

Solvent extraction of Sc(III) from sulfuric acid solution by bis(2-ethylhexyl) phosphinic acid in toluene

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(Received 2 July, revised 30 October 2001)

Liquid-liquid extraction of scandium(III) from sulfuric acid solution using bis(2-ethylhexyl) phosphinic acid (PIA-8) in toluene has been studied. The extraction of scandium(III) was found to be quantitative with 0.03 M PIA-8 in toluene in the acidic range of 0.1–0.5 M and 6.0–8.0 M H₂SO₄. The effect of the reagent concentration and other parameters on the extraction of scandium(III) was also studied. The stoichiometry of the extracted species of scandium(III) was determined on the basis of the slope analysis method. The extraction reaction proceeds *via* the cation exchange mechanism in the H₂SO₄ concentration range of 0.1–0.5 M and the extracted species is ScR₃·3HR. However, at higher acidity (6.0 M–8.0 M H₂SO₄) it proceeds by solvation. The extracted species is HSc(SO₄)₂·4HR. The temperature dependencies of the extraction equilibrium constants were examined to estimate the apparent thermodynamic functions (ΔH , ΔS and ΔG) for the extraction reaction.

Keywords: scandium(III), solvent extraction, bis(2-ethylhexyl) phosphinic acid, sulfate.

INTRODUCTION

Bis(2-ethylhexyl) phosphinic acid, commercially known as PIA-8, was originally developed for the extraction of transition metal ions from ammonium sulfate media.¹ Recent studies considered its application for the extractive separation of metals, such as the selective extraction of nickel(II) from aqueous sulfate solution containing other metals^{2–4} and the extraction of rare earths.^{5–8} However, the extraction of scandium(III) with PIA-8 from sulfuric acid solutions has not yet been reported.

Therefore, in the present work, the extraction mechanism of scandium(III) from acidic aqueous sulfate solution with PIA-8 in toluene has been studied and the stoichiometry found by slope analysis and IR spectral measurements. The effects of reagent concentration and temperature on the extraction of scandium(III) with PIA-8 are also discussed.

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EXPERIMENTAL

Apparatus and reagent

The extractant, bis(2-ethylhexyl) phosphinic acid (PIA-8) was supplied by Dai-hachi Chemical Industries, Japan and used without further purification. A known amount of scandium trioxide was treated with conc. H_2SO_4 for about 2 h. The insoluble residue was filtered off and the filtrate was standardised by a literature method.⁹ All the other chemicals used were of analytical grade. An Elico model LI-120 pH meter with a combined electrode was used for H^+ ion concentration studies and a GBC UV-Visible 911A spectrophotometer with 10 mm quartz cuvettes was employed for the absorbance measurements.

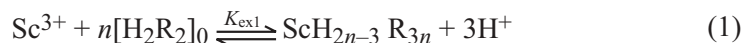
Procedure

An aliquot containing 25 $\mu\text{g}/\text{ml}$ of scandium(III) was equilibrated after adjusting the aqueous solution to the required molarity of H_2SO_4 with 3×10^{-3} M PIA-8 dissolved in toluene. The metal ions from the organic phase containing the extracted species were then stripped back with 4.0 M H_2SO_4 . The amount of metal extracted was determined by the Alizarin Red-S method given in the literature.¹⁰ All the experiments were carried out at room temperature except when the effect of temperature on the distribution equilibria was studied.

