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J. Rajesh Kumar[a,b]; B. Ramachandra Reddy[a]; K. Janardhan Reddy[b]; A. Varada Reddy[b]
[a] Inorganic Chemistry Division, Indian Institute of Chemical Technology (CSIR), Hyderabad, Andhra Pradesh, India [b] Analytical Chemistry Division, Department of Chemistry, Sri Venkateswara University, Tirupati, Andhra Pradesh, India

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J. Rajesh Kumar
Inorganic Chemistry Division, Indian Institute of Chemical Technology
(CSIR), Hyderabad, Andhra Pradesh, India and Analytical Chemistry
Division, Department of Chemistry, Sri Venkateswara University,
Tirupati, Andhra Pradesh, India

B. Ramachandra Reddy
Inorganic Chemistry Division, Indian Institute of Chemical Technology
(CSIR), Hyderabad, Andhra Pradesh, India

K. Janardhan Reddy and A. Varada Reddy
Analytical Chemistry Division, Department of Chemistry,
Sri Venkateswara University, Tirupati, Andhra Pradesh, India

Abstract: Liquid-liquid extraction studies of tetravalent hafnium from acidic chloride solutions have been carried out with bis(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex 301) as an extractant diluted in kerosene. Increase of acid concentration decreases the percentage extraction of metal. Plot of log D vs. log [HCl] gave a straight line with a negative slope of 2 ± 0.1 indicating the exchange of two moles of hydrogen ions for every mole of Hf(IV) extractacted into the organic phase. Extraction of Hf(IV) increases with increase of extractant concentration. The plot of log D vs. log [HA] is linear with slope 2 ± 0.1, indicating the association of two moles of extractant with the extracted metal species. The addition of sodium salts enhanced the percentage extraction of metal, and followed the order NaSCN > Na_2SO_4> $NaNO_3$ > NaCl. Stripping of metal from the loaded organic (LO) with HCl and

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Address correspondence to A. Varada Reddy, Analytical Chemistry Division, Department of Chemistry, Sri Venkateswara University, Tirupati, 517 502, Andhra Pradesh, India. Fax: +91-877-2249611; E-mail: ammireddyv@yahoo.co.in

H_2SO_4 indicated sulphuric acid as the best stripping agent. Increase of temperature increases the percentage extraction of metal indicating the process is endothermic. Regeneration and recycling capacity of Cyanex 301, extraction behavior of associated elements such as Zr(IV), Ti(IV), Al(III), Fe(III), and IR spectra of the Hf(IV)-Cyanex 301 complex was studied.

Keywords: Hafnium(IV), liquid-liquid extraction, Cyanex 301, associated metals

INTRODUCTION

Organophosphorus compounds containing the phosphoryl group ($P = O$) have been widely used as analytical extractants, however only in the 1960's studies on the corresponding sulfur analogs were initiated. Organophosphorus extractants have been used commercially for the extraction of many transition metals. Some particular advantages of the use of organophosphorus extractants in LLE processing are its chemical stability, generally good kinetics of extraction, good loading and stripping characteristics. Recently there has been an increased interest in the potential applications of phosphonic and phosphinic acids in the separation of cobalt-nickel (1).

Thioorganoposphorus extractants such as Cyanex 302 (bis(2,4,4-trimethylpentyl) monothiophosphinic acid), and Cyanex 301 (bis(2,4,4-trimethylpentyl) dithiophosphinic acid) were originally developed for use in the selective recovery of zinc from solutions containing magnesium and particularly, calcium. Since their introduction in 1985 and 1988, respectively, several more potential applications for these reagents have been examined. Two of these are

1. the recovery of cadmium from wet process phosphoric acid and
2. the separation of cobalt from nickeliferous solutions that also contain manganese (2).

Sulfur containing organic compounds finds application in metallurgical processing as flotation reagents, exhibiting high specificity and selectivity for many minerals.

Cyanex 301 (bis(2,4,4-trimethylpentyl) dithiophosphinic acid) is a sulfur containing compound and a much stronger acid than its analogous oxy-acid, Cyanex 272 (bis(2,4,4-trimethylpentyl) phosphinic acid). As such, it is capable of extracting many metals at low pH (<2). Although it does not discriminate between heavy metals in this pH range, it does exhibit a high degree of selectivity for heavy metals vs. alkaline and alkali earths. Particularly useful for the extraction of cobalt and nickel at low pH (laterite ores) and the selective recovery of zinc from effluents; again at low pH (2). In spite of a large number of studies on the extraction of transition metals with Cyanex 301, it has not been reported for the liquid-liquid extraction (LLE) of tetravalent hafnium.

