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Synergistic Enhancement and Separation of Zirconium(IV) and Hafnium(IV) with 3-Phenyl-4-Benzoyl-5-Isoxazolone in the Presence of Crown Ethers

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Abstract: 3-Phenyl-4-benzoyl-5-isoxazolone (HPBI) was synthesized and examined with regard to the synergistic solvent extraction behavior of zirconium(IV) and hafnium(IV) in the presence of various crown ethers (CEs), namely, 18-crown-6 (18C6), dicylohexano-18-crown-6 (DC18C6) and benzo-15-crown-5 (B15C5) from hydrochloric acid solutions. The results demonstrated that zirconium(IV) and hafnium(IV) were synergistically extracted into chloroform with mixtures of HPBI and CEs as $ZrO(PBI)_2 \cdot CE$ and $HfO(PBI)_2 \cdot CE$, respectively. The complexation strength follows the order DC18C6 >18C6 > B15C5. The addition of CEs not only enhances the extraction efficiency of zirconium(IV) and hafnium(IV) but also significantly, especially in the presence of B15C5, improves the selectivity ($Zr/Hf = 4.73$) between these metal ions as compared to HPBI alone ($Zr/Hf = 2.09$). On the other hand, selectivity has been moderately decreased by the addition of 18C6 or DC18C6 to the metal-chelate system.

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Keywords: 3-Phenyl-4-benzoyl-5-isoxazolone, crown ethers, hafnium(IV), synergistic extraction, zirconium(IV)

INTRODUCTION

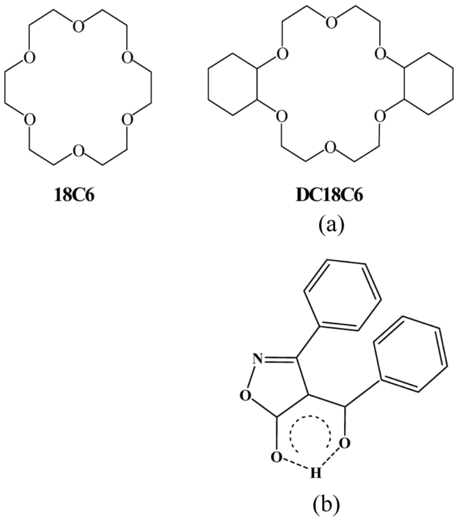
Zirconium and hafnium are two of the most important nuclear materials. The use of zircaloy in construction of fuel elements and other structural components in reactor cores meets many physical and technological requirements (1). Zirconium metal should contain less than 100 ppm hafnium for use in nuclear reactors. The advantage of zirconium in nuclear applications is its low thermal neutron capture cross-section (0.18 *b/a*), whereas hafnium has 640 times higher neutron absorption (2). Zirconium and hafnium have similar atomic radii, (1.45A° and 1.44 A°, respectively) and similar configuration of valence electrons ($4d^2$ $5s^2$ and $5d^2$ $6s^2$ for Zr and Hf respectively). Due to their similarity, in recent years, the problem of separation of zirconium and hafnium has acquired significant importance. There are three established technologies for the zirconium and hafnium separation i.e., multiple crystallization of potassium zirconium fluoride, the solvent extraction process, and extractive distillation (1–3). However, the crystallization process is a batch process, in the solvent extraction process MIBK soluble in water and flash point and decomposition of thiocyanate in the presence of hydrochloric acid and sophisticated technology and energy consumption required for the extractive distillation process could lead to search for new zirconium and hafnium separation process (4). The development of an effective separation method still attracts the attention of many separation chemists; solvent extraction (5,6), synergistic solvent extraction (7,8), and alternative process (9–11) have recently been proposed. However, most existing methods have exhibited poor selectivity between zirconium(IV) and hafnium(IV). This prompted us to develop alternate liquid-liquid extraction systems for the selective extraction and separation of zirconium(IV) and hafnium(IV) from acidic chloride solutions.

The introduction of cation selectivity into synergistic solvent extraction is well accomplished by the use of crown ethers that both form stable in-cavity complexes with the target cation and have adequate fictionalization to impart organophilicity (12). When these two criteria are met, the crown ether is both an effective extractant and an effective synergist. The former criterion requires some understanding of the coordination chemistry and, particularly, knowledge of the solution speciation of the cation and extractants, but remarkably few studies of synergistic extraction have probed the cation coordination environment. Synergistic extraction systems offer unique benefits in cation separations, and it can be argued that such systems hold the best promise for the large-scale application of crown ethers in separation science. Significant fundamental and developmental research is still required. However, only with well-planned and carefully executed research will the full potential of size-selective synergism be realized.

The most versatile class of ion-specific extractants is arguably the crown ethers, in which the macrocyclic cavity size, chelate ring size, macrocycle rigidity, and number and type of donor atoms may be tuned to provide a high degree of metal ion selectivity (13,14). Despite the clear potential of crown ethers in separation science that was immediately evident in Pedersen's initial report in 1967 (15), it was not until almost 13 years later that the use of crown ethers in synergistic solvent extraction was first reported (16–19). Macrocyclic crown ethers have unique complexation properties for metal ions, i.e., the size selectivity originate from the correct fit of a metal ion into the cavity of the crown ether. This property of crown ethers renders them attractive as size-selective extractants for the extractive separation of a series of metals such as alkali, alkaline earths, and possibly lanthanoids and actinides (20–24).

