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Solvent extraction separation of uranium (VI) with acetatecalix[*n*]arene and β-diketone (HTTA)

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Abstract

We have studied a new method for the solvent extraction separation of UO_2^{2+} by four calix[*n*]arenes from acetate solutions. The solvent extraction of UO_2^{2+} with these calix[*n*]arenes and thenoyltrifluoroacetone (HTTA) in toluene has been studied in the presence or absence of alkali ion (Na^+). The efficiency of extraction increases drastically in the presence of alkali ions, due to the formation of heteronuclear complexes. Synergistic extraction was observed with calix[*n*]arenes and thenoyltrifluoroacetone (HTTA). Absorption spectra show shifts of characteristics bands of calix[*n*]arenes from the ultraviolet region to the visible region with a gap of 100 nm when HTTA is in the solution

Keywords: Uranyl ion; Calix[*n*]arenes; Solvent extraction; Thenoyltrifluoroacetone; Synergistic extraction

1. Introduction

The selective extraction of uranium has attracted extensive attention from chemists because of its importance in relation to energy problems. In order to design a ligand that can selectively extract uranyl ions (UO_2^{2+}), one has to overcome a difficult problem, i.e. the ligand must discriminate strictly between UO_2^{2+} and other metal ions present in great excess in sea water and waste solutions. A possibly unique solution to this difficult problem is provided by the unusual coordination structure of UO_2^{2+} complexes which require either a pseudoplanar pentacoordinate or hexacoordinate ligand structure. This suggests that a macrocyclic host molecule having a nearly coplanar arrangement of either five or six ligand groups would act as a specific ligand for UO_2^{2+} (i.e. as uranophile) [1–4].

The calix[*n*]arenes constitute the most extensively characterized series of simple macrocyclic ligands known, all species containing from four to 20 phenolic units being available. The annular space in calix[*n*]arene compounds provides a unique basket-like structure which is useful for trapping metal ions in their three-dimensional network. Calix[*n*]arenes have several attractive features as macrocycles of a higher degree of preorganization. They are formed by *para*-phenolic units linked by methylene bridges *ortho* to the OH functions. As shown in this work, calix[*n*]arenes can be chemically modified by substitution of the phenolic hydrogens with various types of functions known for their affinity for the molecule of interest. Furthermore, phenolic groups can be functionalized on the *para*-position to make the calix[*n*]arene either lipophobic or lipophilic. In this study the calix[*n*]arene is composed of rings of six and four phenolic units used as molecular substructures, on which preorganized ligands, such as six and four acetate groups, are assembled to provide the required structure (Fig. 1) [5–12].

In this paper, the application of a lipophilic calix[*n*]arene (1,2,3,4-tetraacetatocalix[4]arene (2_4)) and 1,2,3,4,5,6-hexaacetatocalix[6]arene (2_6) and HTTA is reported for the extraction of UO_2^{2+} from acetate and nitric media with pH close to that of sea water.

2. Experimental

2.1. Reagents and apparatus

A UV visible spectrophotometer (Model CARY 1) with 10 mm matched quartz cells was used for this study.

The *p*-tert-butyl calix[4]arene (1_4) and *p*-tert-butyl calix[6]arene (1_6) were from Aldrich. *p*-Tert-butyl-tetra-acetate-calix[4]arene and *p*-tert-butyl-hexa-acetate-calix[6]arene were synthesized by the acylation method according to procedures described previously by Gutche [6] and summarized below. The solvent used was washed several

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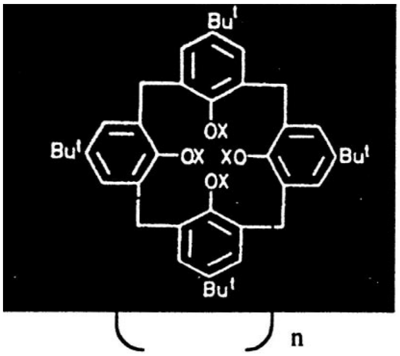