THEORY

Cation exchange reaction

It is well known that PIA-8 is present as a stable dimer in lower polarity organic solvents¹¹ and scandium exists as Sc^{3+} in aqueous media over a wide range of acidity.¹² Assuming that the overall extraction of scandium(III) from acidic sulfate solution by PIA-8 in toluene may be represented by the cation exchange reaction expressed by Eq. (1), the equilibrium constant, K_{ex1} , can be described by Eq. (2).



$$K_{\text{ext1}} = \frac{[\text{ScH}_{2n-3}\text{R}_{3n}]_0 [\text{H}^+]^3}{[\text{Sc}^{3+}] [\text{H}_2\text{R}_2]_0^n} \quad (2)$$

The distribution ratio, D , of scandium(III) is given by Eq. (3).

$$\log D = \log K_{\text{ex1}} + n \log [\text{H}_2\text{R}_2]_0 - 3 \log [\text{H}^+] \quad (3)$$

Solvation reaction

When the acidity of the aqueous phase is high, species such as $\text{HSc}(\text{SO}_4)_2$ exist. If it is assumed that extraction involves the combination of m molecules of PIA-8 dimer, H_2R_2 , which is bonded with the scandium species by the solvation reaction as,



then

$$K_{\text{ext2}} = \frac{[\text{HSc}(\text{SO}_4)_2 \cdot 2m\text{HR}]_0}{[\text{HSc}(\text{SO}_4)_2] [\text{H}_2\text{R}_2]_0^m} \quad (5)$$

and

$$\log D = \log K_{\text{ex2}} + m \log [\text{H}_2\text{R}_2] \quad (6)$$

RESULTS AND DISCUSSION

Dependence of the extraction on the sulfuric acid and reagent concentration

Sulfuric acid plays a dominant role in the extraction, hence the study of the extraction of scandium(III) was carried out in sulfuric acid media. The distribution ratio of scandium(III) decreases with increasing H₂SO₄ concentration below 3.0 M, but above this acidity the extraction curve rises (Fig. 1). It was observed that the extraction was quantitative in the H₂SO₄ concentration range of 0.1–0.5 M when the extraction pro-

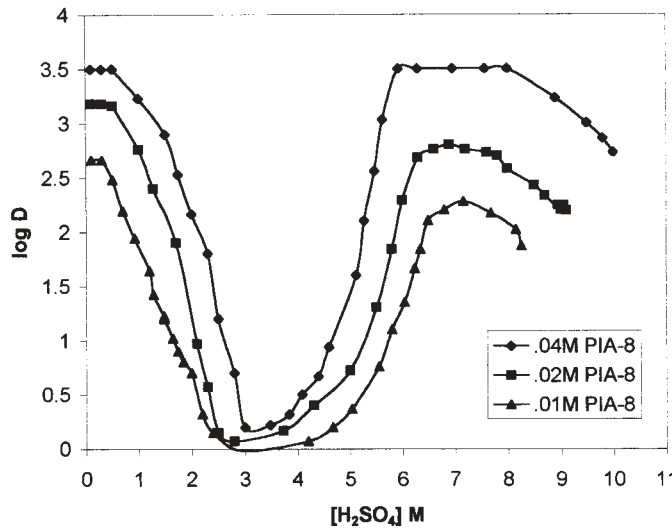


Fig. 1. Effect of sulfuric acid concentration on the extraction of scandium(III) with different concentration of PIA-8 in toluene.