4-Acyl-5-isoxazolones are a class of fascinating chelating extractants capable of extracting metal ions from strong acid solutions due to its lower pK_a values as compared to conventional β-diketones such as HTTA ($pK_a = 6.25$). Among 4-acyl-5-isoxazolones, 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) has come to occupy a special place in the solvent extraction of metal ions due to its lower pK_a value (1.23) (25–28). The lower pK_a value of HPBI is due to the electron delocalization induced by the isoxazolone moiety. This property makes 3-phenyl-4-acyl-5-isoxazolones an interesting class of β-diketones with potential application as reagents in the extraction separation of metal ions from strong acid media (8,23,29–31).

The above factors prompted us to investigate new synergistic systems involving crown ethers (**a**) as synergistic agents and heterocyclic lipophilic ketone, namely, 3-phenyl-4-benzoyl-5-isoxazolone (HPBI: **b**) as chelating agent with the goal of elucidating the nature of the complexes extracted into the organic phase and also to determine the selectivity between zirconium(IV) and hafnium(IV).



EXPERIMENTAL

Instrumentation

A Hitachi (Tokyo, Japan) 220 double-beam microprocessor-controlled spectrophotometer was used for measuring absorbances. An Orion (USA) 720A Ion Analyzer was used for the pH measurements. A Nicolet FT-IR 560 Magna spectrometer using KBr (neat) was used to obtain the infrared spectra of the synthesized compounds. The analysis of C, H, and N elements were performed with a Perkin-Elmer Series 2 Elemental Analyzer 2400. The Bruker 300 MHz NMR spectrometer was used to obtain the ^{1}H NMR spectra of the ligands. ^{31}P NMR spectra of the synergistic complexes (in $CDCl_3$ and 85% H_3PO_4 as an external standard) were recorded using a Bruker 121.47 MHz NMR spectrometer.

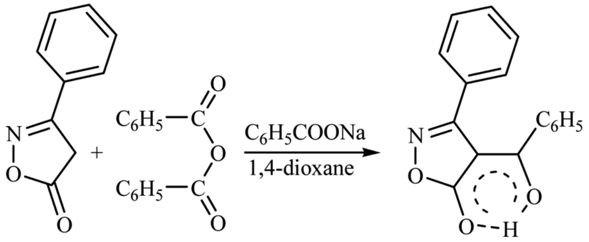
Materials

Crown ethers, 18-crown-6 (18C6), dicyclohexano-18-crown-6 (DC18C6), benzo-15-crown-5 (B15C5) were obtained from Aldrich Chemical Company. Chloroform (Analytical reagent, Merck, India), was used as a diluent in the present study. Xylenol orange (Gravimetric reagent, Lobachemie Pvt. Ltd., India) was used for the spectrophotometric determination of Zr(IV) and Hf(IV). All other chemicals used were of analytical reagent grade.

$ZrOCl_2 \cdot 8H_2O$ (Fluka, 98%) and $HfCl_4$ (Fluka, 98%) were used for the preparation of zirconium(IV) and hafnium(IV) metal ion solutions. Freshly prepared solutions of zirconium(IV) and hafnium(IV) were used for the extraction experiments due to the continuous change in composition of Zr(IV)/Hf(IV) species arising from hydrolysis and polymerization phenomena in the aqueous phase. Suitably diluted stock solutions of metal ions were used in the extraction and analytical studies. The ionic strength was maintained at 1.0 mol dm^{-3} using sodium chloride.

Synthesis of 3-Phenyl-4-benzoyl-5-isoxazolone (HPBI): HPBI was synthesized by the benzoylation of 3-phenyl-5-isoxazolone (8,32–33) (Scheme 1). 3-Phenyl-5-isoxazolone, benzoic anhydride, and sodium benzoate were refluxed in dry 1,4-dioxane for 3 hrs. The reaction mixture was cooled and filtered. The filtrate was diluted with distilled water and acidified with HCl. The precipitate was filtered, dried, and recrystallized from ethyl acetate. Synthesized compounds were characterized by IR, ^1H NMR and elemental analysis.

In the ^1H NMR spectra of HPBI (Fig. 1), the peaks observed at δ 5.90 correspond to the enolic –OH in the HPBI, which was found to have been exchanged with the addition of D_2O. This confirmed the existence of the HPBI in the enolic form. The absence of a peak at δ 3.8 corresponding to the methylene proton at the fourth position of the isoxazolone ring, further confirms the existence of 3-phenyl-4-benzoyl-5-isoxazolone quantitatively in the enolic form.



Scheme 1. HPBI : M.P. = 146°C; ^1H NMR data: δ 6.94–8.06 (m, 10H, phenyl) (Fig.1); IR (KBr) data ($\upsilon\,cm^{-1}$) : 3052, 1699, 1613, 1489, 831; Elemental analysis: Calc. for $C_{16}H_{11}NO_3$, C, 72.45; H, 4.15; N, 5.28. Found: C, 72.27; H, 4.18; N, 5.17 %.

