Liquid-liquid Distribution of the Tetravalent Zirconium, Hafnium and Thorium with a New Tetradentate Naphthol-derivative Schiff Base

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Received June 26, 2007

A fundamental study was developed concerning the novel solvent extraction of the tetravalent metal ions: zirconium(IV), hafnium(IV) and thorium(IV). Their extraction behavior in toluene was investigated with a recently synthesized naphthol-derivative Schiff base, 1-({[4-(4-{[(E)-1-(2-hydroxy-1-naphthyl)methyliden]-amino}phenoxy) phenyl]imino}methyl)-2-naphthol (HAPMN). The spectrophotometrical examination of the complex formation between HAPMN and the Zr(IV), Hf(IV) and Th(IV) ions in acetonitrile revealed the formation of stable 1:1 complexes in the solution. After the thorium extraction in toluene, it was found that [Th(OH)$_3$HA] was the respective deriving substance. While, in the case of zirconium and hafnium extraction, the extracted adduct was found to be [M$_4$(OH)$_8$(H$_2$O)$_{16}$Cl$_6$2HA]. The stoichiometric coefficients of these extracted species were determined by the slope analysis method. The extraction reaction followed a cation exchange mechanism.

Key Words : Liquid-liquid extraction, Zirconium(IV), Hafnium(IV), Thorium(IV), Schiff base

Introduction

Hugo Schiff described the condensation between an aldehyde and an amine leading to a Schiff base in 1864.[1] The Schiff base ligands are able to coordinate metal ions through imine nitrogen and other groups usually linked to the aldehyde. The Schiff base ligands are nowadays called "privileged ligands", being active, well-designed and easy to prepare through the aldehyde-amine condensation.[2] When two equivalents of salicylaldehyde are combined with one equivalent diamine, a particular chelating Schiff base is produced, which is also called a Salen ligand. The ligand illustrates four coordinating sites and two axial sites open to ancillary ligands. Salens are very much like porphyrins, but they are easier to prepare.

These ligands present a high sensitivity for various metal ions and structural rigidity.[3-8] The resulting 1:1 complexes have been frequently used as catalysts in diverse processes such as oxygen- and atom-transfer,[9,11] enantioselective epoxidation[10-12] and mediating organic redox reactions.[13] In fact, the Schiff bases are able to stabilize many different metal ions in various oxidation states, controlling the metal performance in a large variety of useful catalytic transformations.[8] In the recent years, the Salen ligands have been employed as ion carriers in a variety of analytical applications, including liquid-liquid and solid phase extractions,[14-18] liquid membrane transport[19] and ion selective PVC membrane electrodes.[20-22]

As far as thorium is concerned, it is a radioactive element that occurs naturally at low concentrations (10 ppm) in the earth's crust. This element has wide applications in various

arrays of products and processes, including the production of ceramics, carbon arc lamps, alloys and in mantles for lanterns. In addition, thorium is used as a representative element for tetravalent actinides in their separation studies.[23-27]

On the other hand, zirconium and hafnium co-exist in nature, but they have opposite nuclear characteristics. Zirconium is used in the nuclear industry as a fuel rod cladding, as a catalyst in organic reactions and, additionally, in the manufacture of water repellent textiles, in metal alloys and in dye pigments and ceramics.[28] Hafnium is used in alloys with iron, titanium, aluminum and other metals. This metal is also employed for the construction of nuclear control rods and is an efficient "getter" for scavenging oxygen and nitrogen.[28,29] Due to the widespread applications of these ions and the vital importance of separation of the tetravalent lanthanides and actinides from nuclear wastes,[30,31] the development and improvement of efficient techniques for the separation of these ions are among the main subjects of the separation investigations.

The present study reports the solvent extraction behavior and stoichiometry of the extracted complexes of Th(IV), Zr(IV) and Hf(IV) with a newly-synthesized tetradentate naphthol-derivative Schiff base 1-({[4-(4-{[(E)-1-(2-hydroxy-1-naphthyl)methyliden]amino}phenoxy)phenyl]imino}methyl)-2-naphthol (HAPMN) in toluene.