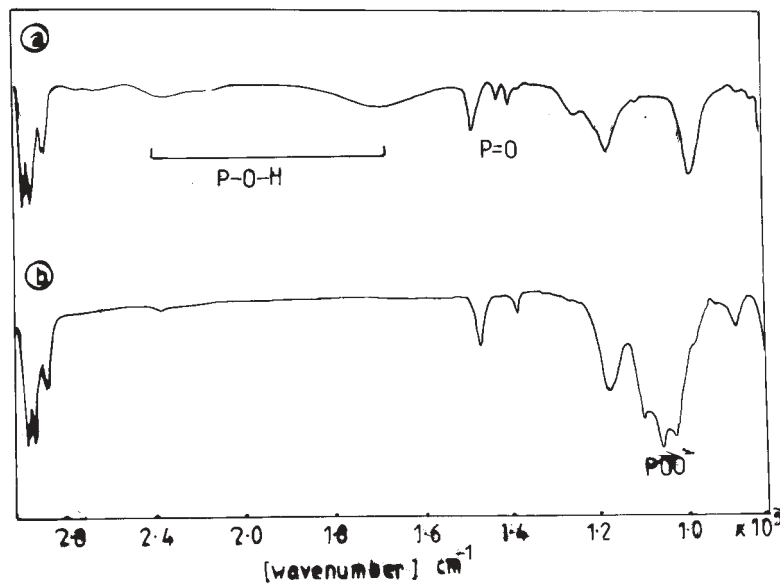


Fig. 2. IR spectra of (a) PIA-8 in CCl₄ (b) Sc-PIA-8 in CCl₄.

ceeds by the cation exchange reaction. Also, when the acidity of the solution is further increased, the extraction again becomes quantitative in H_2SO_4 concentration range of 6.0 – 8.0 M when the extraction proceeds by the solvation reaction.

Extraction of scandium(III) was carried out by varying the reagent concentration from 1×10^{-4} to 1×10^{-1} M while keeping the acidity of the aqueous solution constant at 0.3 M H_2SO_4 . It was observed that the extraction increased with reagent concentration and with 3×10^{-2} M PIA-8 dissolved in toluene gives a quantitative extraction.

IR spectral analysis

In the infrared spectra of both PIA-8 and Sc-PIA-8, (Fig. 2), the absorption bands representing C–H stretching ($2930, 2873$ and 2860 cm^{-1}) and C–H deformation (1461 and 1379 cm^{-1}) obviously appear at the same frequency without any shift. In the spectrum of Sc-PIA-8, the absorption bands between 2700 – 1740 and 965 cm^{-1} , representing aggregative hydrogen bonds and P–O–(H) bonds, are weak in intensity as compared to those observed in the spectrum of PIA-8. The P=O stretch was found at 1442 cm^{-1} with a decrease in intensity. An additional band at 1027 cm^{-1} was observed which was assigned to POO^- vibration mode. These results suggest that Sc(III) replaces the hydrogen of P–OH group from the extractant dimer and that the oxygen in the P=O group also takes part in the coordination with Sc(III). This also confirms the cation exchange mechanism.

Stoichiometry of extracted species

The stoichiometry of the extracted species was determined by analysing the experimental data. The conventional slope analyses method was used. Whether the extracted species of scandium(III) by PIA-8 in toluene is mononuclear or polynuclear was investigated by varying the initial Sc(III) concentration in the aqueous phase and determining the distribution ratio (D). It was observed that the distribution ratio was independent of the Sc(III) concentration which is clear indication that the extracted species

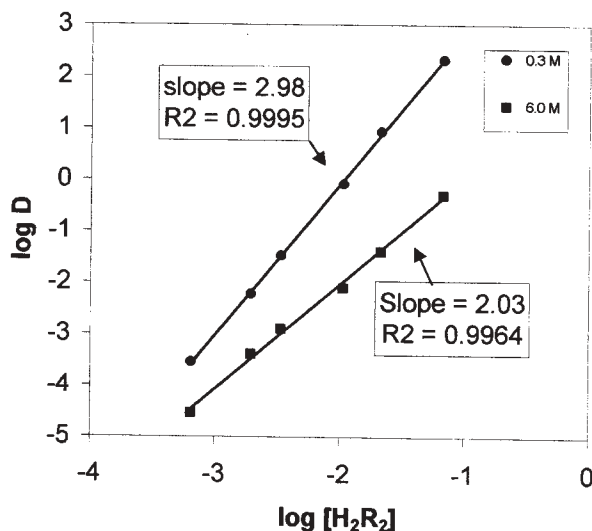


Fig. 3. Dependency of the distribution ratio of scandium(III) on the concentration of PIA-8 in toluene $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$ and 8.0 M .