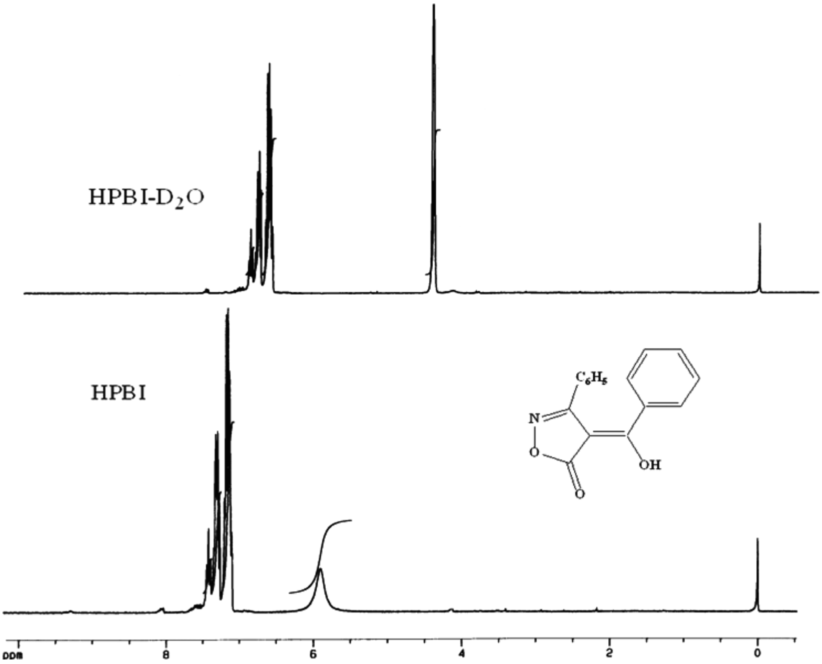


Figure 1. ^{1}H NMR spectrum of HPBI.

Liquid–liquid Extraction and Analytical Procedures

Distribution ratios were determined by shaking equal volumes of aqueous and organic phases for 60 min in a glass stoppered vial using a mechanical shaker at 303 ± 1 K. Preliminary experiments showed that the extraction equilibrium was attained within 30 min for zirconium(IV) and hafnium(IV). The solutions were then allowed to settle, the phases separated, and Zr(IV) and Hf(IV) in the aqueous phases determined spectrophotometrically ($\lambda_{max} = 535$ nm; detection limit = 0.06×10^{-6} mol dm^{-3} for both the metal ions) using the xylenol orange method (34). The concentration of metal ion in the organic phase was then obtained by mass balance. The distribution ratio, *D*, was defined as the ratio of the concentration of metal ion in the organic phase to that in the aqueous phase. All experiments were performed in duplicate, and the general agreement between the distribution ratio values obtained was within ±5%. Due to the solubility limitations of 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) in various industrially employed diluents, in the present study, chloroform has been chosen as a diluent.

RESULTS AND DISCUSSION

Effect of Crownether Concentration on Extraction of Zirconium(IV) and Hafnium(IV) with Crown Ethers

The extraction of zirconium(IV) and hafnium(IV) from $0.2\,\mathrm{mol\,L^{-1}}$ hydrochloric acid solutions with crownethers, 18C6, B15C5 or DC18C6 (1.0×10^{-4} $-3.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$) into chloroform has been studied and results as shown in the Fig. 2. The equilibrium concentration of 18C6 was calculated using the partition coefficient ($\log K_{D,\mathrm{18C6}} = 0.8$) taken from the literature (28). Since the partition coefficients of DC18C6 and B15C5 [$\log K_{D,\ \mathrm{DC18C6}} = 3.52$ (35); $\log K_{D,\ \mathrm{B15C5}} = 2.5$ (36)] are known to be quite large, no correction is necessary for the partitioning of CEs into the aqueous phase. It was found that the extraction of zirconium(IV) and hafnium(IV) with the above crown ethers (CE) were increased with increasing crownethers concentration. The separation factors (S.F.) between zirconium(IV) and hafnium(IV), defined as the ratio of respective distribution coefficients with CE systems at $0.2\,\mathrm{mol\,L^{-1}}$ HCl solutions have been calculated and are given in Table 1. The selectivity of these metal ions improves, especially with B15C5 (Zr/Hf = 4.73), which was compared to 18C6 (Zr/Hf = 2.02), DC18C6(Zr/Hf = 2.12) and HPBI alone (Zr/Hf = 2.09) (8). This can be explained on the basis of steric factors and basicity value of B15C5.