HAPMN
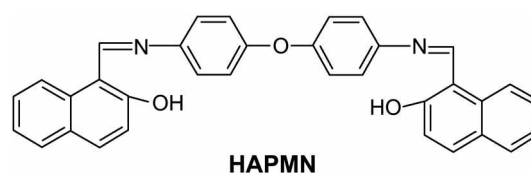
Experimental

Reagents. All reagents were of pro-analysis grade, purchased from the Merck Company. The zirconium, hafnium and thorium stock solutions of 1000 µg mL^{-1} were prepared by dissolving appropriate amounts of ZrOCl$_2$·8H$_2$O. HfOCl$_2$·8H$_2$O and Th(NO$_3$)$_4$·6H$_2$O (all from Merck) in 1000 mL of 0.1 M hydrochloric acid. The solutions were standardized complexometrically.[32]

Synthesis of the HAPMN Schiff Base: HAPMN was prepared by a usual Schiff base condensation in methanol (50 mL) of 2-hydroxy-1-naphthaldehyde (3.44 g. 20 mmol) with bis(4-aminophenyl)ether (2.02 g. 10 mmol). The solution was stirred and refluxed for 4 h. The orange precipitate was filtered, washed by a small amount of methanol and dried in vacuum. Yield 88%, m.p. 164 °C. Anal. Calcd. for C$_{34}$H$_{24}$N$_2$O$_3$: C: 80.30; H: 4.76; N: 5.51%. Found: C: 80.18; H: 4.63; N: 5.63%. Main IR bands (KBr. cm^{-1}): 2956. 2907. 2868. 1619 (C=N). 1495. 1439, 1243. 1170, 849 and 831. ^{1}H-NMR (CDCl$_3$): δ 15.3 (2H, s. -OH). 9.4 (2H, s. CH=N). 7.11 (4H, d, aminophenyl), 7.34 (4H, d, aminophenyl), 7.48 (4H. s, naphthyl). 7.52 (4H, s, naphthyl), 7.75-8.33 (4H. s, naphthyl). In the UV-Vis spectra, the tetradentate Schiff base ligand exhibited similar absorptions at three intense bands at *ca.* 278, 333 and 364 nm. The former two absorptions at 278 and 333 nm could be assigned to the Π → Π* transition of the benzene and phenol rings. The latter absorption at 364 nm is attributed to the charge transfer transition within the delocalized system in the molecular structure.

Apparatus. The determination of zirconium, hafnium and thorium was performed on a Varian model Liberty 150 AX inductively coupled plasma optical emission spectrometer (ICP–OES). A Cary-3 UV-visible spectrophotometer with 10 mm quartz cells was used to record the absorption spectra and measure the absorbance. A Metrohm model 744 digital pH-meter, equipped with a combined glass-calomel electrode. was employed for the pH adjustments.

Solvent Extraction Procedure. In the extraction studies involving pH variation. the concentrations of zirconium(IV). hafnium(IV) and thorium(IV) were 10 µg mL^{-1}. whereas the Schiff base concentration in toluene was 1.0 × 10^{-3} M. The ionic strength was maintained at 0.1 M with KCl. Equal volumes (10 mL) of the aqueous phase. containing Zr(IV). Hf(IV) or Th(IV), and the organic phase, containing the extractant Schiff base in toluene. were equilibrated for 80 min, using a mechanical shaker. The preliminary experiments on the metal extraction kinetics showed that the equilibrium was achieved within 60 min of contact. After the phase disengagement. the aqueous phase was separated and the metal concentrations were determined by ICP-OES. The metal concentration in the organic phase was calculated from the corresponding mass balance. The distribution ratio (D) was calculated as the metal concentration present in the
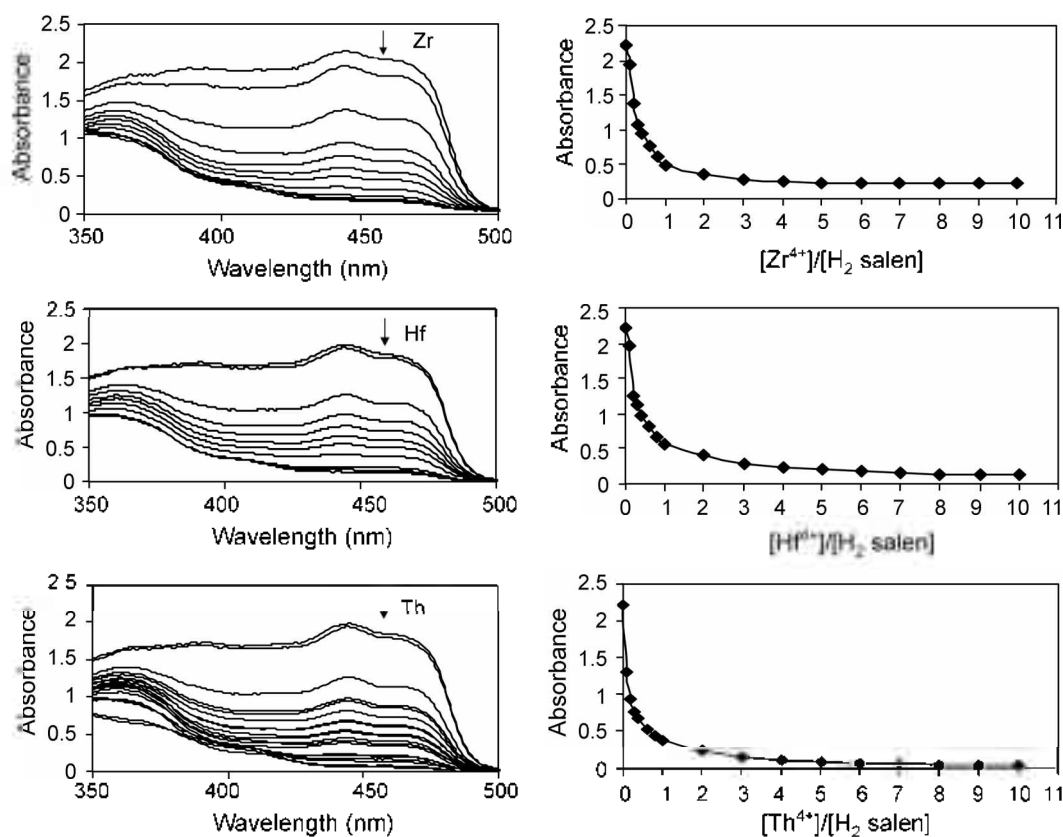

