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Enhanced Extraction and Separation of Zr(IV) and Hf(IV) from Acidic Chloride Solutions Using 4-Sebacoyl*bis*(1-phenyl-3-methyl-5-pyrazolone) in Presence of Crown Ethers

JANARDHAN REDDY KODURU[1,*], LAKSHMI PRASANNA LINGAMDINNE[2], YOON-YOUNG CHANG[2] and C. RAMACHANDRAIAH[3]

[1]Graduate School of Environmental Studies, Kwangwoon University, Seoul, 139-701, Republic of Korea
[2]Department of Environmental Engineering, Kwangwoon University, Seoul, 139-701, Republic of Korea
[3]Srikalahastheeswara Institute of Technology, Srikalahasti-517 640, India

*Corresponding author: Fax: +82 2 9185774; Tel: +82 2 9405496; E-mail: reddyjchem@gmail.com

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Synergistic extraction behaviour and selectivity in the separation of Zr(IV) and Hf(IV) were examined using synthesized 4-sebacoyl*bis*(1-phenyl-3-methyl-5-pyrazolone) (H_2SbBP) in presence of various crown ethers (CEs), such as 18-crown-6 (18C6), dicylohexano-18-crown-6 (DC18C6) and benzo-15-crown-5 (B15C5) from acidic chloride solutions. The preceding results demonstrate that Zr(IV) and Hf(IV) were synergistically extracted into chloroform with H_2SbBP and crown ethers as $ZrO(HSbBP)_2$-CE and $HfO-(HSbBP)_2$-CE, respectively. The synergistic complexation strength of Zr(IV) and Hf(IV) was follows in order DC18C6 > 18C6 > B15C5. The addition of crown ethers to H_2SbBP in chloroform not only enhance the extraction but also improves the selectivity in the separation of Zr(IV) and Hf(IV), especially, in presence of B15C5 (Zr(IV)/Hf(IV) = 13.18), where compared to H_2SbBP alone (Zr(IV)/Hf(IV) =1.17) and other typical reports in literature. On the other hand the selectivity moderately decreased by the addition of DC18C6 and 18C6 to the synergistic solvent system.

Keywords: Zr(IV) and Hf(IV) separation, Extraction, Synergistic solvent extraction, Pyrazolones, Crown ethers.

INTRODUCTION

Zirconium and hafnium are well known materials due to their importance in nuclear reactors[1], catalyzed reactions[2] and their use in separation of rare earths[3,4]. Because of their similar atomic radii, the separation of Zr(IV) and Hf(IV) has great interest in the field of solvent extraction, due to the difference in their thermal neutron capture cross-section property[5,6] There are some existing extraction techniques for extractive separation of Zr(IV) and Hf(IV)[1,3,5] However, those have some limitations, such as soluble of organic solvent in aqueous medium, decomposition of thiocynate with HCl and high energy consumption of extractive distillation still requires a sophisticated technology to overcome these limitations[7-9]. These leads to search an alternative solvent extraction technique, such as synergistic solvent extraction[10-13] for effective separation of Zr(IV) and Hf(IV).

Pyrazolones[14,15] and crown ethers[16-20] were widely used for the separation of various lanthanides and actinides. Recently, we also reported a synergistic solvent extraction mechanism for selective separation of Zr(IV) and Hf(IV) using 4-acyl*bis*pyrazolones or 4-acyl*bis*isoaxazolones in the presence of neutral organophosphorous compounds (*i.e.*, TOPO, TBP, Cyanex-923) and 4-acyl*bis*isoaxazolones in the presence of crown ethers (CEs) (*i.e.*,18-crown-6 (18C6), dicyclohexano-18-crown-6 (DC18C6), benzo-15-crown-5 (B15C5)). However, a better selectivity was achieved between Zr(IV) and Hf(IV) with mixtures of HPBI + CEs, especially, in the presence of B15C5 (S.F. = 5.23) than alones, such as HPBI (S.F. = 2.09) and B15C5 (S.F. = 4.73). On the other hand, the 4-sebacoyl*bis*(1-phenyl-3-methyl-5-pyrazolone) (H_2SbBP) was achieved a better extraction efficiency towards Zr(IV) and Hf(IV)[7,9,12]. These results prompted us to develop an alternative liquid-liquid extraction technique for selective separation of Zr(IV) and Hf(IV) from acidic chloride solutions using 4-acyl*bis* pyrazolones in presence of crown ethers..

