Identification of the Active Species for Scandium Extraction by Phoslex DT-8

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Air-exposed di(2-ethylhexyl) dithiophosphate (Phoslex DT-8®) has been previously shown to be able to selectively extract scandium ions from waste water produced during zirconium refining. In the absence of exposure to air, Phoslex DT-8® is not effective for scandium ion extraction, therefore, a compound produced by air-oxidation was suspected to be responsible for the selective extraction of the metal. In the present study, we employed 31P NMR spectroscopy and mass spectrometry in order to identify this active species. We revealed that a sulfur atom of Phoslex DT-8® was substituted for an oxygen atom on oxidation yielding O,O-bis(2-ethylhexyl) hydrogen thiophosphate (BOHTP). This compound was subsequently synthesized in high purity, and was confirmed to possess similar extraction capabilities for scandium as the oxidized Phoslex DT-8®.

1. Introduction

Since scandium was identified as being an excellent electrode material for solid oxide fuel cells, its demand has greatly increased [1]. The element is mainly obtained by recovery from metal mining waste water, as no Sc ores exist on Earth [2]. A variety of chelate extractants for Sc have attracted attention and their selectivities and extraction performances have been evaluated [3–8]. Sc is a hard acid and is therefore easily extracted from aqueous solution with conventional hard base extractants such as alkyl phosphorous compounds. However, most of this type of extractants combine with Sc3+ so strongly that it becomes bound to the organic phase and can’t be effectively stripped by acid [9]. It is hypothesized that a soft base type extractant in the form of an S,S-ligand would bind Sc3+ weakly, enabling the metal to be easily stripped from the loaded organic phase by acid treatment. Bis(trimethylpentyl) dithio-phosphinic acid (Cyanex 301) is the most commonly used S,S-ligand, however, in the present study, di(2-ethylhexyl)dithiophosphate (Phoslex DT-8®, I in Figure 1) was instead selected owing to its good availability in Japan. Phoslex DT-8® is manufactured by a domestic company for use as an extreme-pressure additive for lubricating oil. Whilst this compound has been
evaluated for the extraction of Ag, it has not been studied for the extraction of Sc$^{3+}$ [10]. Therefore, we investigated air-exposed Phoslex DT-8® as a potential extractant for Sc and assessed its ability to recover the metal from waste water produced in zirconium refining [11]. As brand-new Phoslex DT-8® stored under an anaerobic condition is known to have poor extractability, it was speculated that an unknown species was formed by air-oxidation with this being the active compound for Sc$^{3+}$ extraction rather than the Phoslex DT-8® itself.

In this study, we utilized $^{31}$P NMR-spectroscopy and mass spectrometry (MS) to determine that the active species produced by air exposure of Phoslex DT-8® was $O,O$-bis(2-ethylhexyl) hydrogen thiophosphate (BOHTP, II in Figure 1). In addition, BOHTP was synthesized by reacting $O,O$-bis(2-ethylhexyl) hydrogen phosphonate with elemental S and it was verified that BOHTP was able to selectively extract scandium ions.

![Figure 1. Air oxidation of Phoslex DT-8®.](image)

### 2. Experimental

#### 2.1 Reagents and chemicals

Sample 1 was commercial Phoslex DT-8®, and was supplied by SC Organic Chemical Co. Ltd., Japan, and used without further purification. Commercial Phoslex DT-8® (250 mL) was maintained at room temperature for 150 and 350 h under a stream of air at a flow rate of 1.1 L min$^{-1}$ in a gas washing bottle. The resulting samples were termed 2 and 3 for the 150 and 350 h treated samples, respectively. Chloroform-$d$ ($\text{CDCl}_3$) was purchased from Wako Pure Chemical Industries. All other reagents were of analytical reagent grade and were used as received.

#### 2.2 Measurements

$^{1}$H, $^{13}$C, and $^{31}$P NMR spectra were recorded at 500, 125, and 202 MHz, respectively, on a JNM-ECA500 spectrometer (JEOL) equipped with a variable temperature controller. The samples were dissolved in $\text{CDCl}_3$. The chemical shifts were reported in delta ($\delta$) units relative to tetramethyl silane ($\delta = 0$) as an internal standard for $^1$H and $^{13}$C. The chemical shift for $^{31}$P was calibrated with the signal of trimethyl phosphite in acetone-$d_6$ ($\delta = 140$) as an external standard. The solute concentration was approximately 60 g L$^{-1}$ and maintained at 30 °C ($\pm 0.1$ °C) during spectra acquisition.