Figure 1. Absorption spectra of a 1.0 × 10^{-4} M HAPMN solution in acetonitrile upon addition of increasing amounts of zirconium, hafnium and thorium ions together with the corresponding mole ratio plots.

organic phase to the metal concentration present in the aqueous phase at equilibrium. All the experiments were conducted at room temperature (25 ± 1 °C).

Results and Discussion

In order to obtain a clue about the stoichiometry and stability of the HAPMN complexes with the Zr(IV), Hf(IV) and Th(IV) ions, preliminary studies were performed for the investigation of the HAPMN complexation with the Zr(IV), Hf(IV) or Th(IV) ions in acetonitrile solution spectrophotometrically. In these experiments, the HAPMN concentration in acetonitrile was kept constant at 1.0×10^{-4} M and a concentrated Zr(IV), Hf(IV) or Th(IV) solution in the same solvent was then added. The UV-Visible spectra of the resulting solution at various M^{4+}/HAPMN mole ratios were recorded, until the desired mole ratio was reached. The corresponding spectra and the resulting mole ratio plots obtained at 445 nm are depicted in Figure 1. As it is obvious from Figure 1, the HAPMN absorption spectra show distinct inflection points upon complexation with the metal ions in the solution at a molar ratio of about 1, indicating the formation of a stable 1:1 (HAPMN:M(IV)) complex in the acetonitrile solution. The overall stability constant of the resulting 1:1 complexes was evaluated by computer fitting the absorbance vs. the cation/ligand mole ratio plots to a corresponding equation [33]. The resulting log K values for the Zr(IV), Hf(IV) and Th(IV) complexes with HAPMN were 5.2 ± 0.3, 5.1 ± 0.3, 5.5 ± 0.2, respectively. Based on the above observations, we decided to examine the HAPMN suitability as a complexing agent for the solvent extraction of the zirconium(IV), hafnium(IV) and thorium(IV) ions.

The pH of aqueous solution was the first parameter, which was investigated for the extraction of the above-mentioned ions. For this study, the liquid-liquid extraction of zirconium(IV), hafnium(IV) and thorium(IV) with HAPMN into toluene was carried out at different pH values. The metal ion separation by liquid-liquid process involved the initial formation of a metal ion-Schiff base adduct with sufficient hydrophobicity to be extracted into the organic phase. Figure 2 exhibits the pH dependence of the extraction of zirconium(IV), hafnium(IV) and thorium(IV) with HAPMN into toluene. As is obvious from Figure 2, the extraction of the
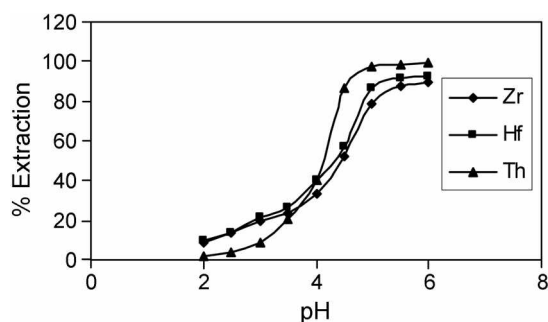
metal ions increased with the pH increase of the aqueous medium in the range of 2.0-6.0. The maximum extraction occurred at a pH value of 5 for thorium, while for zirconium and hafnium the optimum pH value was found to be 5.5.