In the present study, 4-sebacoyl*bis*(1-phenyl-3-methyl-5-pyrazolone) (H_2SbBP) with crown ethers (as synergistic agent), such as 18C6 or DC18C6 or B15C5 was used for the synergistic extraction studies of Zr(IV) and Hf(IV) from hydrochloric acid solutions. It also includes the development of an extraction mechanism for Zr(IV) and Hf(IV) and observed the selectivity in the separation of them. The interfering studies of associated metal ions, such as Fe(III), Al(III) and Ti(III) were also included in this study. The comparison of present results with some reported results (Table-1)[7,9,13,21-26]

TABLE- 1
COMPARISON OF PRESENT RESULTS WITH SOME OTHER RELATED EXTRACTION SYSTEMS

Extraction system	Conditions	% Extraction		S.F. (Zr/Hf)	Remarks	Ref.
		Zr(IV)	Hf(IV)			
Cyanex 301	pH 4.0 in presence of NaCl	NR	NR	7.0	Use of low acidic nitrate solutions, the lack of using of thiocyanate and a higher extraction of hafnium relative to zirconium	21
Glycidylmethacrylate/divinylbenzene/Fe_3O_4	Chloride media	94	24	3.9	93.3 and 98.3 % of Zr(IV) and Hf(IV), respectively regenerated using 1 mol L^{-1} HNO_3	22
Amberjet 4200 Cl	9.5 mol L^{-1} HCl	NR	NR	9.0	High acid concentration causes for polymerization	23
TBP/Cyanex 923	HNO_3/$NaNO_3$	< 98.1 %	< 90.9 %	< 12.25	Acid and salt sensitive extraction	24
Diphonix®	0.5 mol L^{-1} H_2SO_4 at 22 °C	45 %	55 %	<1.0	Temperature sensitive extraction	25
Salicylaldoxime/Neutral organophosphorus extractants	HCl medium	< 95 %	NR	NR	Not discussed about separation of Zr(IV) and Hf(IV)	26
Pyrazolones/Crown ethers	0.1 mol L^{-1} H^+	98.9 %	77 %	13.18	Better extraction and separation between Zr(IV) and Hf(IV)[a]	

[a]In the present study; NR: Not reported

indicates that the present method was more selective and sensitive method for extractive separation of Zr(IV) and Hf(IV).

EXPERIMENTAL

To measure absorbances of Zr(IV) and Hf(IV) xylenol orange colour complexes, 220 double-beam microprocessor-controlled spectrophotometer was used (Hitachi, Tokyo, Japan). An Orion (USA) 720A Ion Analyzer was used for the pH measurements. A Nicolet FT-IR 560 magna spectrometer (USA) using KBr (neat) was used to obtain the infrared spectra of the synthesized compounds. C, H and N analysis were performed with a Perkin-Elmer Series 2 Elemental Analyzer 2400 (USA). The Bruker 300 MHz NMR spectrometer (UK) was used to obtain the ^{1}H NMR spectra of the ligands.

All chemicals were used of analytical reagent grade otherwise stated here. $ZrOCl_2.8H_2O$ (Fluka, 98 %) and $HfCl_4$ (Fluka, 98 %) were used for the preparation of Zr(IV) and Hf(IV) metal ion solutions. Freshly prepared solutions of Zr(IV) and Hf(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 mol dm^{-3} using sodium chloride. Gravimetric reagent grade xylenol orange (Lobachemie Pvt. Ltd., India) was used for the spectrophotometric determination of Zr(IV) and Hf(IV). Crown ethers, 18-crown-6 (18C6), dicyclohexano-18-crown-6 (DC18C6) and benzo-15-crown-5 (B15C5) were obtained from Aldrich Chemical Company. Analytical reagent grade chloroform (Merck, USA), was used as diluents in the present study.