Fourier transform-MS measurements were carried out using an Exactive mass spectrometer (Thermo Fisher Scientific) consisting of an Orbitrap analyzer and electrospray ionization (ESI) source. The experimental conditions were as follows: spray voltage, -4.0 kV; capillary temperature, 300 °C; sample flow rate, 200 μL min$^{-1}$; injection volume, 10 μL; mobile phase, methanol. All sample solutions were prepared by diluting the NMR sample solutions 2000 times with chloroform, and measurements were acquired from $m/z$ 50 to 800 in negative ion mode.

The atomic ratios for carbon and hydrogen were determined by using an organic elemental
2.3 Synthesis of O,O-bis(2-ethylhexyl) hydrogen thiophosphate (BOHTP)

BOHTP was synthesized in accordance with the method reported by Kabachnik et al. [12]. Briefly, O,O-bis(2-ethylhexyl) hydrogen phosphonate (30.6 g, 0.1 mol) and elemental S (3.2 g, 0.1 mol) were dissolved in toluene (20 g). To the reaction mixture, ammonia water (25 wt%, 10 g) was added at 30 °C or lower, and the mixture was stirred under N₂ at 30 °C for 8 h. The reaction mixture was washed twice with 40% aqueous sulfuric acid and once with water. The organic phase was condensed to yield pure BOHTP as a clear liquid (33 g, 98% yield).

The chemical structure and purity were confirmed as follows: Elemental analysis (%) for C₁₆H₃₅O₃PS found (calcd): C, 56.50 (56.77); H, 10.55 (10.42). ¹H NMR (CDCl₃, 500 MHz) δ 3.98 (m, 4H), 1.59 (m, 2H), 1.39 (m, 4H), 1.34–1.24 (m, 12H), 0.92–0.86 (m, 12H). ¹³C NMR (CDCl₃, 125 MHz) δ 70.6 (t), 70.5 (t), 40.0 (d), 30.0 (t), 29.0 (t), 23.4 (t), 23.0 (t), 14.1 (q), 11.0 (q).

2.4 Quantitative analysis by ³¹P NMR spectroscopy

For the quantitative NMR analysis, adjustments of the pulse width and relaxation delay for each sample is very important. In the ³¹P NMR measurements, the pulse width was determined using the air-exposed sample. The relaxation delay was set to ten times that of the longitudinal relaxation time (T₁) which was measured using the inversion recovery method. The inverse-gated decoupling technique was employed to carry out quantitative analysis. The π/2 pulse width, data acquisition time, and relaxation delay were 10.4 (11.4) μs, 3.23 (6.98) s, 40 (5) s, respectively, where the values in parentheses are for the ¹H NMR experiments.

2.5 Extraction procedure

Extraction was carried out using a conventional batch method in a thermostatted room at 25 °C (±1 °C). The organic phase was prepared by dissolving the chelate extractant in hexane to a concentration of 0.1 mol dm⁻³. An aqueous solution (10 mL) containing 1.0 mmol dm⁻³ of metal ion and 0.10 mol dm⁻³ of tripotassium citrate as a masking reagent of known pH was shaken mechanically with the same volume of the organic phase for 1 h. The pH of the aqueous phase was adjusted with 3 mol dm⁻³ HCl and 3 mol dm⁻³ KOH solutions. The phases were subsequently separated by centrifugation at 2000 rpm for 20 min, and the pH of the aqueous phase was measured. The metal distributed to the organic phase was stripped with 3.0 mol dm⁻³ HCl, and then the metal concentrations in the aqueous phase and the stripped HCl liquor were determined using inductively coupled plasma-atomic emission spectroscopy (Vista-Pro ICP-AES spectrophotometer, Varian).

3. Results and Discussion

3.1 Analysis of Phoslex DT-8®

¹H and ¹³C NMR measurements could not distinguish between the different chemical species as the chemical shifts were too similar. Therefore, ³¹P NMR measurements were performed in order to permit quantitative analysis. Figure 2 shows the ³¹P NMR spectra of samples 1, 2, and 3, with the most significant peaks labeled. The relative integrated values, which were normalized by the sum of the integrated areas of the peaks on each spectrum, were obtained (Table 1), and these were considered to be the ratio of the chemical species in each sample.
Figure 2. $^{31}$P NMR spectra of (a) sample 1, (b) sample 2, (c) sample 3, and (d) BOHTP. The values of the chemical shifts are indicated beside each peak. All spectra were expanded on the Y-axis for clarity.

The most intense peak at 85.5 ppm (A, Figure 2) was attributed to dithiophosphate 1. Peak B can be observed in the spectra of samples 1, 2, and 3 (Figure 2a–c), with the relative integrated values being almost the same (Table 1). This result suggests that peak B was caused by an impurity present in the Phoslex DT-8®, due to its industrial synthesis. On the other hand, peaks C and D are only present in the spectra of the air-exposed samples. The relative integrated values of peaks C and D can be seen to increase with air exposure time, while that of peak A decreased. Accordingly, it seems that dithiophosphate 1 was converted to different chemical species by exposure to air. It is known that the $^{31}$P peak from dithiophosphate is shifted upfield on substitution of one of its S atoms with an O atom, and that this shift increases further on substitution of both S atoms [13]. Therefore, the peaks C and D were attributed to the oxidized derivatives of dithiophosphate 1.

