

Extractive Separation of Scandium, Yttrium, Lanthanum, Iron, and Tin in Hydrochloric Acid System with 1,10-Bis(1-phenyl-3-methyl-5-oxopyrazol-4-yl)decane-1,10-dione

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The separation of Sc(III), Y(III), La(III), Fe(III, II), and Sn(IV, II) in hydrochloric acid solution by the extraction method with 1,10-bis(1-phenyl-3-methyl-5-oxopyrazol-4-yl)decane-1,10-dione has been investigated. The solid extracts of Sc(III) and Fe(III) have been prepared by this method, and their solubility, molar conductivity, thermal stability, UV, IR, and ^1H NMR spectra have been determined. Their extraction mechanism and the structure of the extractive are discussed, too.

Due to ferrophilic and rockphilic geochemical properties, disperse of resource, complex of components, and properties similar to those of the lanthanoids, the separation of scandium from either lanthanoids or iron is an important subject-matter extensively studied.

1,10-Bis(1-phenyl-3-methyl-5-oxopyrazol-4-yl)decane-1,10-dione (BPMOPD, H_2A) is an acyclic quadridentate β -diketone chelating agent, which has two terminal pyrazolonyls linked by a flexible aliphatic α,ω -diacyl [1]. Its chelating function is twice as large as that of the 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (PMBP) and its $\text{p}K_a$ value (3.76) is smaller than that of PMBP (4.04). So we hope it is possible to extract metal ion in strongly acidic medium. The extraction of Sc, Y, La, Fe, and Sn with this chelating agent has not been reported so far [1]. In this communication, we attempt to separate scandium from lanthanoids and some other elements by the extraction with BPMOPD under suitable conditions.

EXPERIMENTAL

Methods and Materials

The microanalysis of scandium was made by a photometer and using Arsenazo III as developer. The analysis of C, H, and N was performed with a 1106 elemental analyzer. IR spectra were measured with a Nicolet 170SX spectrometer and using KBr discs for the middle infrared region and a nujol for the far infrared one. ^1H NMR spectra were measured with an FT-80A spectrometer using CDCl_3 as solvent and TMS as internal standard. The thermal

analyses were recorded with a PCT-2 thermo-balance in the atmosphere.

The ligand H_2A was prepared as described in literature [1]. The product obtained are the colourless needle crystals, yield 91 %, m.p. = 134–135 °C. UV spectrum (CHCl_3), $\lambda_{\text{max}}/\text{nm}$: 271, 242. IR spectrum, $\tilde{\nu}/\text{cm}^{-1}$: 1625 m $\nu(\text{C}=\text{O})$, 1552 s $\nu(\text{C}-\text{O})$. ^1H NMR spectrum, δ : 10.60 (s, br, 2H, $\text{C}=\text{C}-\text{OH}$), 7.78 (m, 10H, phenyl), 2.74 (t, 4H, $=(\text{OH})\text{CH}-$), 2.47 (s, sh, 6H, CH_3), 1.40–1.65 (m, 12H, CH_2).

Extraction

10 cm^3 of the solution of Sc^{3+} or Y^{3+} , La^{3+} , Fe^{3+} , Fe^{2+} , Sn^{4+} , Sn^{2+} (Fe^{2+} obtained by the reduction and Sn^{2+} protected from oxidation by using $\text{NH}_2\text{OH} \cdot \text{HCl}$) ($c = 1 \times 10^{-4}$ mol dm^{-3}) and NaCl ($l = 0.1$ mol dm^{-3}) was shaken with equal volume of $\text{H}_2\text{A}-\text{CHCl}_3$ for 30 min (2 h for Fe) at (25 ± 0.5) °C. After separating of the aqueous phase, pH and content of Sc (or Y, La, Fe, and Sn) were determined. This content in organic phase can be obtained by the difference method.

Preparation of Solid Extractive

In a separating funnel aqueous ScCl_3 (1.6 mmol) and $\text{H}_2\text{A}-\text{CHCl}_3$ (0.8 mmol) (the pH value of aqueous phase was adjusted to 1.0 with the solution of NaOH), aqueous FeCl_3 (1.6 mmol) and $\text{H}_2\text{A}-\text{CHCl}_3$ (0.8 mmol) (the pH value of aqueous phase was adjusted to 2 with the solution of NaOH) were added and stirred for 30 min at (25 ± 0.5) °C in

a thermostat (2 h for Fe). After separating of the layers, the organic phase was separated off, evaporated to a half of original volume and suitable amounts of petroleum ether were added. The resulting precipitate was collected by centrifugation, washed twice with a mixed solution of chloroform and petroleum ether and dried under vacuum.