Synthesis of 4-Sebacoyl*bis* (1-phenyl-3-methyl-5-pyrazolones) (H_2SbBP): 4-Sebacoyl*bis* (1-phenyl-3-methyl-5-pyrazolones) (H_2SbBP) was prepared by the acylation of 1-phenyl-3-methyl-5-pyrazolone with the sebacoyl acid dichloride by following the method described elsewhere[9,13]. Chloroform-hexane mixture was used for recrystallization of the crude compound and was dried under reduced pressure. The purity of the compound was checked by elemental analysis, IR and ^{1}H NMR spectral data, which are given here[9,13]: m.p. = 135-136 °C; Elemental analysis (%): Calc. for $C_{30}H_{34}O_4N_4$: C, 70.03; H, 6.61; N, 10.89. Found: C, 69.48; H, 6.51; N, 10.67 %; ^{1}H NMR data ($CDCl_3$/TMS): δ 7.81-7.84, 7.42-7.47, 7.28-7.30 (m, 10H, Ph); 2.71-2.76 (t, 4H, $(CH_2)_2$); 2.48 (s, 6H, CH_3); 1.73-1.77 (m, 4H, $(CH_2)_2$); 1.39 (m, 8H, $(CH_2)_4$) IR (KBr, ν_{max}, cm^{-1}): 3430 (br, OH); 1633 (s, C=O); 1593 (s, phenyl C=C);1553 (s, pyrazolone ring).

Liquid-liquid extraction and analytical procedures: Metal ion distribution ratios were determined by shaking equal volumes of aqueous and organic phases for 2 h in a glass stoppered vial using a mechanical shaker at 303 ± 1 K. Preliminary experiments showed that the extraction equilibrium was attained within 1 h for Zr(IV) and 2h in case of Hf(IV). After phases disengagement, the aqueous phase was separated and determined the metal ions concentration by spectrophotometrically (λ_{max} = 535 nm; detection limit = 0.06×10^{-6} mol L^{-1} for both the metal ions) using the xylenol orange method[7,9,12,27]. The distribution ratio (D) was taken as the ratio of the concentration of metal ion in organic phase to that in the aqueous phase. All experiments were performed in duplicate and the general agreement between the distribution ratios values obtained was within ± 5 %. In the present study, chloroform was used as diluent due to the solubility limitations of H_2SbBP in various industrially employed diluents.

RESULTS AND DISCUSSION

Synergistic extraction of Zr(IV) and Hf(IV) with mixtures of H_2SbBP and crown ethers: The mixtures of H_2SbBP (1×10^{-2}-3×10^{-2} mol L^{-1}) and 18C6 or B15C5 or DC18C6 (1×10^{-3}-3.5×10^{-3} mol L^{-1}) in chloroform were used to examine the synergistic extraction behavior of Zr(IV) and Hf(IV) from 0.2 mol L^{-1} hydrochloric acid solutions. It was found that the extraction of Zr(IV) and Hf(IV) with mixtures of H_2SbBP and crown ethers, considerable synergistic enhancement (synergistic enhancement factor (S.E.F.) = $D_{mix}/(D_{H2SbBP} + D_{CE})$, where D_{mix} = distribution ratio with H_2SbBP + CE; D_{H2SbBP} = distribution ratio with H_2SbBP alone; D_{CE} = distribution ratio with CE alone) has been observed in the extraction of these metal ions (Table-2). However, the extraction of Zr(IV) and Hf(IV) with the above crown ethers (CEs) alone were negligible under the present experimental conditions which were published in our earlier paper[7]. It is clear from Table-2

TABLE-2
SYNERGISTIC ENHANCEMENT FACTORS OF ZR(IV) AND HF(IV) WITH H_2SBBP IN THE PRESENCE OF CROWN ETHERS

Crown ether (CE)	$[CE]_{initial, \times 10^{-3}}$ (mol L^{-1})	$[H_2SbBP]_{initial, \times 10^{-2}}$ (mol L^{-1})	Synergetic enhancement factors	
			Zr(IV)	Hf(IV)
18C6	1	1	3.50	1.71
	2	1	4.25	2.16
	3	1	4.54	2.37
DC18C6	1	1	4.25	1.39
	2	1	5.02	1.62
	3	1	5.35	1.74
B15C5	1	1	3.57	1.01
	2	1	4.21	1.91
	3	1	4.53	2.72

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 of complexation of various crown ethers with metal chelates in the synergistic extraction systems. The extent of complexation essentially depends on relative sizes of the cation and the crown cavity, 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[7,9,28,29].