Extraction studies of hafnium with TBP (3, 4), D2EHPA (5), Cyanex 923 (6), Cyanex 925 (7), bidentate/tridentate organophosphorus compounds (8, 9), dibutyl-sulfoxide (10, 11) and DC-18-crown-6 (12) has been reported. In our recent investigations on tetravalent hafnium, we have reported the extraction studies under different experimental conditions with organophosphorus (13) (PC 88A), thioorganophosphorus (14) (Cyanex 302) and 2-hydroxy-5-nonylacetophenoneoxime (15) (LIX 84I-C) as extractants from chloride media.

The present study reports the LLE behavior of tetravalent hafnium from low acidic chloride solutions with Cyanex 301 in kerosene. The experimental parameters studied are the effect of acid, extractant, metal concentration, salts, nature of diluents, loading capacity, stripping of metal from loaded organic (LO), temperature, regeneration and recycling capacity of extractant, extraction of associated elements, and infrared spectral data of metal complex.

EXPERIMENTAL

Apparatus and Reagents

The concentration of Hf(IV) and Zr(IV) in the aqueous phase was determined by the xylenol orange (XO) method (16) at 535 nm and Ti(IV) by hydrogen peroxide method (16) at 410 nm using a GBC CINTRA 10e UV-VIS-DRS spectrometer. Analysis of Fe(III) and Al(III) was obtained using Perkin Elmer Model A 300 AAS. The IR spectrum of the solid complex was recorded using FTIR-Nicolet (USA)-740-spectrophotometer and aromatic content of distilled kerosene in $CDCl_3$ using Avance-300 MHz ^1H NMR instrument. Julabo shaker (Temp SW 22 model) was used for temperature effect. Cyanex 301 supplied by Cytec, Canada was used without purification. As a source of Hf(IV), $HfCl_4$ (Fluka, 98%) was used. Working solutions of Hf(IV) were prepared fresh and used for the extraction experiments. Distilled kerosene (160–200°C) was used as a diluent. It was colorless, aliphatic and the aromatic contents were 96.2% and 3.8%, respectively as determined by NMR spectra. All other reagents used were analar grade.

Liquid-Liquid Extraction Procedure

Equal volumes (10 mL) of the aqueous phase containing desired concentrations of Hf(IV)/or other metals and organic phase containing the extractant, Cyanex 301 was equilibrated for 30 min in glass stopped bottles using a mechanical shaker. Preliminary experiments on the kinetics of metal extraction showed that equilibrium was achieved within a 20 min contact. After phase disengagement, the aqueous phase was separated and its metal concentrations were estimated by XO method. The concentration of the metal in the organic phase was calculated from the mass balance. All the experiments were conducted at room temperature (30 ± 1°C) excepting that involving temperature effect and the general agreement with D values obtained was within ±5%.

Preparation of Solid Complex

Hf(IV)-Cyanex 301 solid complex was prepared by repeated contact of $0.002\ \mathrm{mol \cdot L^{-1}}$ Cyanex 301 in chloroform with fresh portions metal ($0.001\ \mathrm{mol \cdot L^{-1}}$) each time for 30 min till the extractant becomes completely loaded with the metal. Finally, the loaded organic (LO) phase was separated and filtered through a Whatman phase separator (1 PS). Most of the diluent from the LO is removed by a rotavac pump; a drop of the Hf(IV) complex is kept on a KBr pellet and placed under the IR lamp to evaporate chloroform completely. IR spectrum of the extracted metal complex and pure Cyanex 301 was recorded for comparison.