$\mathbf{1_4}$; n=4 X =H
$\mathbf{1_6}$; n=6 X =H
$\mathbf{2_4}$; n=4 X =-CO-CH_3
$\mathbf{2_6}$; n=6 X=-CO-CH_3

Fig. 1. The calix[*n*]arene family.

times with distilled water. Uranium nitrate solutions were prepared from a known amount of the corresponding oxide (U_3O_8) by dissolution in hot concentrated nitric acid and uranium acetate solutions were prepared from a weighed amount of $UO_2(CH_3CO_2)_2$ (Mallinckrodt). All other reagents used in this work were analytical grade.

2.2. Synthesis of n-acetate calix[n]arene

The syntheses of tetraacetatecalix[4]arene and hexaacetatecalix[6]arene derivatives were carried out following an acylation reaction as described by Gutche [6]. About 2.0 g of tert-butyl-calix[*n*]arene was treated with 50 ml acetic anhydride as well as two drops of concentrated sulfuric acid. Recrystallization of the crude product from chloroform/methanol gave white pellets. IR spectra were recorded from CsI disks using nujol with a BOMEN spectrophotometer. The ^{1}H-NMR spectra were recorded on a NMR AC at 200 MHz using deuterated chloroform as solvent.

2.3. Absorption spectra measurements

Absorption spectra of organic phase calix[*n*]arene/toluene with and without HTTA and uranium complexes were recorded using an ultraviolet–visible spectrometer (Cary 1) in the range 190–900 nm because calix[*n*]arenes have characteristic bands in this range.

2.4. Extraction

The solvent extraction experiments were carried out in a stoppered glass vial using a 2:1 volume aqueous to organic phase relationship.

The organic phases *p*-tert-butylcalix[*n*]arenes and *n*-acetocalix[*n*]arenes/HTTA/toluene and aqueous phase containing UO_2^{2+} nitrate and acetates were mixed and the extraction equilibrium was reached after 30 min under continuous stirring. The extraction systems were than centrifuged to complete the separation of the phases before the aqueous phase was analyzed. The UO_2^{2+} in the aqueous phase was measured in a spectrophotometer using an Arsenazo III method [13]. The stock solutions were also standardized by two methods, spectrophotometry and liquid chromatography.

Distribution ratios, $D_{UO_2^{2+}}$, were calculated according to the equation

$$D_{UO_2^{2+}} = [UO_2^{2+}]_{org}/[UO_2^{2+}]_{aq} \tag{1}$$

where $[UO_2^{2+}]_{org}$ and $[UO_2^{2+}]_{aq}$ are the molar concentration of uranyl at equilibrium.

The percent extraction is given by

$$\%E = \{[UO_2^{2+}]_{org}/[UO_2^{2+}]_{feed}\} \times 100 \tag{2}$$

where $[UO_2^{2+}]_{org}$ and $[UO_2^{2+}]_{feed}$ are the molar concentrations of uranyl ion in the organic phase and in the feed solution, respectively.

The synergistic factors (SF) and (SC) are defined as

$$SF = D_{syn}/(D_{HTTA} + D_{CALIX}) \tag{3}$$

and

$$SC = \log SF \tag{4}$$

where D_{syn} is the distribution coefficient of the synergistic mixture. SF and SC give a measure of the degree of synergism brought about by the individual calix[*n*]arene in the extraction of β-diketones with UO_2^{2+}.

3. Results and discussion

3.1. Synthesis and identification of modified calix[n]arenes

The modified compounds were characterized by IR, ^{1}H-NMR and UV–vis techniques. Table 1 lists IR and ^{1}H-NMR data for calix[*n*]arenes derivatives.

3.2. Solvent extraction

The parameters affecting the extraction of the cation from the aqueous phase are mainly: pH of the aqueous solution, diluent, and ionic strength.