The effect of H_2SbBP concentration (1×10^{-2} to 3×10^{-2} mol L^{-1} in chloroform) on the extraction efficiency of Zr(IV) and Hf(IV) has been studied at constant metal ion (1×10^{-3} mol L^{-1}), hydrochloric acid (0.2 mol L^{-1}) and crown ether (2×10^{-3} mol L^{-1} of 18C6, DC18C6 and B15C5) concentrations and the results are shown in Fig. 1. The extraction efficiency of both metal ions increases linearly with increasing concentration of H_2SbBP in the organic phase. It is clear from the plots of log D *vs*. log [H_2SbBP]free that at constant crown ether concentration, only two molecules of H_2SbBP are involved in the synergistically extracted metal complexes.

The effect of various crown ether concentrations on the synergistic extraction of Zr(IV) and Hf(IV) from 0.2 mol L^{-1} has been investigated at constant H_2SbBP concentration (1×10^{-2} mol L^{-1} in chloroform) and the results are shown in Fig. 2. The synergistic extraction efficiency increases linearly with increasing crown ether concentration. The plots of log D *vs*. log $[CE]_{free}$ at constant H_2SbBP concentration gave slopes of 1 ± 0.35 for both the metal ions, indicating the participation of only one CE molecule in the synergistic extracted species.

The synergistic extraction behaviour of Zr(IV) and Hf(IV) with mixture of H_2SbBP (1×10^{-2} mol L^{-1}) and various crown ethers (2×10^{-3} mol L^{-1} 18C6 or B15C5 and DC18C6) in chloroform as a function of hydrogen ion concentration at constant metal (1×0^{-3} mol L^{-1}) and chloride ion (1 mol L^{-1}) concentrations has been examined using HCl + NaCl mixtures and the results are given in Fig. 3. The synergistic extraction behaviour shows an inverse dependence on the acidity. The log-log plots gave slope of -2 ± 0.01, reveals that the release of two hydrogen ions to the aqueous phase by reacting with two H_2SbBP molecules.

The synergistic extraction efficiency of Zr(IV) and Hf(IV) with H_2SbBP (1×10^{-2} mol L^{-1}) in the presence of crown ethers (2×10^{-3} mol L^{-1} 18C6 or B15C5 and DC18C6) in chloroform at constant concentration of metal (1×10^{-3} mol L^{-1}) and