RESULTS AND DISCUSSION

Extraction Mechanism and Species

The extraction of tetravalent hafnium from low hydrochloric acid solutions with Cyanex 301 may be represented as:

$$\mathrm{HfO^{2+}_{(aq)}} + 2\mathrm{HA_{(org)}} \overset{K_{ex}}{\longleftrightarrow} \mathrm{HfOA_{2(org)}} + 2\mathrm{H^{+}_{(aq)}} \tag{1}$$

Where K_{ex} denotes the equilibrium constant and HA refers to the monomeric form of Cyanex 301 (17, 18).

$$K_{ex} = \frac{[\mathrm{HfOA_2}][\mathrm{H^+}]^2}{[\mathrm{HfO^{2+}}][\mathrm{HA}]^2} \tag{2}$$

$$K_{ex} = \frac{D[\mathrm{H^+}]^2}{[\mathrm{HA}]^2} \tag{3}$$

$$\text{Where } D = \frac{[\mathrm{HfOA_2}]}{[\mathrm{HfO^{2+}}]} \tag{4}$$

Taking logarithm of Eq. (3) and rearranging

$$\text{Log } D = \log K_{ex} + 2\log[\mathrm{HA}] - 2\log[\mathrm{H^+}] \tag{5}$$

The extraction of 0.001 M Hf(IV) with $0.002\ \mathrm{mol \cdot L^{-1}}$ Cyanex 301 as a function of hydrochloric acid concentration ($0.01\text{–}0.5\ \mathrm{mol \cdot L^{-1}}$) has been studied, the extraction behavior showed an inverse dependence on acidity.

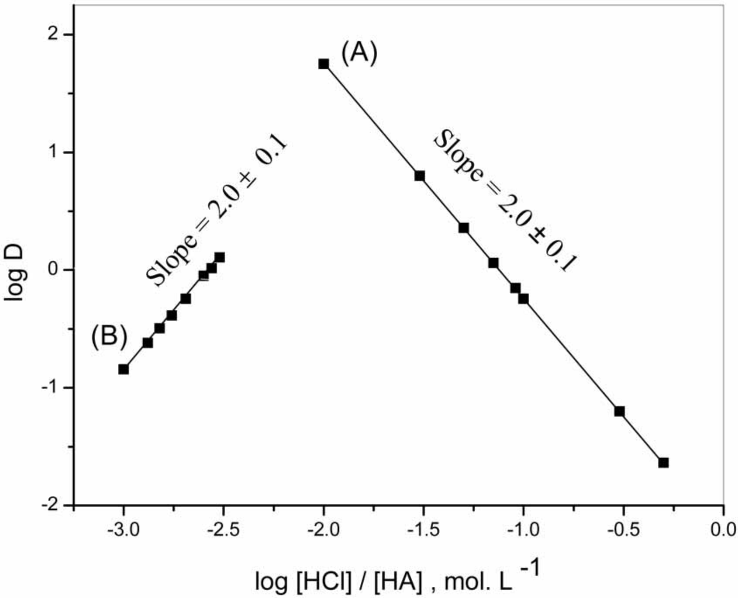

Figure 1. Effect of hydrochloric acid/or extractant concentration on the distribution ratio of hafnium. (A) HCl: Hf(IV): 0.001 mol · L^{-1}, Cyanex 301: 0.002 mol · L^{-1}. (B) Extractant: Hf(IV): 0.001 mol · L^{-1}, HCl: 0.1 mol · L^{-1}.

Log D vs. log [HCl] plot (Fig. 1A) gave a straight line with a negative slope of 2 ± 0.1, indicating the exchange of two moles of H^+ for every mole of metal ion during the extraction process. The variation of extractant concentration (0.001 to 0.003 mol · L^{-1}) on the extraction of Hf(IV) (0.001 mol · L^{-1}) from 0.1 mol · L^{-1} HCl indicated increase in the percent extraction of hafnium with increase in extractant concentration. The log D versus log [HA] plot (Figure 1B) is linear with slope of 2 ± 0.1, confirming that two molecules of the extractant (HA ≡ Cyanex 301) is involved in the extracted complex of Hf(IV). The effect of hafnium concentration on the extraction process has been investigated using 0.002 mol · L^{-1} Cyanex 301 from 0.1 mol · L^{-1} HCl. The log-log plot (Fig. 2) of equilibrium organic phase metal concentration against aqueous phase metal concentration is linear with a slope of unity indicating the extraction of monomeric species into the organic phase. Based on these studies, the species extracted into the organic phase was established as $HfOA_2$.