Extraction of Zirconium(IV) and Hafnium(IV) with Mixtures of HPBI and Crown Ethers

The synergistic extraction of zirconium(IV) and hafnium(IV) from $0.2\,\mathrm{mol\,L^{-1}}$ hydrochloric acid solutions with mixtures of HPBI (1.0×10^{-3} -3.0×10^{-3} $\mathrm{mol\,L^{-1}}$) and 18C6 (1.0×10^{-4} $-3.5 \times 10^{-4}\mathrm{mol\,L^{-1}}$), B15C5 ($1.0 \times 10^{-4}$ $-3.5 \times 10^{-4}\mathrm{mol\,L^{-1}}$) or DC18C6 ($1.0 \times 10^{-4}$–$3.5 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$) into chloroform has been studied. It was found that the extraction of zirconium(IV) and hafnium(IV) with the above crown ethers (CE) were negligible under the present experimental conditions. However, with mixtures of HPBI and crown ethers, considerable synergistic enhancement (synergistic enhancement factor (S.E.F.) $= D_{mix}/(D_{HPBI} + D_{CE})$, where D_{mix} = distribution ratio with HPBI + CE; D_{HPBI} =distribution ratio of metal ion with HPBI alone; D_{CE} = distribu-distribution ratio of metal ion with CE alone) in the extraction of these metal ions has been observed (Table 2). It is clear from that the synergistic enhancement factor increases with the increase in concentration of the crown ether. This may be due to the difference in the extent

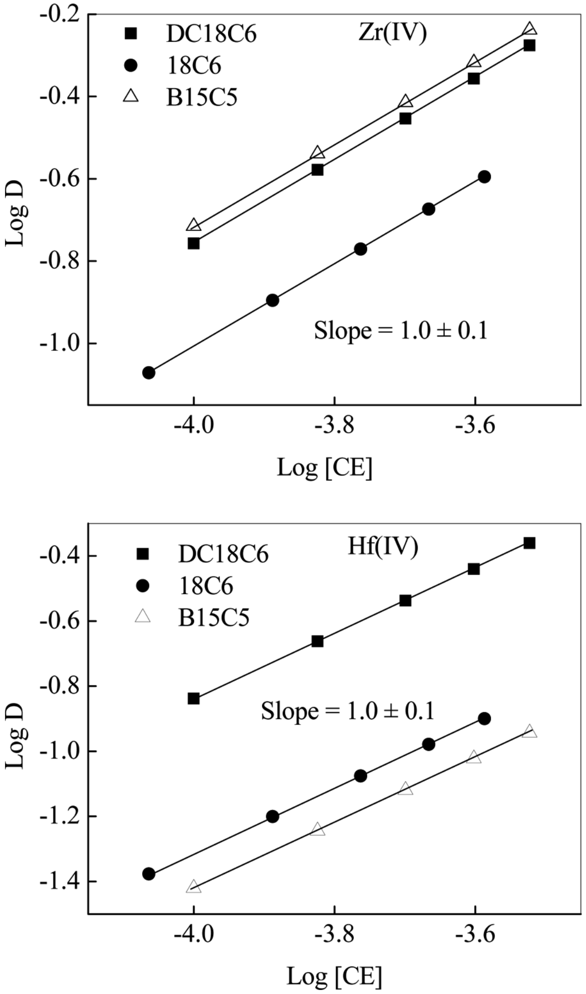


Figure 2. Effect of crown ethers concentration on the extraction of Zr(IV) or Hf(IV) (1.0×10^{-4} mol L^{-1}) from 0.2 mol L^{-1} hydrochloric acid solutions, without HPBI.

of complexation of various CEs with metal chelates in the synergistic extraction systems. The extent of complexation essentially depends on relative sizes of the cation and the crown cavity, the number of oxygen atoms in the polyether ring, coplanarity of the oxygen atoms, symmetrical placement of oxygen atoms, basicity of the oxygen atoms, steric hindrance in the polyether ring, and electrical charge on the metal ion (15).

The effect of HPBI concentration (1.0×10^{-3} -3.0×10^{-3} mol L^{-1} in chloroform) on the extraction efficiency of zirconium(IV) and hafnium(IV)

Table 1. Two phase distribution coefficients (D) and separation factors (S.F.) for Zr (IV)-CE-chloroform and Hf(IV)-CE-chloroform systems at [CE] = 0.00025 mol L^{-1}

	D		S.F.
Extraction system	Zr(IV)	Hf(IV)	Zr/Hf
B15C5	0.451	0.095	4.73
DC18C6	0.440	0.363	1.21
18C6	0.212	0.105	2.02

has been investigated at constant metal ion (1.0×10^{-4} mol L^{-1}), hydrochloric acid (0.2 mol L^{-1}) and crown ether (2.5×10^{-4} mol L^{-1} of 18C6, DC18C6 and B15C5) concentrations, and the results are depicted in Fig. 3. The extraction efficiency of both the metal ions increased linearly with increasing concentration of HPBI in the organic phase. It is clear from the plots of log D vs, log $[HPBI]_{free}$ that at constant crown ether concentration, only two molecules of HPBI are involved in the synergistically extracted complexes.