Zirconium and hafnium extraction. The nature of the extracted species has been deduced from the linear plot of log D vs. pH.[34] in the pH range of 2.0-6.0 at a constant HAPMN concentration of 1.0×10^{-3} M, where D is the distribution ratio of zirconium(IV) or hafnium(IV). The plot displays a slope of about 0.5 (Figure 3). When the HAPMN concentration was varied from 1.0×10^{-4} to 1.0×10^{-3} at the constant pH value of 5.0, the slope of the log D vs. the log [HAPMN] was also found to be 0.5.

In the studied pH range, zirconium and hafnium form many hydrolyzed species such as $MO(OH)^+$, $M(OH)_2^{2+}$, $M(OH)_3^-$ and also polymerized species with the general form of $[M(OH)_x^{4-x}]_n$. The great tendency of the tetravalent zirconium and hafnium ions for hydrolysis is mainly due to the relatively large charge of the metal ions (4+) and their small diameters (0.74 and 0.75 Å, respectively).

It was found that at this pH range, zirconium and hafnium are present in the solution principally in the form of tetramers $[Zr_4(OH)_8]^{8+}$ and $[Hf_4(OH)_8]^{8-}$.[35] In the recent years, the compositions of the Zr(IV), Hf(IV) species in chloride

Figure 2. Percent extraction of Zr(IV), Hf(IV) and Th(IV) as a function of pH. Metals concentration, 10 µg mL^{-1}; HAPMN, 1.0×10^{-3} M.
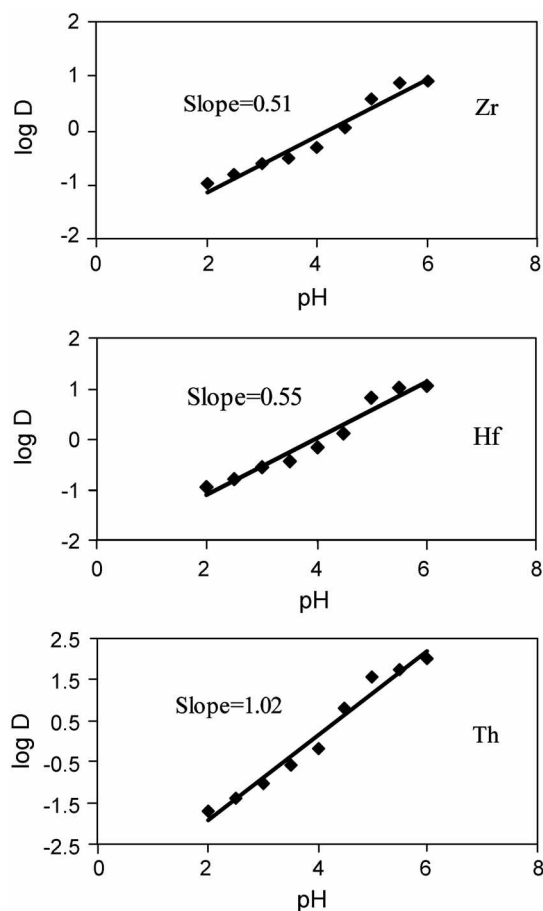

Figure 3. Effect of the solution pH on the distribution ratio of Zr(IV), Hf(IV) and Th(IV). Metals concentration, 10 µg mL^{-1}; HAPMN: 1.0×10^{-3} M.
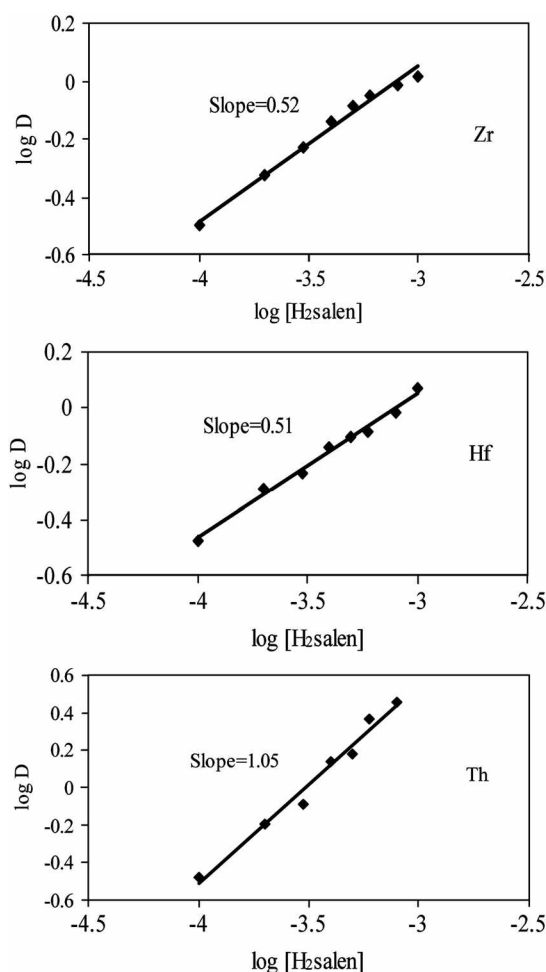
Figure 4. Influence of the extractant concentration on the distribution ratio of Zr(IV), Hf(IV) and Th(IV). Metals concentration, 10 μg mL⁻¹; pH, 5.0.