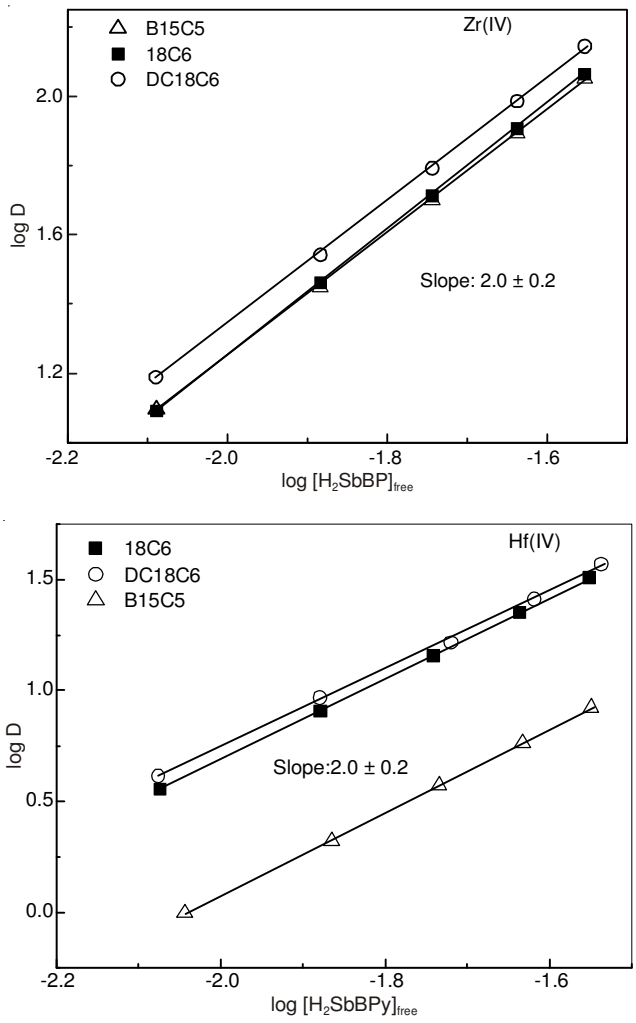

Fig. 1. Synergistic extraction of Zr(IV) and Hf(IV)(1×10^{-3} mol L^{-1}) from 0.2 mol L^{-1} hydrochloric acid solutions (1 mol L^{-1} Cl^-) using H_2SbBP in presence of constant crown ether concentration = [B15C5] = [DC18C6] = [18C6] = 2×10^{-3} mol L^{-1} in $CHCl_3$

hydrogen ion (0.2 mol L^{-1}) concentrations as function of chloride ion concentration (0.2-1 mol L^{-1}) has been observed and the results shown that the extraction efficiency of metal ions are independent of the chloride ion concentration.

The synergistic extraction process of Zr(IV) and Hf(IV) from 0.2 mol L^{-1} hydrochloric acid solutions as a function of metal ion concentration (1×10^{-3}-3×10^{-3} mol L^{-1}) has been studied with H_2SbBP (1×10^{-2} mol L^{-1}) in the presence of

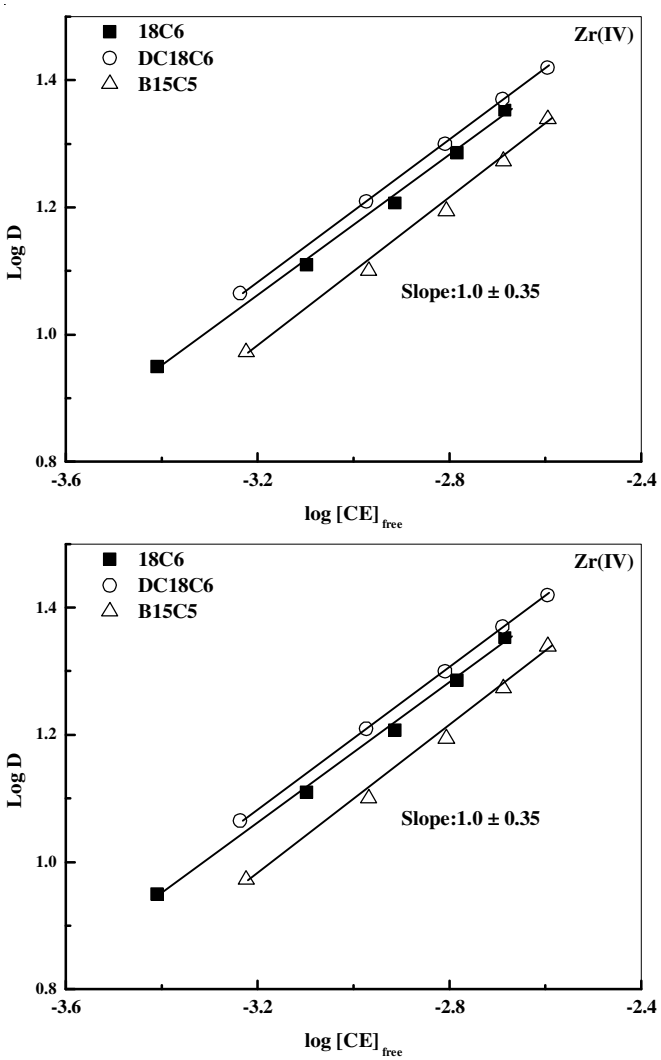

Fig. 2. Synergistic extraction of Zr(IV) and Hf(IV)(1×10^{-3} mol L^{-1}) from 0.2 mol L^{-1} hydrochloric acid solutions(1 mol L^{-1} Cl^{-1}) using CEs in presence of constant H_2SbBP(1×10^{-2} mol L-1) in $CHCl_3$