The effect of various crown ether concentrations on the extraction of zirconium(IV) and hafnium(IV) at constant HPBI concentration (1.0 ×

Table 2. Synergistic enhancement factors of Zr(IV) and Hf(IV) with HPBI in the presence of Crown Ethers

			Synergistic enhancement factors	
CE	$[HPBI]_{initial}$ mol $L^{-1} \times 10^{-3}$	$[CE]_{initial}$ mol $L^{-1} \times 10^{-4}$	Zr(IV)	Hf(IV)
B15C5	1.0	1.5	1.05	2.06
	1.0	2.0	1.13	2.34
	1.0	2.2	1.20	2.38
	1.0	2.5	1.31	2.53
	1.0	3.0	1.48	2.63
DC18C6	1.0	1.5	1.31	2.65
	1.0	2.0	1.64	3.11
	1.0	2.2	1.74	3.03
	1.0	2.5	1.89	3.20
	1.0	3.0	2.14	3.25
18C6	1.0	1.5	1.06	5.68
	1.0	2.0	1.36	6.31
	1.0	2.5	1.63	6.78
	1.0	3.0	1.89	7.15
	1.0	3.5	2.13	7.46

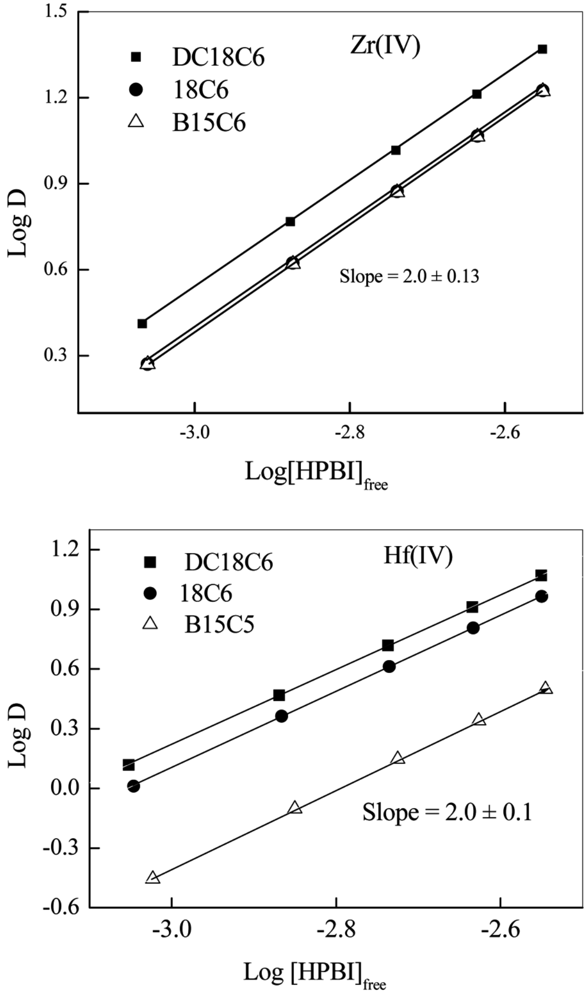


Figure 3. Effect of HPBI concentration on the extraction of Zr(IV) or Hf(IV) (1.0×10^{-4} mol L^{-1}) from 0.2 mol L^{-1} hydrochloric acid solutions. [B15C5] = [DC18C6] = [18C6] = 2.5×10^{-4} mol L^{-1} in $CHCl_3$.

10^{-3} mol L^{-1} in chloroform) has been examined from 0.2 mol L^{-1} HCl solutions, and the results are shown in Fig. 4. The plots of log D vs log [CE]$_{free}$ at constant HPBI concentration gave slopes of unity for both the metal ions, indicating the participation of only one CE molecule in the synergistic extracted species.

The extraction of zirconium(IV) and hafnium(IV) with 1.0×10^{-3} mol L^{-1} HPBI in the presence of various crown ethers (2.5×10^{-4} mol L^{-1} 18C6 or