In order to elucidate the identity of this derivative, BOHTP was synthesized as a potential candidate, and its $^{31}$P NMR spectrum was obtained (Figure 2d). The chemical shift of BOHTP can be observed to differ only slightly ($\pm 1$ ppm) from that of peak C in the spectra of samples 2 and 3. Moreover, we measured the concentration-dependent $^{31}$P NMR spectra of BOHTP, and found that the peak shifted upfield with increasing concentration.

To obtain a more detailed analysis, MS was carried out on each of the samples. As shown in

<table>
<thead>
<tr>
<th>Peak$^a$</th>
<th>Sample (air-exposure time)</th>
<th>$1$ (0 h)</th>
<th>$2$ (150 h)</th>
<th>$3$ (350 h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td>94.8</td>
<td>89.1</td>
<td>74.6</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>4.6</td>
<td>4.8</td>
<td>4.3</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>0</td>
<td>6.2</td>
<td>13.5</td>
</tr>
<tr>
<td>D</td>
<td></td>
<td>0</td>
<td>0</td>
<td>4.8</td>
</tr>
</tbody>
</table>

$^a$ Peaks less than 1% are not listed.
Figure 3, the m/z 353 signal corresponding to [M-H] of dithiophosphate I was mainly observed for samples 1 and 3. In addition, the m/z 337 signal was found only for sample 3. According to the exact mass analysis, the chemical composition of the derivative was deduced to be C_{16}H_{35}O_{3}PS, which corresponds to BOHTP. It should be noted that tautomerism of P=S(OH) ⇌ P=O(SH) could occur, however, the dialkythiophosphinic acid group generally exists in its thiono form, P=S(OH) (Figure 1), in solution [13]. The possibility that the RO-P bond in (C_{6}H_{17}O)_{2}PS(SH) would cleave to form (C_{6}H_{17}O)PS(SH)(OH) on air-oxidation was considered, however, this was rejected as the m/z 242 signal corresponding to this product was not present in any of the mass spectra. Thus, the obtained MS data agreed with the hypothesis that peak C in the $^{31}$P NMR spectra was due to BOHTP. Incidentally, the signals corresponding to peak D in the $^{31}$P NMR spectra were not observed in the MS experiments, which were attributed to either the low concentration of the species or low ionization efficiency.

![Figure 3. MS spectra of (a) Sample 1 and (b) Sample 3. The peak strengths of each spectrum were normalized.](image)

The oxidation of Cyanex 301 (R_{2}P=S(SH)) to R_{2}P=S(OH) on exposure to 5 mmol dm$^{-3}$ HNO$_{3}$ has been previously reported [14]. As even a strong oxidant such as HNO$_{3}$ only brought about the monosubstitution of P=S(SH) to P=S(OH), it is unlikely that a weak oxidant such as air would be able to cause further conversion of the species. Therefore, all the evidence points toward the main product of air-exposure of Phoslex DT-8® being BOHTP (Figure 1).

### 3.2 Extractability of Sc(III) and ZrO(II) with BOHTP

Based on the above results, pure BOHTP was synthesized, and its ability to extract Sc(III) and ZrO(II) was examined. The 350 h air-exposed Phoslex DT-8® (sample 3) was also used for metal extraction for comparison purposes. As shown in Figure 4, the extraction behaviors of 3 and air-exposed Phoslex DT-8® were quite similar, although pure BOHTP gave better extractability of
Sc(III) and better selectivity for Sc(III) over ZrO(II) at all pH values examined. As reported previously, for the Phoslex DT-8® extraction system, the percent extraction of Sc³⁺ increased with increasing length of air exposure. Although the concentrations of air-exposed Phoslex DT-8® and BOHTP were set to be same at 0.1 mol L⁻¹, the concentration of BOHTP in air-exposed Phoslex DT-8® was estimated to be around 0.013 mol L⁻¹ judging from the results shown in Table 1. This difference can be ascribed to the difference in the concentration of the active species, BOHTP.

4. Conclusion

The molecular structure of the unknown active species for Sc³⁺ extraction produced in Phoslex DT-8® by air-oxidation was determined to be BOHTP by employing ³¹P NMR spectroscopy and MS. Pure BOHTP was subsequently synthesized, and demonstrated superior extractability for Sc³⁺ to that of air-exposed Phoslex DT-8®. These results demonstrate the possibility for industrial recovery of Sc from the waste water from zirconium refining.

References