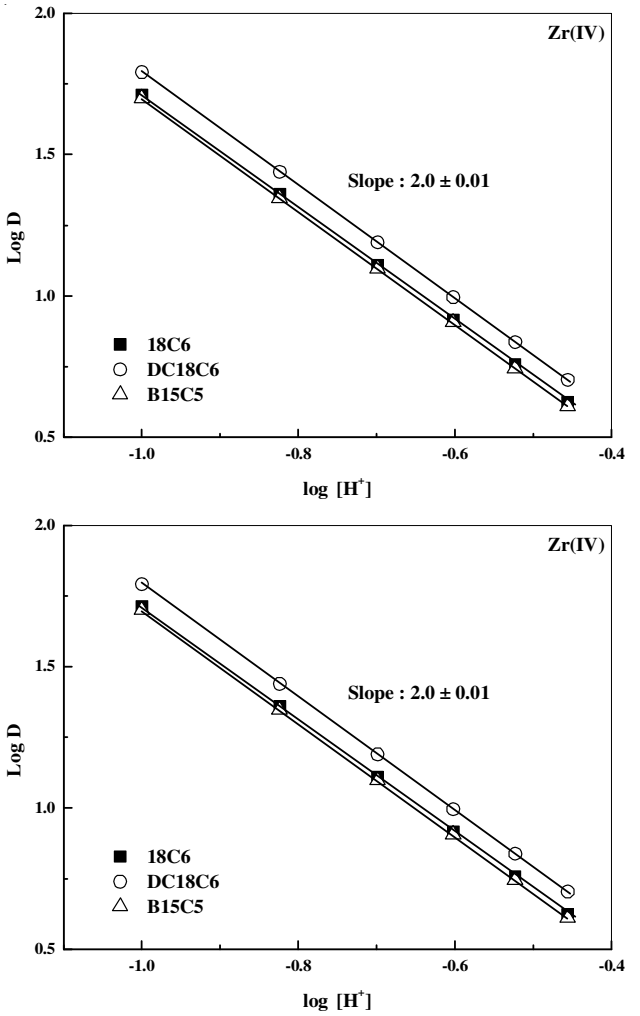

Fig. 3. Effect of hydrogen ion concentration on extraction of Zr(IV) and Hf(IV). Aqueous phase = 1×10^{-3} mol L^{-1} Zr(IV) or Hf(IV) + 1 mol L^{-1} Cl^- ; Organic phase = H_2SbBP (1×10^{-2} mol L^{-1}) + CE (2×10^{-3} mol L^{-1} 18C6 or B15C5 and DC18C6)

various crown ethers (2×10^{-3} mol L^{-1} 18C6 or B15C5 and DC18C6), has shown that the extraction is independent of metal ion concentration in the investigated range. The log-log plots 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.

Thus the extraction equilibrium of Zr(IV) and Hf(IV) from hydrochloric acid solutions with H_2SbBP in the presence of various crown ethers (CEs) may be represented as:

$$MO^{2+}_{aq} + 2H_2SbBP_{org} + CE_{org} \overset{K_{syn}}{\rightleftharpoons} MO(HSbBP)_2.CE_{org} + 2H^+_{aq} \quad (1)$$

where K_{Syn} represents the synergistic equilibrium constant and is given by,

$$K_{syn} = \frac{[MO(HSbBP)_2CE]_{org}[H^+]^2_{aq}}{[MO^{2+}]_{aq}[H_2SbBP]^2_{org}[CE]_{org}} \quad (2)$$