Table 1
Infrared and NMR data for *n*-acetate calix[*n*]arenes

Compound	Infrared νC=O	^{1}H-NMR δ
Tetraacetate calix[4]arene	1740 cm^{-1}	6.81 (s, 8, ArH) 3.61 (br, s, 8, CH_2) 2.31, 2.11, 1.92 (s, 15, $COCH_3$) 1.42, 1.36, 1.21 (s, 36, $C(CH_3)_3$)
Hexaacetate calix[6]arene	1743 cm^{-1}	7.26 (s, 8, ArH) 3.74, 3.50 (br, s, 2, CH_2) 2.31, 1.58 (br, s, $OCOCH_3$) 1.42, 1.36, 1.21 (s, 9, $C(CH_3)_3$)

3.2.1. Effect of pH

Acetic acid solutions of different pH were used to study the effect of the hydrogen ion concentration on the distribution of U(VI). In Fig. 2, the distribution data are plotted against the variation of pH on a semilogarithmic scale. The extraction decreases from pH 1 to pH 3 for all the extraction systems, begins to increase from pH 4 and is saturated at around pH 5.0 showing about 90% extractability.

3.2.2. Effect of diluent

Extraction systems of hexaacetate calix[6]arene were prepared using diluents of different dielectric constant. As the dielectric constant increases, the extraction capacity of UO_2^{2+} by the calix[*n*]arene also increases. The data obtained for the extraction systems using acetatocalix[6]arene/toluene and acetatocalix[6]arene/HTTA/toluene are: toluene (2.13%), chloroform (12.33%) and dichlorobenzene (31.78%), and toluene (71.62%), chloroform (88.70%) and dichlorobenzene (90.20%), respectively. These systems were chosen due to their solubility in the chloroform, toluene and dichlorobenzene solvents. The acetatecalix[4]arene was insoluble in these solvents except for toluene. The system without HTTA exhibits a larger alteration in the extraction percentage than the system with HTTA. The contact time in all processes was 30 min.

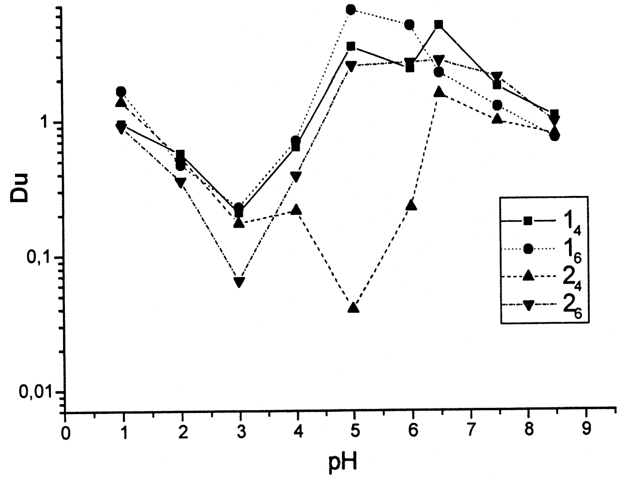

Fig. 2. Distribution of ratios for the extraction of UO_2^{2+} by calix[*n*]arenes at 298 K in toluene as a function of pH. $[UO_2^{2+}]_{feed}=8.4\times10^{-4}$ M buffered with borate solution; [calix[*n*]arenes]$=5\times10^{-3}$ M; [HTTA]$=5\times10^{-3}$ M.