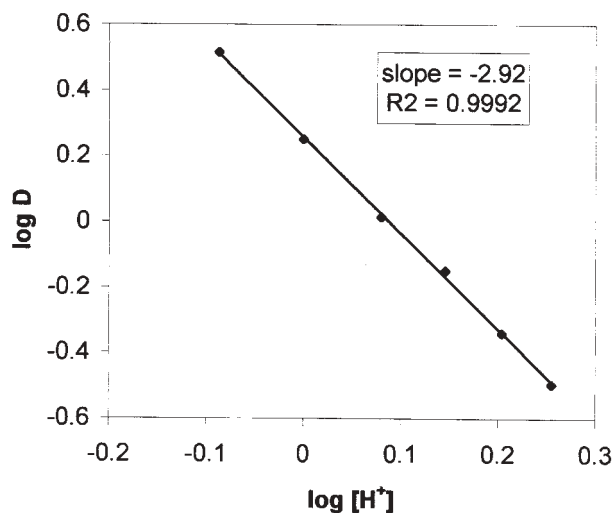


Fig. 4. Dependency of the distribution ratio of scandium(III) on the H^+ ion concentration. ($[PIA-8] = 3 \times 10^{-2} M$).

is mononuclear over the whole range of experimental study. The plot of $\log D$ versus $\log [H_2R_2]$ is a linear graph with a slope of 3.06, which is close to 3, for 0.3 M H_2SO_4 and at high acidity, 6.0 M H_2SO_4 , the plot of $\log D$ versus $\log [H_2R_2]$ also gives a straight line with a slope of 1.91, which is close to 2.0, Fig. 3. These results suggest that three ligands react with one Sc(III) ion. The relationship between $\log D$ and $\log [H^+]$ is shown in Fig. 4. The obtained slope of 3.15 is in good agreement with the predicted value of 3.0, confirming that three protons are released during the cation exchange reaction. In brief, it was observed that scandium ion forms a complex of the type $ScR_3 \cdot 3HR$ and the overall cation exchange can be expressed as follows



and solvation reaction as



Temperature effect

The change of the apparent equilibrium constant (K_{ex1}) with temperature is expressed by the Van't Hoff equation

$$\frac{\partial(\log K_{ex1})}{\partial(1/T)} = -\frac{\Delta H}{2.303 R} \quad (9)$$

The plot of $\log K_{ex1}$ versus $1/T \times 1000$ is illustrated in Fig. 5. The graph is linear with a slope of 2.40 and the enthalpy change of the extraction reaction carried out at a concentration of H_2SO_4 of 2.0 M was evaluated as $\Delta H = -45.67$ kJ/mol, which means an exothermic reaction. The free energy ΔG and entropy ΔS were also calculated from Eqs. (10) and (11), respectively, and are shown in Table I

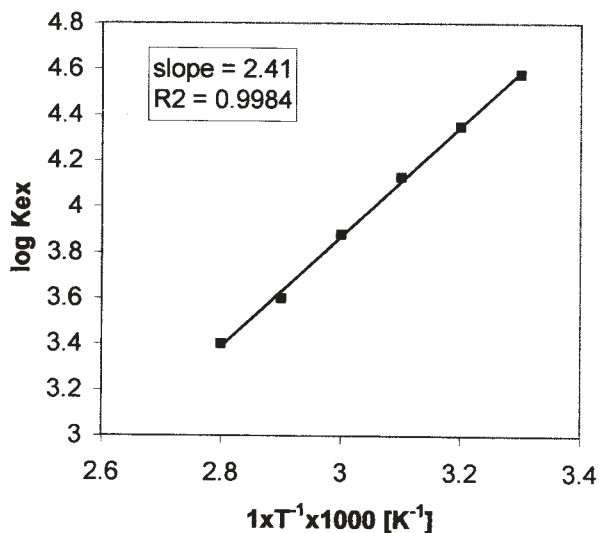


Fig. 5. Temperature effect on the extraction of scandium(III). $[\text{H}_2\text{SO}_4] = 2.0 \text{ M}$; $[\text{PIA-8}] = 3 \times 10^{-2} \text{ M}$.