where $$[CE]_{org} = [CE]_{initial} / \left(1 + \frac{1}{K_D}\right) \quad (3)$$

The equilibrium concentration of 18C6 was calculated using the partition coefficient (log $K_{D,18C6}$ = 0.8), which was taken from the literature[7,29]. No correction is necessary in the partitioning of equilibrium concentration of DC18C6 and B15C5, due to their partition coefficients (log $K_{D,DC18C6}$ = 3.52[7,30]; log $K_{D,B15C5}$ = 2.5[7,31]) are known to be quite large. The interaction between the chelating agent and a neutral oxo-donor are weaker when compared with the chloroform interactions with the oxo-donors[7,32-34] Hence, it was assumed that there is negligible interaction between H_2SbBP and crown ethers in chloroform. The initial concentrations of H_2SbBP and crown ethers chosen in the present study moderately equal to the initial metal ion concentration and hence free ligand concentrations were calculated and used in the respective log-log plots (Figs. 1 and 2).

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

$$MO(HSbBP)_{2org} + CE_{org} \overset{K_{CE}}{\rightleftharpoons} MO(HSbBP)_2.CE_{org} \quad (4)$$

$$K_{CE} = K_{Syn}/K_{ex.M(IV)} \quad (5)$$

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

$$MO^{2+}_{aq} + 2H_2SbBP_{org} \overset{K_{ex,M(IV)}}{\rightleftharpoons} MO(HSbBP)_{2org} + 2H^+ \quad (6)$$

The synergistic equilibrium constants (K_{syn}) of the above extracted complexes of these metal ions were deduced by nonlinear regression analysis and results were given in Table-3. The adduct formation constants (K_{CE}), for the organic phase synergistic reactions of ZrO-$(HSbBP)_2$ chelate and HfO-$(HSbBP)_2$ chelate with various crown ethers were also calculated and are given in Table-3.

The synergistic complexation strength of Zr(IV) and Hf(IV) with various crown ethers follows the order: DC18C6 > 18C6 > B15C5. It reflects increasing steric hindrance and decreasing basicity of crown ethers. 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[7,35]. The cyclohexano group has a less dramatic effect on the stability of the complex and on cation selectivity[7,36]. A better understanding of the interactions of crown ethers with metal-chelate systems requires more investigations of the solution structures of these complexes.

Separation of Zr(IV) and Hf(IV) using H_2SbBP in presence of crown ethers: The separation factors (S.F.) between Zr(IV) and Hf(IV), defined as the ratio of respective equilibrium constants with H_2SbBP + CE systems at 0.2 mol L^{-1} HCl solutions have been calculated (Table-3). It is interesting to note that the addition of crown ethers not only enhances the extraction efficiency of these metal ions but also significantly improves the selectivity between these metal ions, especially, in the presence of B15C5 (Zr/Hf = 13.18), which is a better selectivity when compared to H_2SbBP [Zr(IV)/Hf(IV) = 1.17] or B15C5 (Zr(IV)/Hf(IV) = 4.73) alone, their synergistic systems[7,9] and as well as in other typical or related extraction systems reported elsewhere (Table-1)[21-26] This can be explained on the basis of steric hindrance and basicity factors of B15C5. On the other hand, selectivity between Zr(IV) and Hf(IV) has been moderately decreased by the addition of 18C6 or DC18C6 to the metal-chelate system.

Effect of interfering metal ions: Effect of interfering metal ions, such as Fe(III), Al(III) and Ti(III) (1×10^{-3} mol L^{-1}) on liquid-liquid extraction of Zr(IV) and Hf(IV) (1×10^{-3} mol L^{-1}) has been studied as a function of HCl concentration using mixture of 1×10^{-2} mol L^{-1} H_2SbBP and 2×10^{-3} mol L^{-1} B15C5 in chloroform and were shown in Fig. 4. The results indicates that the percentage extraction of Zr(IV), Hf(IV) and Fe(III) are decreased with increasing HCl concentration where as Al(III) and Ti(III) are quantitatively extracted up to 60 % under present experimental conditions.