Effect of Diluents

The extraction of 0.001 mol · L^{-1} Hf(IV) from 0.1 mol · L^{-1} HCl using 0.002 mol · L^{-1} Cyanex 301 in various diluents has been investigated. The

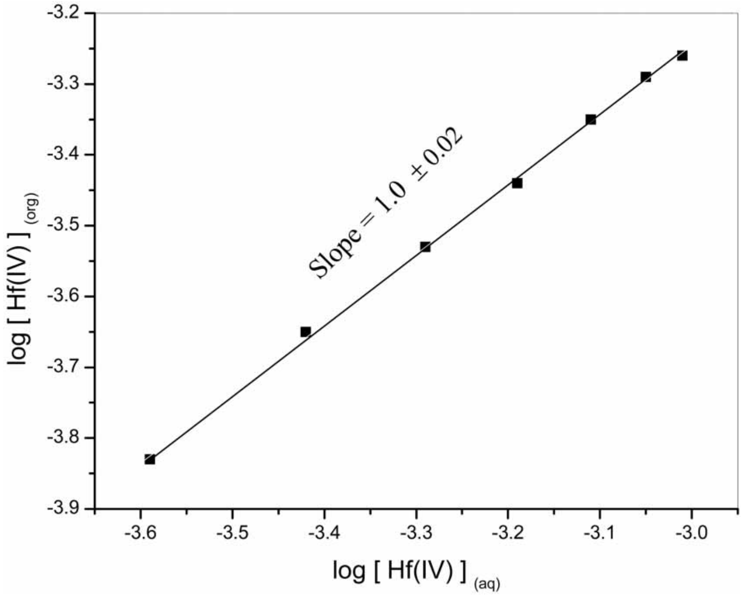

Figure 2. Effect of the metal concentration on the extraction of hafnium. HCl: 0.1 mol · L^{-1}, Cyanex 301: 0.002 mol · L^{-1}.

results indicate that the extraction of Hf(IV) varies with the nature of diluents and follows the order (%E): Toluene (41.2) > kerosene (36.3) > nitrobenzene (33.8) > n-hexane (30.1) > xylene, chloroform (27.5) > benzene (24.8) > carbon tetrachloride (22.5) > cyclohexane (17.4). However, in the present study, kerosene was used as a diluent as it is low cost and commercially available for industrial separation and recovery of metals in pure form for a wide range of applications.

Effect of Salts

The effect of salts such as NaCl, Na_2SO_4, $NaNO_3$, and NaSCN was studied in the concentration range 0.1–1.0 mol · L^{-1} on the extraction behavior of 0.001 mol · L^{-1} Hf(IV) from 0.1 mol · L^{-1} HCl with 0.002 mol · L^{-1} Cyanex 301 and the results are given in Fig. 3. The enhancement in percent extraction in the presence of added salts may be perhaps due to a common ion effect as well as the presence of mixed metal salt species that makes the metal more favorable for extraction (19). The results clearly demonstrate that at a given concentration of hafnium, Cyanex 301, and HCl, the percentage extraction follows in the increasing order NaSCN > Na_2SO_4> $NaNO_3$ > NaCl.

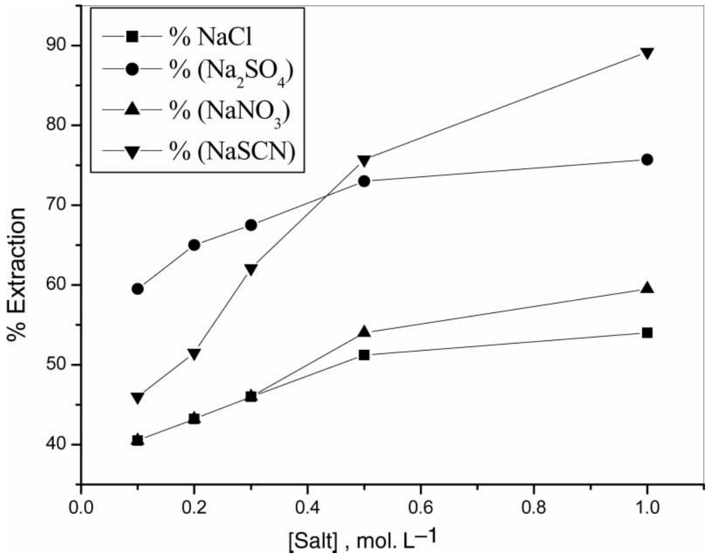

Figure 3. Effect of sodium salts on hafnium extraction. Hf(IV): 0.001 mol · L^{-1}, HCl: 0.1 mol · L^{-1}, Cyanex 301: 0.002 mol · L^{-1}.