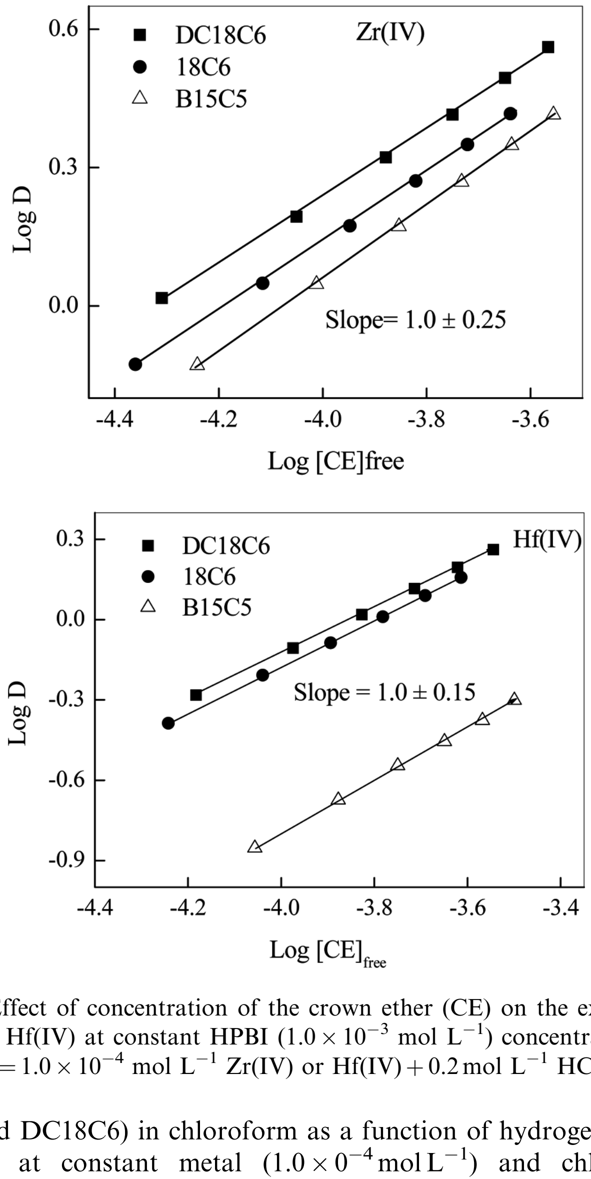


Figure 4. Effect of concentration of the crown ether (CE) on the extraction of Zr(IV) and Hf(IV) at constant HPBI (1.0×10^{-3} mol L^{-1}) concentration. Aqueous phase $= 1.0 \times 10^{-4}$ mol L^{-1} Zr(IV) or Hf(IV) + 0.2 mol L^{-1} HCl.

B15C5 and DC18C6) in chloroform as a function of hydrogen-ion concentration at constant metal (1.0×0^{-4} mol L^{-1}) and chloride ion (1.0 mol L^{-1}) concentrations has been studied using HCl +NaCl mixtures and the results are given in Fig. 5. The extraction behavior shows an inverse dependence on the acidity. The log-log plots gave a slope of -2.0 ± 0.1, indicating the release of two hydrogen ions to the aqueous phase by reacting with two HPBI molecules. The effect of chloride ion concentration (0.2 – 1.0 mol L^{-1}) on the extraction efficiency of zirconium(IV)

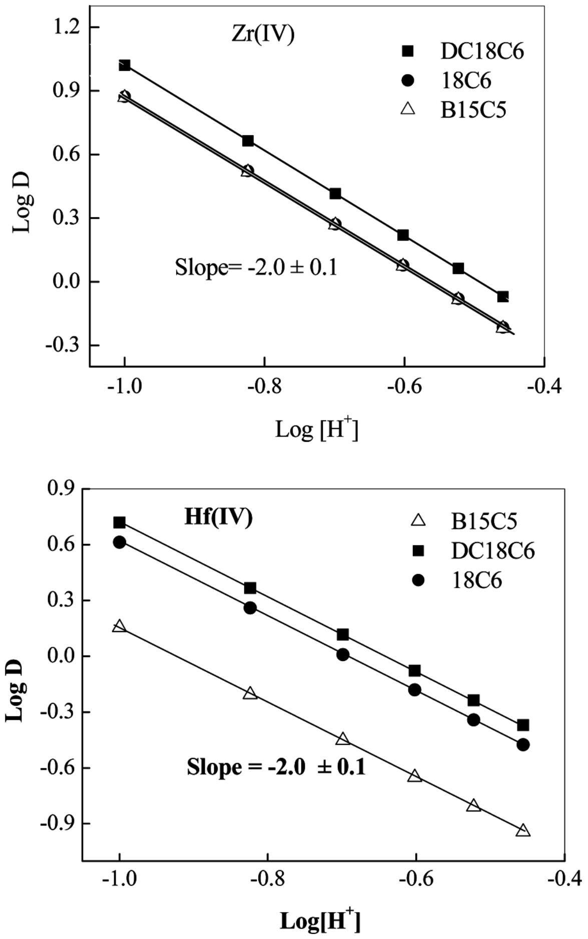


Figure 5. Effect of hydrogen ion concentration on extraction of Zr(IV) and Hf(IV). Aqueous phase = 1.0×10^{-4} mol L^{-1} Zr(IV) or Hf(IV) + 1.0 mol L^{-1} Cl$^-$; Organic Phase = HPBI (1.0×10^{-3} mol L^{-1}) +CE (2.5×10^{-4} mol L^{-1} 18C6 or B15C5 and DC18C6).

and hafnium(IV) with HPBI (1.0×10^{-3} mol L^{-1}) in the presence of crown ethers (2.5×10^{-4} mol L^{-1}18C6 or B15C5 and DC18C6) in chloroform at constant metal (1.0×10^{-4} mol L^{-1}) and hydrogen ion (0.2 mol L^{-1}) concentrations has shown that the extraction efficiency of metal ions are independent of the chloride ion concentration.

The effect of metal ion concentration ($9.5 \times 10^{-5} - 1.8 \times 10^{-4}$ mol L^{-1}) on the extraction process of zirconium(IV) and hafnium(IV) from 0.2 mol dm^{-3} hydrochloric acid solutions has been studied with HPBI

(1.0×10^{-3} mol dm^{-3}) in the presence of various crown ethers (2.5×10^{-4} mol L^{-1} 18C6 or B15C5 and DC18C6). It has shown that the extraction is independent of metal ion concentration in the investigated range. The log–log plots (Fig. 6) of equilibrium organic phase metal ion concentration against aqueous phase metal ion concentration are linear with a slope of unity, indicating the extraction of mononuclear species into the organic phase.