TABLE I. Thermodynamic functions for the extraction of scandium(III) from sulfate solution. $[\text{PIA-8}] = 3 \times 10^{-2} \text{ M}$

Temp/K	$-\log D$	$\log K_{ex1}$	$-\Delta G/\text{kJ mol}^{-1}$	$-\Delta S/\text{kJ mol}^{-1} \text{ K}^{-1}$	$-\Delta H/\text{kJ mol}^{-1}$
303	0.201	4.600	26.64	60.05	
313	0.440	4.360	26.08	60.4	
323	0.680	4.120	25.437	60.9	45.67
333	0.932	3.880	24.697	61.9	
343	1.177	3.640	23.865	61.6	
353	1.411	3.401	22.948	62.4	

$$\Delta G = -2.303 RT \log K_{ex1} \quad (10)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (11)$$

The negative values of the change in free energy imply that the reaction is spontaneous. Further, it is clear from the experimental data that the extraction increases with increasing temperature.

CONCLUSION

The stoichiometry of the extracted species was determined by the conventional slope analysis method. From the obtained results it was observed that scandium(III) in 0.1–0.5 M sulfuric acid is extracted with PIA-8 by the cation exchange mechanism into the organic phase as $\text{ScR}_3 \cdot 3\text{HR}$ and at higher acidities it proceeds by the solvation reaction, the extracted species being $\text{HSc}(\text{SO}_4)_2 \cdot 4\text{HR}$. The apparent equilibrium constants

and the thermodynamic functions ΔH , ΔS and ΔG in the extraction of Sc(III) with PIA-8 were evaluated. The extraction is an exothermic process. The extraction of Sc(III) with PIA-8 decreases with increasing temperature.

Acknowledgment: The authors are thankful to Dai-hachi Chemical Industries, Japan for the gift of a sample of PIA-8.

NOMENCLATURE

D – distribution coefficient

ΔG – free energy change, kJ mol^{-1}

ΔH – enthalpy change, kJ mol^{-1}

HR – monomer of PIA-8

H_2R_2 – dimer of PIA-8

K_{ex1} – extraction equilibrium constant of the chemical exchange reaction

K_{ex2} – extraction equilibrium constant of the solvation reaction

ΔS – entropy change, $\text{kJ mol}^{-1} \text{K}^{-1}$

T – temperature, K

ИЗВОД

ЕКСТРАКЦИЈА Sc(III) ИЗ СУМПОРНОКИСЕЛИХ РАСТВОРА ПОМОЋУ РАСТВОРА БИС(2-ЕТИЛХЕКСИЛ)ФОСФИНСКЕ КИСЕЛИНЕ У ТОЛУЕНУ

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Проучавана је течност–течност екстракција скандијума(III) из сумпорнокихиселих раствора коришћењем раствора бис(2-етилхексил) фосфинске киселине (PIA-8) у толуену. Нађено је да је екстракција квантитативна при коришћењу 0,03 M PIA-8 у толуену из раствора сумпорне киселине у области концентрација 0,1 – 0,5 M и 6,0 – 8,0 M. Проучаван је утицај концентрације реагенса и других параметара на екстракцију скандијума(III). Стехиометрија екстраховане врсте Sc(III) одређивана је методом анализе нагиба. У области концентрација 0,1 – 0,5 M H_2SO_4 процес екстракције тече по механизму размене катјона, а екстрахована врста је $\text{ScR}_3 \cdot 3\text{HR}$. Међутим, у киселијим срединама (6,0 – 8,0 M H_2SO_4) у питању је процес солватације. Екстрахована врста је $\text{HSc}(\text{SO}_4)_2 \cdot 4\text{HR}$. Испитана је температурна зависност равнотежне константе екстракције за процену привидних термодинамичких функција (ΔH , ΔS и ΔG) процеса екстракције.

(Примљено 2. јула, ревидирано 30. октобра 2001)

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