Temperature Effect

The effect of temperature in the range of 303–333 K (±1°) on the extraction of metal from an aqueous solution containing 0.001 mol · L^{-1} Hf(IV) and 0.1 mol · L^{-1} HCl using 0.002 mol · L^{-1} Cyanex 301 showed increase of extraction from 36.3 to 85.8%. The calculated value of ΔH from the plot of log D vs. (1/T) K^{-1} for the extraction reaction was 8.354 k J mol^{-1}, indicating the endothermic nature of extraction process.

Loading Capacity of Cyanex 301

An aliquot of (10 mL) 0.002 mol · L^{-1} Cyanex 301 was repeatedly contacted for 30 min with the same volume of aqueous solution containing 0.00014 mol · L^{-1} of Hf(IV) and 0.1 mol · L^{-1} HCl. After equilibration, the phases were separated and analyzed for metal content in the aqueous phase. The amount of metal transferred into the organic phase in each contact was calculated by difference and the cumulative concentration of hafnium in the organic phase after each stage of contact was presented in Fig. 4. It is clear that most of the hafnium existing in the aqueous phase is extracted into the organic phase up to the seventh stage and analysis of L.O contains 71 mg.L^{-1} Hf(IV).

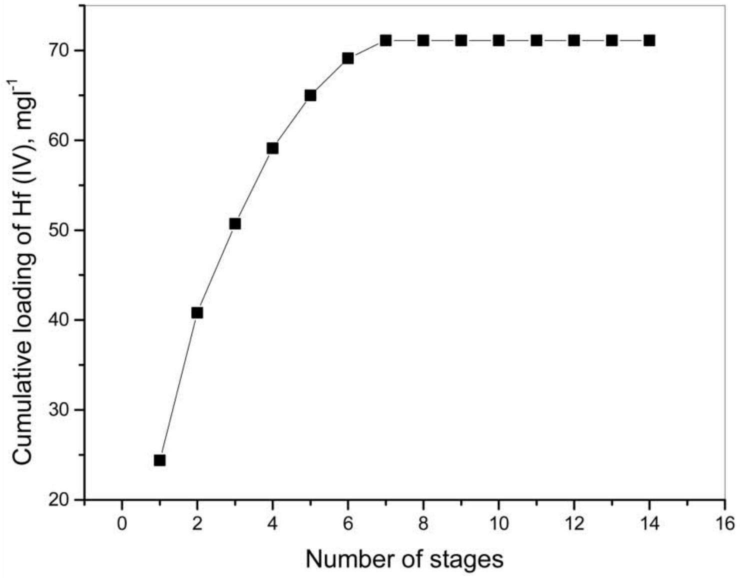

Figure 4. Loding capacity of Cyanex 301. Hf(IV): $0.00014\,mol \cdot L^{-1}$, HCl: $0.1\,mol \cdot L^{-1}$, Cyanex 301: $0.002\,mol \cdot L^{-1}$.

Table 1 gives the equilibrium constant (K_{ex}) values of Hf(IV) from the following experiments such as acid effect, extractant effect, metal ion influence, and loading capacity of the Cyanex 301.

Stripping Studies

Hafnium stripping from $0.002\,mol \cdot L^{-1}$ Cyanex 301 L.O containing 71 mg.L^{-1} Hf(IV) has been investigated using HCl and H_2SO_4 in the range $0.5 - 8\,mol \cdot L^{-1}$ (Table 2). As expected, percentage stripping increases with increase in acid concentration and indicate that at any given acid, the stripping efficiency of H_2SO_4 is more than that of HCl.