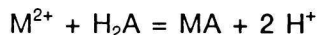
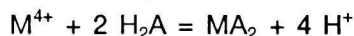
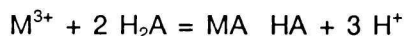
RESULTS AND DISCUSSION

Extraction of Sc^{3+} , Y^{3+} , La^{3+} , Fe^{3+} , Fe^{2+} , Sn^{4+} , and Sn^{2+} by H_2A

The relationships of extraction efficiency—pH and distribution ratio—pH which are obtained from the system Sc^{3+} , Y^{3+} , La^{3+} , Fe^{3+} , Fe^{2+} , Sn^{4+} , Sn^{2+} , HCl , $\text{NaCl}/\text{H}_2\text{A}$ — CHCl_3 are shown in Figs. 1 and 2.

It can be seen from Fig. 2 that the slope of Sc^{3+} , Y^{3+} , La^{3+} , and Fe^{3+} is equal to 3, but those of Fe^{2+} and Sn^{2+} are equal to 2 and that of Sn^{4+} is 4.

The extraction can be indicated as follows



The $\text{pH}_{1/2}$ values and respective apparent extraction constants of these extracted compounds are listed in Table 1.

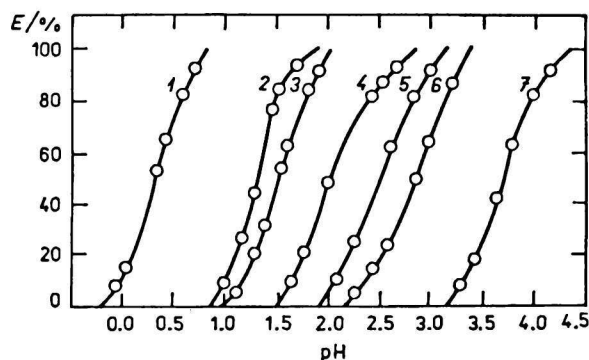


Fig. 1. Effect of pH on the extraction efficiency. 1. Sc^{3+} ; 2. Sn^{4+} ; 3. Fe^{3+} ; 4. Sn^{2+} ; 5. Fe^{2+} ; 6. Y^{3+} ; 7. La^{3+} .

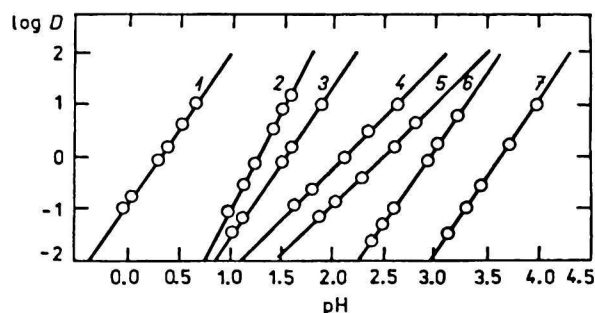


Fig. 2. Effect of pH on the distribution ratio. 1. Sc^{3+} ; 2. Sn^{4+} ; 3. Fe^{3+} ; 4. Sn^{2+} ; 5. Fe^{2+} ; 6. Y^{3+} ; 7. La^{3+} .

Table 1. The $\text{pH}_{1/2}$ Values and Extraction Constants

Extracted compound	$\text{pH}_{1/2}$	$\log K_{\text{ex}}$
$\text{ScA} \cdot \text{HA}$	0.37	-1.70
$\text{YA} \cdot \text{HA}$	2.88	-5.17
$\text{LaA} \cdot \text{HA}$	3.65	-7.41
$\text{FeA} \cdot \text{HA}$	1.50	-1.09
FeA	2.51	-1.62
SnA_2	1.33	-1.92
SnA	2.02	-0.60

The pH values of these extracted compounds are smaller than those obtained by HNO_3 . It is possible that Sc is separated from Y, La, Fe, and Sn, when using deoxygenated H_2A — CHCl_3 system as extractant, controlling pH value and changing the valence of Fe and Sn in the solution. In order to confirm rationality of this deduction, we add $\text{NH}_2\text{OH} \cdot \text{HCl}$ (or other reductants such as ascorbic acid) which reduces Fe^{3+} to Fe^{2+} , into the solutions of Sc (36 mg), Y (72 mg), La (112 mg), Fe (54 mg), and Sn (72 mg) in hydrochloric acid ($\text{pH} = 0.8$, Sc is extracted completely) and we extract by the deoxygenated solution of H_2A in CHCl_3 . The organic phase was washed twice with water, then re-extracted with 2 M-HCl. The obtained solution was evaporated to remove a great quantity of HCl, the pH value was adjusted to 4, and the solution was precipitated with oxalic acid. The sample obtained by burning the precipitate was determined spectrometrically (WPC-100 planar grating spectrograph). The contents of Y (0.003 %), La (0.001—0.003 %), Sn (0.03 %), and Fe (0.01 %) show that Sc has been separated satisfactorily from Y, La, Sn, Fe.