media have been reported in several articles.[36-38] In the chloride medium, the only present zirconium and hafnium substance was reported to be partly hydrolyzed as $[M_4(OH)_8(H_2O)_{16}Cl_6]^{2+}$. In these complexes, the metal ion was 8-coordinated: four M atoms take a square planar arrangement, each M(IV) has two -OH bridging and carries four H_2O molecule as coordinated ligands, whereas six Cl⁻ ions take their positions in the secondary coordination sphere of the complexes. The OH⁻/M⁴⁻ ratio of these complexes is equal to 2. With respect to the existence of such zirconium and hafnium compounds in the solution as well as the experimental results obtained for the zirconium and hafnium extractions with the HAPMN Schiff base, the following equation was suggested for the extraction reactions for this system:

$$[M_4(OH)_8(H_2O)_{16}Cl_6]_{aq}^{2+} + 2H_2A$$
$$\rightarrow [M_4(OH)_8(H_2O)_{16}Cl_62HA]_{org} + 2H^+$$
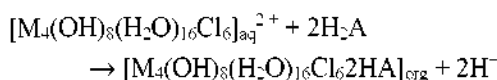
where HA is a monoanionic ligand. Since the increase in the zirconium and hafnium concentration results in extensive polymerization,[39] the slope analysis of the log $[M^{4+}]_{aq}$ vs. log $[M^{4+}]_{org}$ was not attempted in this work.

Thorium extraction. The resulting data for the pH influence of the solution (in the range of 2.0-6.0) and the HAPMN ligand concentration $(1.0 \times 10^{-4}$ to 2.0×10^{-3} M) on the thorium(IV) extraction from a 0.1 M chloride solution are presented in Figures 3 and 4, respectively. The slope of the linear plot of log [D] vs. pH for thorium(IV) was almost 1. This was supported by the slope of the log [D] vs. log [HAPMN] linear plot, due to the variation in the Schiff base concentration from 1.0×10^{-4} to 2.0×10^{-3} M at the pH value of 5. Because of the larger size of the thorium(IV) ion, as compared with that of the zirconium and hafnium ions, the thorium(IV) tendency for hydrolysis in aqueous solutions was lower than that of the zirconium and hafnium ions. However, thorium forms various monomeric hydroxo-species, owing to its partial hydrolysis in the solution.[40,41] Based on the experimental evidence, primarily on the slope analyses of the extraction results, the following equation was recommended for the thorium ions extraction by HAPMN into toluene:

$$[Th(OH)_3]^+ + H_2A \rightarrow [Th(OH)_3HA] + H^-$$
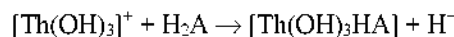
where HA is the monoanionic Schiff base.

Conclusion

In this research, the solvent extraction of zirconium(IV), hafnium(IV) and thorium(IV) from aqueous solutions with the help of a H_2salen ligand (HAPMN) was described. In line with the derived data, the metal transfer followed a cation exchange mechanism. The log D-pH plots illustrated that the zirconium(IV) and hafnium(IV) compounds, extracted from the solutions, were a partly hydrolyzed $[M_4(OH)_8(H_2O)_{16}Cl_6]^{2+}$ adduct, while the thorium(IV) extracted compound was a monomeric $[Th(OH)_3]^-$ cation. The spectrophotometrical assessment of the complexation between the H_2salen ligand and the Zr(IV), Hf(IV) and Th(IV) ions in acetonitrile revealed that all cations formed stable 1:1 complexes with HAPMN.

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