Table 1. Two phase equilibrium constants of various experiments using Cyanex 301 as extractant in kerosene

Experiment name	log K_{ex}
Effect of acid	6.1576 ± 0.005
Effect of extractant	6.1559 ± 0.003
Effect of metal ion concentration	6.148039 ± 0.03
Loading capacity of extractant	6.4647 ± 0.2

Table 2. Stripping of Hf(IV) from loaded organic phase (71 mg $\cdot$ L^{-1} Hf)

Stripping reagent (HCl, mol $\cdot$ L^{-1})	Hf stripping (%)	Stripping reagent (H_2SO_4, mol $\cdot$ L^{-1})	Hf-stripping (%)
1.0	21.7	0.5	31.2
2.0	31.2	1.0	38.8
3.0	38.5	2.0	47.6
4.0	47.6	4.0	67.2
6.0	51.0	6.0	88.5
8.0	60.0	8.0	100

Regeneration and Recycling Capacity of Cyanex 301

The recycling capacity of 0.002 mol $\cdot$ L^{-1} Cyanex 301 for the extraction of Hf(IV) (using 0.001 mol $\cdot$ L^{-1} metal and 0.1 mol $\cdot$ L^{-1} HCl was carried out by first loading the extractant with Hf(IV) and then stripping with 8 mol $\cdot$ L^{-1} H_2SO_4 at unit phase ratio. Single stage extraction resulted in L.O containing 64.6 mg.L^{-1} metal. The stripped organic phase was washed with distilled water once and then used for extraction. The results revealed practically insignificant change in the extraction and stripping efficiency of these extractants up to ten cycles of extraction.

Comparison of Extraction Behavior of Hf(IV) with other Associated Metal Ions

The hafnium/zirconium separation process is the challenging task to researchers. In spite of commercial Hf/Zr separation process such as TBP and MIBK there has been continues effort in the development of new extractants for title metal recovery, separation, extraction and ultimate use in commercial separation of above metal ions if possible. In this endeavor, the extraction behavior of Zr(IV), Ti(IV), Al(III), and Fe(III) (0.001 mol $\cdot$ L^{-1} each) are generally associated in the leach liquors obtained from the treatment of Hf/Zr containing natural zircon sand, has been investigated as a function of HCl concentration using 0.002 mol $\cdot$ L^{-1} Cyanex 301 in kerosene (Figs. 5 and 6). It is clear from these results that the percentage extraction of Hf(IV), Zr(IV), and Fe(III) decreases with increasing acid concentration. On the other hand, the extraction of Ti(IV) and Al(III) is nil. Thus, these results indicate that it is possible to separate Hf(IV) from metal ions such as Ti(IV), Al(III) and Fe(III).

IR Spectra of the Hafnium(IV)-Cyanex 301 Complex

The IR spectra of hafnium complex with Cyanex 301 and pure extractant for comparison were recorded. The spectrum of Cyanex 301 shows bands at

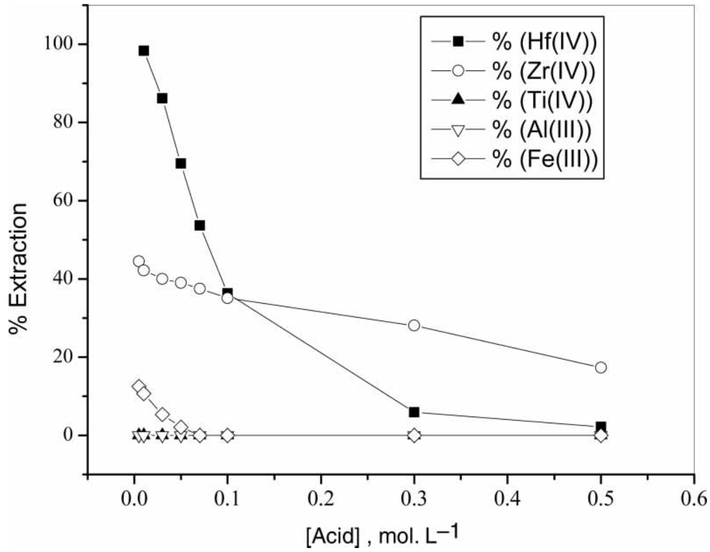

Figure 5. Extraction of associated metals as a function of acid concentration. Metal: 0.001 mol · L^{-1}, Cyanex 301: 0.002 mol · L^{-1}.

