reported previously.\(^{20,28,47}\) First, 120 mg of CTA, 160 mg of D2EHAF, and 120 mg of 2NPOE were dissolved in 10 mL of dichloromethane. This membrane composition was optimized in our previous study.\(^{48}\) The solution was poured into a glass ring (7.5 cm diameter) on a glass plate, and covered with a filter paper and a watch glass for 24 h at room temperature. After evaporation of dichloromethane, the membrane was peeled off the glass plate. The average thickness of the PIMs obtained in this way was determined as 54 \(\pm\) 4 \(\mu\)m using a digital caliper (MDC-25MX, Mitutoyo). A circular disc of 45 mm in diameter was cut from the central part of the PIM and used in the transport experiments.

A transport system (PERMCELL KH-55P, Vidrex) with the PIM sandwiched between the feed and receiving compartment was used for membrane transport experiments and is shown in Figure 8.\(^{48,59}\) The membrane surface area exposed to the solutions was 4.9 \(\times\) 10\(^{-4}\) m\(^2\). The initial feed solution was prepared in the same manner as in the solvent extraction experiments. The feed and receiving solutions (50 cm\(^3\) each) were added in the two compartments of the transport system and mechanically stirred at 1200 rpm using magnetic stirrers and small cross-head magnets (8 \(\times\) 910). Water maintained at 25.0 \(\pm\) 0.5 °C using a thermostimulator was circulated through the jacket of the transport system. Samples (1 cm\(^3\)) of the feed and receiving solutions were taken at regular time intervals. The solution removed for sampling was replaced by the same.
volume of the corresponding initial solution. The concentrations of the metal ions were measured by inductively coupled plasma optical emission spectrometry (ICP-OES).

The transport kinetics $k$ (h$^{-1}$), initial flux $J_0$ (mol m$^{-2}$ s$^{-1}$), and recovery factor RF (%) were calculated by eqs 12–14, respectively.

$$\ln \left( \frac{C_{M,t}}{C_{M,0}} \right) = -kt$$

(12)

$$J_0 = \frac{V}{A} kC_{M,0}$$

(13)

$$RF = \frac{C_{M,t}}{C_{M,0}} \times 100$$

(14)

where $t$ is time (h), $C_{M,0}$ and $C_{M,t}$ are the concentrations of the metal ions in the feed aqueous solution (mol m$^{-3}$) at $t = 0$ and $t > 0$, respectively, $V$ (m$^3$) is the volume of the feed solution, and $A$ (m$^2$) is the surface area of the membranes exposed to each of the two solutions.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b02540.

Additional experimental data for the time dependence of the percentage extraction and stripping of Sc(III) and Fe(III) (PDF)

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The manuscript was written through contributions of all the authors. All the authors have given approval for the submission of the manuscript.

**Notes**

The authors declare no competing financial interest.

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