3.2.3. Ionic strength

Fig. 3 shows the effect of sodium ions on the extraction of rare earth metals in a liquid–liquid extraction system. The degree of extraction of uranium strongly increased with sodium ion concentration close to 0.04 M and decreased at higher concentrations. Fig. 4 illustrates the extraction behavior when the concentration of Na^+ is constant $[Na^+]=0.04$ M and the pH changes. It can be seen that, at pH 6.5, the systems with the pure calix[*n*]arenes exhibited increased distribution coefficients by a factor of 160 for 1_4 and 1_6 and a factor of 10 for the calixarenes substituted 2_4 and 2_6. For the systems associated with HTTA, it was observed that calix[*n*]arenes of type 1_4 and 1_6 gave the best extraction results at pH 6.5 where the values of *D* obtained were two and four times larger than the result obtained without the presence of sodium. For the calix[*n*]arenes substituted 2_4 and 2_6, larger values of *D* were observed at pH 5 than at pH 6.5. It was determined that the best extraction coefficient, when compared with the results for the effect of ionic strength and without ionic strength, was for the calixarene 2_6. This calix[*n*]arene presents the better behavior and recorded a displacement for a range of pH<5.0. Otho et al. [14] and Montavon et al. [15] investigated the effect of coextracting alkaline ions on rare earth metal extraction with calix[*n*]arene carboxylate derivatives and concluded the following: the calix[4]arene derivative exhibited specificity for sodium ions based on carrier cavity size and sodium ionic diameter; the uptake of sodium ion into the cavity produces molecular structure ‘‘rigidity’’ and ‘‘preorganization’’, thereby improving the extraction of metals through an enhanced chelate effect. The results in this study are explained by a similar observation that sodium calix[*n*]arene complexes affect the extraction behavior of uranyl ions. The data for potassium are quite different and are shown in Fig. 5.

3.2.4. Synergism

The SF values were calculated for $[HTTA]=5\times10^{-3}$ M and [calix[*n*]arenes]$=5\times10^{-3}$ M. The results are given in Table 2. The synergistic effect is observed in the systems with pH>5 and, in general, obeyed the following order:

$2_4<1_4<1_6<2_6$

3.2.5. Absorption spectra

The linear oligomers as well as the cyclic ones have a characteristic pair of absorption bands in the ultraviolet region 280–288 nm. The spectra obtained for the extraction systems with HTTA that were studied in this work showed a displacement of the bands of the calixarenes for

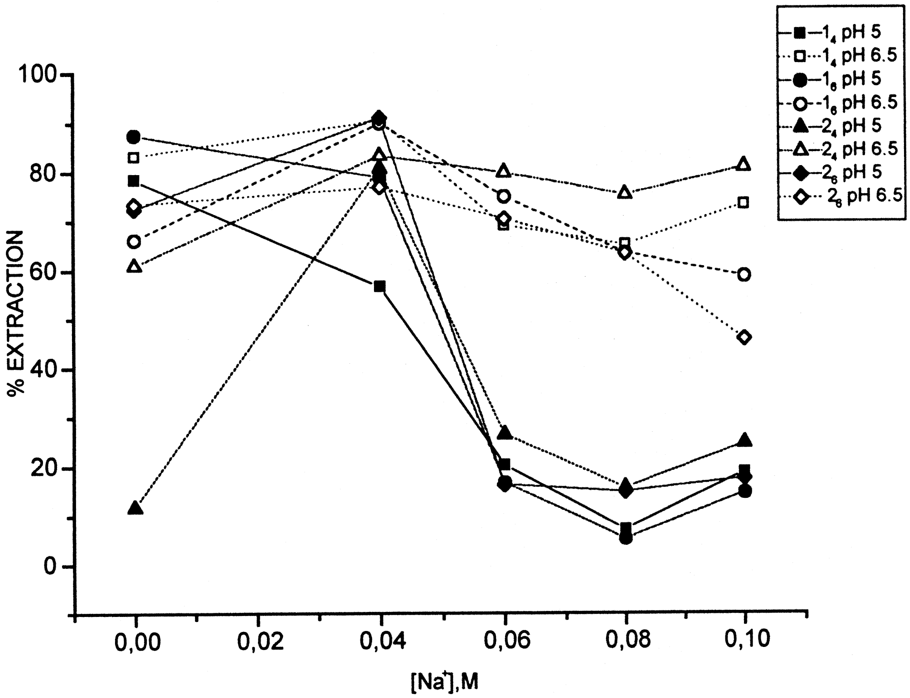

Fig. 3. Distribution of extraction ratios of UO_2^{2+} by calix[*n*]arenes at 298 K in toluene as a function of [Na^+] at pH 5 and 6. $[UO_2^{2+}]_{feed} = 8.4 \times 10^{-4}$ M buffered with borate solution; [calix[*n*]arenes] $= 5 \times 10^{-3}$ M; [HTTA] $= 5 \times 10^{-3}$ M.