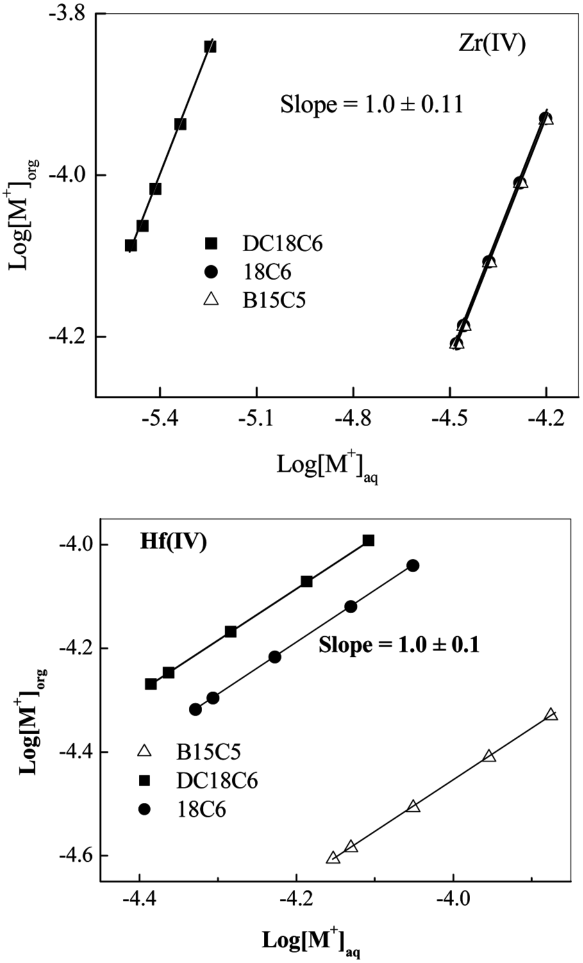


Figure 6. Effect of metal ion concentration on the extraction process of Zr(IV) and Hf(IV) with HPBI (0.001 mol L^{-1}) in the presence of crown ethers (2.5×10^{-4} mol L^{-1} 18C6 or B15C5 and DC18C6). Aqueous phase = 0.2 mol L^{-1} HCl + 0.8 mol L^{-1} Cl^{-}.

Thus the extraction equilibrium of zirconium(IV) and hafnium(IV) from hydrochloric acid solutions with HPBI in the presence of various crown ethers (CE) may be represented as:

$$\mathrm{MO}^{2+}_{\mathrm{aq}} + 2\ \mathrm{HPBI}_{\mathrm{org}} + \mathrm{CE}_{\mathrm{org}}\ 21^{K_{\mathrm{syn},1}}\mathrm{MO(PBI)_2CE}_{\mathrm{org}} + 2\mathrm{H}^{+}_{\mathrm{aq}} \qquad (1)$$

Where $K_{\mathrm{Syn},1}$ represents the synergistic equilibrium constant and is given by,

$$K_{\mathrm{Syn},1} = \frac{[\mathrm{MO(PBI)_2} \cdot \mathrm{CE}]_{\mathrm{org}}\ [\mathrm{H}^+]^2_{\mathrm{aq}}}{[\mathrm{MO}^{2+}]_{\mathrm{aq}}[\mathrm{HPBI}]^2_{\mathrm{org}}\ [\mathrm{CE}]_{\mathrm{org}}} \qquad (2)$$

$$\text{where } [\mathrm{CE}] = [\mathrm{CE}]_{\mathrm{initial}} \Big/ \left(1 + \frac{1}{K_D}\right) \qquad (3)$$

The equilibrium concentration of 18C6 was calculated using the partition coefficient ($\log K_{D,\mathrm{18C6}} = 0.8$) taken from the literature (28). Since the partition coefficients of DC18C6 and B15C5 [$\log K_{D,\mathrm{DC18C6}} = 3.52$ (35); $\log K_{D,\mathrm{B15C5}} = 2.5$ (36)] are known to be quite large, no correction is necessary for the partitioning of CEs into the aqueous phase. The interaction between the chelating agent and a neutral oxo-donor in chloroform are, in general, weaker when the diluent itself has strong interaction with the oxo-donor (27,37,38). Hence, it is assumed that there is negligible interaction between HBPI and CEs in chloroform. The initial concentrations of HPBI and crown ethers chosen in the present study are moderately lower/or equal to the initial metal concentration, and hence free ligand concentrations were calculated and used in the respective log-log plots (Figs. 3 and 4).