The composition of these extracted compounds is invariable although the amounts of the metal ions in the extractive system are greater than that of the ligand.

Solid Extractive of Sc

The composition of the extractive of scandium is $\text{ScA} \cdot \text{HA}$. The extractive is colourless, soluble in chloroform, sparingly soluble in DMF, insoluble in water, ethanol, petroleum ether, acetone, DMSO, and acetonitrile. Its molar conductivity (in CHCl_3 , 25 °C, $c = 1 \times 10^{-3} \text{ mol dm}^{-3}$) is 1.0 mS mol^{-1} , which approaches the value reported for nonelectrolyte [2]. For $\text{C}_{60}\text{H}_{65}\text{N}_8\text{O}_8\text{Sc}$ $w_i(\text{calc.})$: 67.28 % C, 6.07 % H, 10.47 % N, 4.21 % Sc; $w_i(\text{found})$: 67.20 % C, 6.10 % H, 10.42 % N, 4.18 % Sc. UV spectrum (CHCl_3), $\lambda_{\text{max}}/\text{nm}$: 247, 284. IR spectrum (KBr), $\tilde{\nu}/\text{cm}^{-1}$: 1606 m $\nu(\text{C}=\text{O})$, 1534 s $\nu(\text{C}-\text{O})$, 623, 447, 401 m $\nu(\text{Sc}-\text{O})$. ^1H NMR spectrum

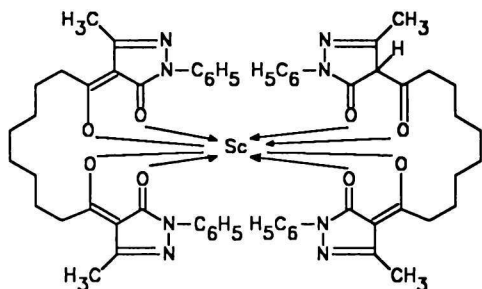


Fig. 3. Possible structure of the ScA · HA complex.

(CDCl₃), δ : 7.2 and 7.7 (m, 20H, phenyl), 2.42 (s, 12H, CH₃), 2.71 (t, 8H, C(O)CH₂), 1.34 and 1.50 (m, 24H, CH₂), 2.76 (s, 1H, *tert*-H). The curve of its TG—DTA has not changed up to 379 °C.

The composition and some properties of the solid extractive of Fe are similar to those of Sc; ¹H NMR spectra are different because the Fe extractive is paramagnetic.

It is shown that the results obtained from the elemental analysis are in agreement with those from the slope method. The bathochromic shift of the two UV characteristics shows that the extractives are formed indeed [3]. The important IR data of the ScA · HA complex show that the wavenumbers of $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$ are shifted bathochromically by 19 and 18 cm⁻¹, respectively, *i.e.* some carbonyls in the ligand can coordinate in keto form

to the Sc ion, and the other in enol form. The new bands at $\tilde{\nu} = 673, 447, \text{ and } 401 \text{ cm}^{-1}$ can be due to $\nu(\text{Sc}-\text{O})$ forming the Sc—O band [4]. The ¹H NMR spectra show that the proton signals in the complex ScA · HA are all shifted upfield with the ligand. In addition, the chemical shifts of the ligand at $\delta = 10.6$ due to the enolic hydroxyl proton disappeared in ScA HA. While a new signal at $\delta = 2.76$ appeared in the complex, it arose from the proton on methylidyne. It can be seen that two out of four carbonyls in the ligand exist in enol form, but only three out of eight carbonyls coordinate to the central ion in enol form, and the others in keto form in this complex. The TG—DTA diagram of the ScA · HA complex has not revealed any apparent heating effect up to 379 °C, *i.e.* the complex does not contain crystal water, is amorphous, does not melt, and is more thermostable.

Summarizing our results, we propose a plausible structure for the complex ScA · HA as shown in Fig. 3.

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