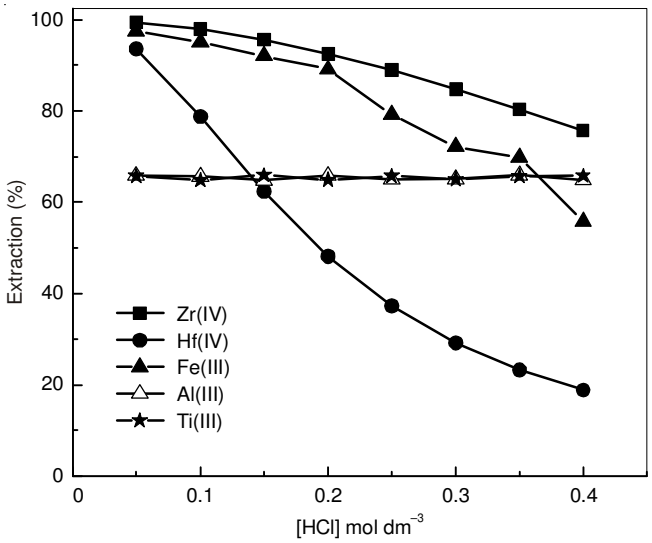

Fig. 4. Effect of HCl concentration on the extraction of interfering metal ions: $[M^+] = 1 \times 10^{-3}$ mol L^{-1}; $[H_2SbBP] = 1 \times 10^{-2}$ mol L^{-1}; [B15C5] = 2×10^{-3} mol L^{-1}

Conclusion

The mixture of H_2SbBP and macrocyclic ligands, such as 18C6 or DC18C6 or B15C5 has been used for the synergistic extraction of Zr(IV) and Hf(IV) from dilute hydrochloric acid solutions and elucidated the extracted complexes as $ZrO(HSbBP)_2$-CE and $HfO(HSbBP)_2$-CE. The addition of CE to the metal-chelate systems considerably improves the extraction efficiency of these metal ions. The complexation strength of H_2SbBP for Zr(IV) and Hf(IV) with various crown ethers follows the order DC18C6 > 18C6 > B15C5. The sharp decrease in the complexation strength from DC18C6 to 18C6 and to B15C5 mostly reflects on decreasing basicity as increasing steric hindrance. A better separation selectivity between Zr(IV) and Hf(IV) has been achieved by the addition of B15C5 to the MO-$(HSbBP)_2$ chelating system (Separation factor: Zr(IV)/Hf(IV) = 13.18 with H_2SbBP+ B15C5) as compared to crown ethers, DC18C6 (Zr(IV)/Hf(IV) = 1.21), 18C6 (Zr(IV)/Hf(IV) = 2.02), B15C5 (Zr(IV)/Hf(IV) = 4.73) and H_2SbBP alone [Zr(IV)/Hf(IV) =1.17] and their synergistic systems[7,9] as well as their related or typical systems[21-26]. These results indicates that the present system was better selective and suitable for the separation of Zr(IV) and Hf(IV). A better understanding of the interactions of crown ethers with Zr(IV)-H_2SbBP or Hf(IV)-H_2SbBP system requires more detailed investigations of the solution structures of these complexes by X-ray absorption fine structure (XAFS) measurements. Thus, the above mixed ligand system may extend its potential application to the extraction and separation of Zr(IV) and Hf(IV) from dilute hydrochloric acid solutions.

TABLE-3
TWO PHASE EQUILIBRIUM CONSTANTS AND SEPARATION FACTORS (S.F.) FOR Zr(IV)-H_2SBBP-CROWN ETHER-CHLOROFORM AND Hf(IV)-H_2SBBP- CROWN ETHER-CHLOROFORM SYSTEMS

Synergetic extraction system	Zr(IV)		Hf(IV)		Separation factor
	log K_{Syn}	log K_{CE}	log K_{Syn}	log K_{CE}	Zr(IV)/Hf(IV)
18C6 + H_2SbBP	6.41 ± 0.032	4.06 ± 0.040	5.86 ± 0.050	3.61 ± 0.045	3.55
DC18C6 + H_2SbBP	6.49 ± 0.045	4.14 ± 0.035	5.92 ± 0.030	3.67 ± 0.050	3.72
B15C5 + H_2SbBP	6.39 ± 0.025	4.05 ± 0.040	5.27 ± 0.025	3.03 ± 0.030	13.18

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