the visible region of approximately 100 nm. This could be attributed to the inclusion of a HTTA molecule by the calixarene (see Fig. 6)

4. Conclusions

Uranium (VI) is synergistically extracted as an HTTA–calix[*n*]arene adduct. This kind of extraction is advantageous for separating metal ions efficiently. The presence of alkali ion strongly influences the extraction of uranium (VI) by calix[*n*]arene systems due to the formation of heteronuclear complexes in the organic phase. The rate of complexation is fast and the curve behaves like an exponential decay. Thus, whereas the calix[*n*]arenes studied display a very poor affinity for the uranyl cation when alone, these ligands behave as very efficient extracting agents for this ion in the presence of HTTA and alkali ions.

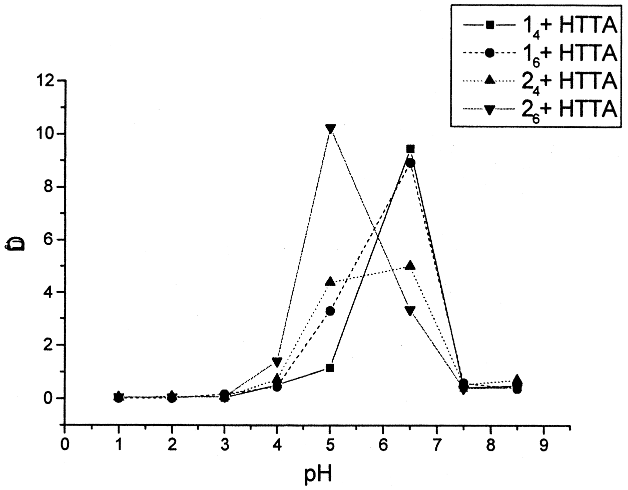

Fig. 4. Distribution of extraction ratios of UO_2^{2+} by calix[*n*]arenes at 298 K in toluene as a function of pH. $[UO_2^{2+}]_{feed} = 8.4 \times 10^{-4}$ M buffered with borate solution; [calix[*n*]arenes] $= 5 \times 10^{-3}$ M; [HTTA] $= 5 \times 10^{-3}$ M; [Na^+] $= 0.04$ M.

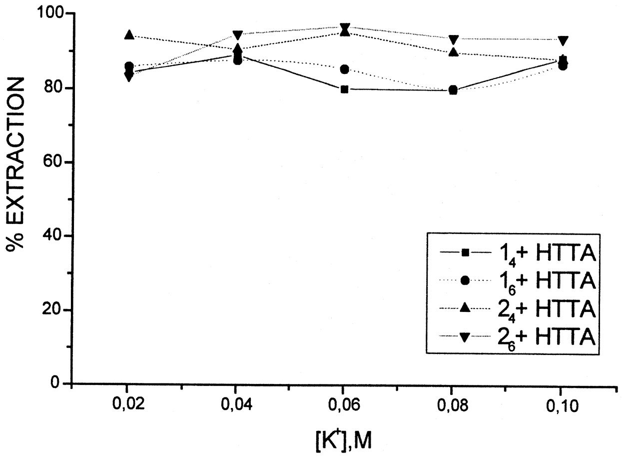

Fig. 5. Distribution of extraction ratios of UO_2^{2+} by calix[*n*]arenes at 298 K in toluene as a function of [K^+] at pH 5. $[UO_2^{2+}]_{feed} = 8.4 \times 10^{-4}$ M buffered with borate solution; [calix[*n*]arenes] $= 5 \times 10^{-3}$ M; [HTTA] $= 5 \times 10^{-3}$ M.