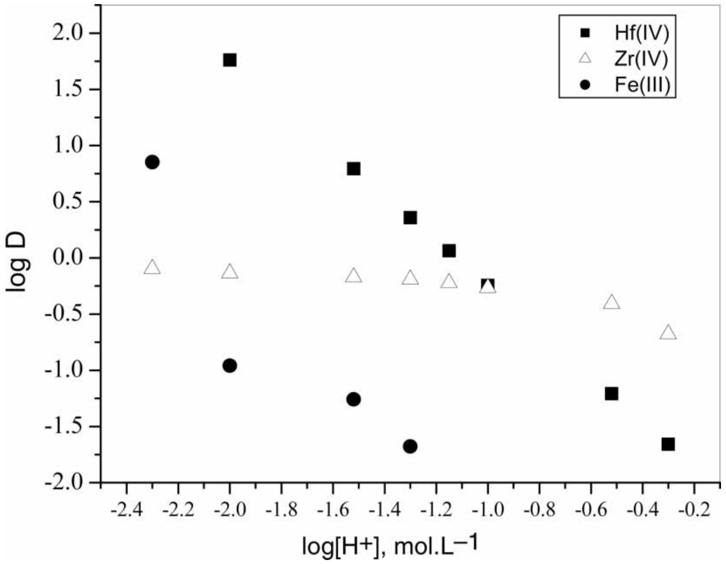

Figure 6. Log vs log plots of hafnium(IV), zirconium(IV) and iron(III) as a function of acid concentration. Metal: 0.001 mol · L^{-1}, Cyanex 301: 0.002 mol · L^{-1}.

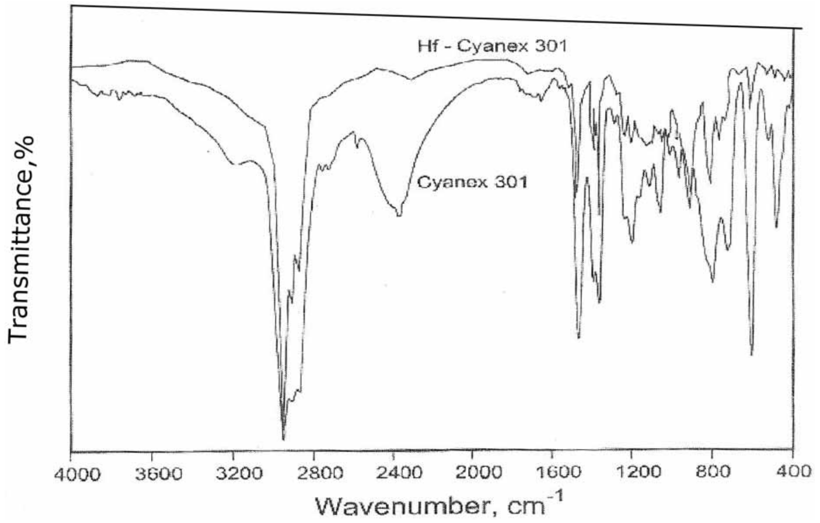

Figure 7. FTIR spectra of Cyanex 301 and Hf(IV)-Cyanex 301 complex. Hf(IV): 0.001 mol · L^{-1}, HCl: 0.1 mol · L^{-1}. Cyanex 301: 0.002 mol · L^{-1}.

~2380 cm^{-1} and also a sharp, small band at ~2575 cm^{-1} that can be assigned to the P-S-H stretching vibration. Further it was reported (20) that the complexity of the broad band at ~2380 cm^{-1} may be due to the presence of a mixture of hydrogen bonded polymers of the type $(R_2P(S)SH)_n$. The S-H group shows band at 400 cm^{-1} and S=P-S group shows band at 800 cm^{-1}. The presence of P=S bond in $R_2P(S)SH$ shows two absorption bands with frequencies within the range 725 cm^{-1} and 595–617 cm^{-1}. In the spectra of Hf-Cyanex 301 complex (Fig. 7), the bands due to the aggregative S-H vibrations in the region 2380–2575 cm^{-1} are absent. The results suggest that when the Cyanex 301 molecule forms a complex with Hf(IV), the hydrogen atom of P-S-H is displaced by hafnium thus confirming the cation exchange mechanism proposed.

CONCLUSIONS

Liquid-liquid extraction of tetravalent hafnium from acidic chloride solutions using Cyanex 301 and IR spectra of metal complex revealed the transfer of metal by cation exchange mechanism. Regeneration and recycling of the extractant indicated stability of Cyanex 301. This study indicates possible separation of Hf(IV) from multivalent metal ions such as Ti(IV), Al(III), and Fe(III).

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