The adduct formation reaction in the organic phase and the stability constant, K_{CE} is given by

$$\mathrm{MO(PBI)_{2org}} + \mathrm{CE}_{\mathrm{org}} \xrightleftharpoons{K_{\mathrm{CE}}} \mathrm{MO(PBI)_2} \cdot \mathrm{CE}_{\mathrm{org}} \qquad (4)$$

$$K_{\mathrm{CE}} = K_{\mathrm{Syn},1}/K_{\mathrm{ex,M(IV)}} \qquad (5)$$

Where $K_{\mathrm{ex,M(IV)}}$ denotes the conditional equilibrium constant for:

$$\mathrm{MO}^{2+}_{\mathrm{aq}} + 2\mathrm{HA}_{\mathrm{org}} \xrightleftharpoons{K_{\mathrm{ex.M(IV)}}} \mathrm{MOA}_{\mathrm{2org}} + 2\ \mathrm{H}^{+}_{\mathrm{aq}} \qquad (6)$$

The synergistic equilibrium constants ($K_{\mathrm{syn},1}$) of the above extracted complexes of these metal ions were deduced by nonlinear regression analysis and are given in Table 3. The adduct formation constants (K_{CE}),

Table 3. Two phase equilibrium constants and separation factors (S.F.) for Zr(IV)-HPBI-CE-chloroform and Hf(IV)-HPBI-CE-chloroform systems

	Log $K_{\mathrm{Syn},1}$		Log K_{CE}		S.F.
Extraction system	Zr(IV)	Hf(IV)	Zr(IV)	Hf(IV)	(Zr/Hf)
HPBI + B15C5	8.49 ± 0.03	7.77 ± 0.05	3.11 ± 0.03	2.70 ± 0.05	5.28
HPBI + DC18C6	8.64 ± 0.04	8.34 ± 0.05	3.27 ± 0.04	3.27 ± 0.05	1.99
HPBI + 18C6	8.54 ± 0.05	8.32 ± 0.03	3.17 ± 0.05	3.25 ± 0.03	1.66

for the organic phase synergistic reactions of Zr-HPBI-chelate and Hf-HPBI-chelate with various CEs were also calculated and are given in Table 3.

The complexation strength of zirconium(IV) and hafnium(IV) with various CEs follows the order: DC18C6 >18C6 > B15C5. The sharp decrease in the complexation from DC18C6 to B15C5 mostly reflects increasing steric effects and decreasing basicity. This seems reasonable, since the extensive thermodynamic studies on cation-crown ether complexation have shown that the cation binding ability of the CE containing benzo groups is lower than that for the parent CE, and demonstrated that the diminished complex stability is due to the decreased electron density of donor oxygens produced by the electron-withdrawing aromatic ring (39). The cyclohexano group has a less dramatic effect on the stability of the complex and on cation selectivity (40). A better understanding of the interactions of CEs with metal-chelate systems requires more detailed investigations of the solution structures of these complexes.

The separation factors (S.F.) between zirconium(IV) and hafnium(IV), defined as the ratio of respective equilibrium constants with HPBI + CE systems at 0.2 mol L^{-1} HCl solutions have been calculated and are given in Table 3. It is interesting to note that the addition of CEs not only enhances the extraction efficiency of these metal ions but also significantly, especially,- in the presence of B15C5, improves the selectivity (Zr/Hf = 5.28) between these metal ions as compared to crownethers, DC18C6(Zr/Hf = 1.21), 18C6 (Zr/Hf = 2.02), B15C5 (Zr/Hf = 4.73) and HPBI alone (Zr/Hf = 2.09) (8). This can be explained on the basis of steric factors and basicity value of B15C5. On the other hand, selectivity has been moderately decreased by the addition of 18C6 or DC18C6 to the metal-chelate system. However, the S.F. values found in the present study are lower than that reported elsewhere with DC18C6 (41). The extraction of zirconium(IV) and hafnium(IV) from hydrochloric acid media using DC18C6 has been investigated by Sudowe et al. (41) and reported that the S.F. value decreases with increasing acid concentration in the aqueous phase (S.F. = Zr/Hf = 2.5 at 7.0 mol L^{-1} HCl; 28 at 8.0 mol L^{-1} HCl and 4.3 at 9.0 mol L^{-1} HCl).

CONCLUSIONS

The synergistic extraction of zirconium(IV) and hafnium(IV) with HPBI in the presence of various macrocyclic ligands such as benzo-15-crown-5, 18-crown-6, and dicyclohexano-18-crown-6 from dilute hydrochloric acid solutions has been studied and the extracted complexes have been elucidated. The extracted complexes have been elucidated as $ZrO(PBI)_2 \cdot CE$ and $HfO(PBI)_2 \cdot CE$ in the presence of crown ethers (CE). The addition of CE to the metal-chelate systems considerably improves the extraction efficiency of these metal ions. The complexation strength of zirconium(IV) and hafnium(IV) with various CEs follows the order DC18C6 > 18C6 > B15C5. The sharp decrease in the complexation from DC18C6 to 18C6 and to B15C5 mostly reflects increasing steric effects and decreasing basicity. A better understanding of the interactions of crown ethers with Zr(IV)-HPBI or Hf(IV)-HPBI system requires more detailed investigations of the solution structures of these complexes by X-ray absorption fine structure (XAFS) measurements. Better selectivity between zirconium(IV) and hafnium(IV) has been achieved in the presence of B15C5 (Separation Factor: Zr/Hf = 5.28 with HPBI +B15C5) as compared to crownethers, DC18C6(Zr/Hf = 1.21), 18C6 (Zr/Hf = 2.02), B15C5 (Zr/Hf = 4.73) HPBI alone (Zr/Hf = 2.19 with HPBI). Thus, the above mixed ligand system may extend its potential application to the extraction and separation of zirconium(IV) and hafnium(IV) from dilute hydrochloric acid solutions.

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