Table 2
The best synergistic coefficients of UO_2^{2+} [a]

System	pH	D_U	SF	SC
5×10^{-3} M 1_4	6.5	3.778	–	–
5×10^{-3} M 1_6	6.5	3.380	–	–
5×10^{-3} M 2_4	6.5	0.573	–	–
5×10^{-3} M 2_6	5.0	0.035	–	–
5×10^{-3} M HTTA	5.0	3.490	–	–
5×10^{-3} M HTTA	6.0	3.270	–	–
5×10^{-3} M $1_6+5\times10^{-3}$ M HTTA	6.5	9.463	1.341	0.127
5×10^{-3} M $1_6+5\times10^{-3}$ M HTTA	6.5	8.931	1.343	0.128
5×10^{-3} M $2_4+5\times10^{-3}$ M HTTA	6.5	4.993	1.300	0.113
5×10^{-3} M $2_6+5\times10^{-3}$ M HTTA	5.0	10.240	2.905	0.463

[a] [Na]=0.04 M.

The compound 2_4 presents different behavior than the others, and this fact was attributed to steric hindrance of the carboxylic group in complex formation.

Further studies are in progress in this laboratory to determine the selective properties of 2_4 and 2_6 calix[*n*]arenes in solvent extraction processes toward other actinide and lanthanide cations in the presence or absence of alkali ions.

Acknowledgements

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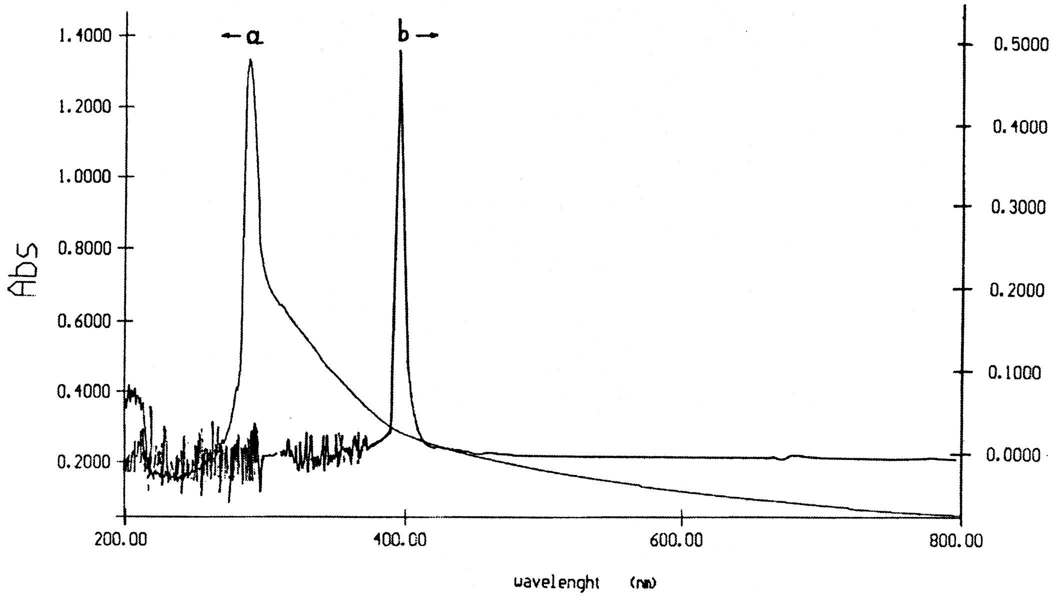

Fig. 6. Absorption spectra of the extraction systems using calix[*n*]arenes as extractor agent. (a) Hexacetate calix[6]arene/toluene; (b) hexaacetate calix[6]arene/HTTA/toluene.