Journal of Inclusion Phenomena and Macrocyclic Chemistry **40:** 225–229, 2001.

Solvent Extraction of Selenate and Chromate Using a Diaminocalix[4]arene

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(Received: 12 January 2001; in final form: 20 April 2001)

Key words: anion recognition, calixarene, selenium, solvent extraction

Abstract

The extraction of Se(VI) and Cr(VI) using a diammoniumcalix[4]arene was investigated. A study of parameters such as ligand concentration, pH or diluent was carried out and allowed to specify the stoichiometry of the extracted species. It was shown that Se(VI) is extracted into $CHCl_3$ as (LH_2^{2+}, Cl^-, $HSeO_4^-$) and ((LH_2^{2+})$_2$, $2Cl^-$, SeO_4^{2-}) species at pH 2.6. An increase of pH or an addition of 5% or 10% decanol in $CHCl_3$ favors the extraction of SeO_4^{2-} over $HSeO_4^-$ but leads to a drastic decrease of selenium extraction. Cr(VI) was shown to be extracted as (LH_2^{2+}, Cl^-, $HCrO_4^-$) at pH 2.6 and probably as (LH^+, $HCrO_4^-$) for higher pH.

Introduction

Selenium is a trace element present in the environment under various forms, the most commonly encountered anionic species being SeO_4^{2-} and SeO_3^{2-} [1]. Its toxicity depends on numerous factors, e.g., chemical form, adsorption pathway, pH. Because of its biological and environmental implications even at very low levels, sophisticated analytical techniques to determine its speciation were developed. However its quantification at trace levels often requires additional preconcentration or derivatisation steps [2–6].

Calixarenes are attractive molecules from their preorganization ability as their use in liquid/liquid extraction could lead to selective concentrations and/or separations. However, only a few studies deal with their use in anion extraction [7–11]. Bis-amidocalix[4]arenes were employed to extract Se(VI) and a partial cone conformation was shown to be more adapted and to lead to the extraction of 10% Se(VI) [9]. A series of calix[4]arenes with amine or amide groups were investigated in the extraction of Se(VI) and the tetramine derivative exhibited the best results [10]. In a previous work, we reported the ability of a diammoniumcalix[4]arene to separate and concentrate Se(VI) from a Se(IV)/Se(VI) mixture. Concentrations of Se(VI), as low as 40 ng Se/g, were determined [11]. The present work is a theoretical study focused on the influence of parameters such as ligand concentration, pH or diluent on the extraction of Se(VI) and Cr(VI) using this calixarene and attempt to elucidate the mechanisms which govern the extraction. A comparison with the extraction of other oxyanions is also presented.

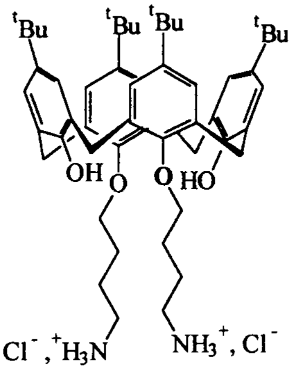

Figure 1. 5,11,17,23-tetra-p-*tert*-butyl-25,27-bis[(butylammonium chloride)-oxy]-26,28-dihydroxy-calix[4]arene LH_2^{2+}, $2Cl^-$).

Experimental

Reagents

All anions were used as their sodium salts. $Na_2SeO_4 \cdot 10H_2O$, (purity min. 99%) and $Na_2CrO_4 \cdot 4H_2O$ (purity min. 99%) were purchased from Aldrich. Na_2SO_4 (purity min. 99%), $Na_2S_2O_3 \cdot 5H_2O$ (purity min. 99.5%), NaH_2PO_4 (purity min. 99%) and NaCl (purity min. 99.5%) were products from Acros. $Na_2SeO_3 \cdot 5H_2O$ (purity min. 99%) was purchased from Merck and $NaNO_3$ (purity min. 99.5%) and $Na_2HAsO_4 \cdot 7H_2O$ (purity min. 98.5%) from Prolabo.

5, 11, 17, 23-tetra-p-*tert*-butyl-25, 27-bis[(aminobutyl)-oxy]-26, 28-dihydoxy-calix[4]arene (L) was synthesized according to the procedure described in [11] and used as its chloride salt, symbolized by (LH_2^{2+}, $2Cl^-$), to prevent any degradation (Figure 1).

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Table 1. Extraction percentages of Se(VI) and Cr(VI) using different ligands having ammonium functions

	L	L^1	L^2	Aliquat 336	Dodecylamine
Se(VI)	96	70	0	0	0
Cr(VI)	85	77	0	83	5

Analytical procedure

The aqueous phase consisted of a sodium salt of Se(VI) or Cr(VI) at a concentration of 5 × 10^{-5} mol L^{-1} in a 0.01 mol L^{-1} (Na, H)Cl solution, in order to obtain the desired pH at equilibrium and maintain the ionic strength constant. The organic phase was obtained by dissolving appropriate amounts of (LH_2^{2+}, $2Cl^-$) in either water-saturated $CHCl_3$ or water-saturated mixtures of $CHCl_3$ and decanol.

Experiments were carried out in thermostated vessels (25.0 ± 0.2) °C. 5 mL of both aqueous and organic phases were magnetically stirred for at least 30 min, the time found experimentally to be sufficient to reach equilibrium. pH was measured at the equilibrium using a potentiometer and a glass electrode (reference: Ag/AgCl). After separation by gravity, each phase was withdrawn and the metal concentration was determined by plasma induced atomic emission spectrometry (ICP/AES) using a Jobin Yvon JY 138 spectrometer (λ_{As} = 193 nm, λ_{Se} = 196 nm, λ_{Cr} = 205 nm). The metal contained in the organic phase was previously stripped using a 0.1 mol L^{-1} NaOH solution.

For the analysis of other anions ion-exchange chromatography followed by a chemical suppression was performed using a AS4A-SC P/N 43174 column, 4 mm i.d. × 280 mm. The eluent was composed of a 50/50 mixture of Na_2CO_3 2.7 × 10^{-3} mol L^{-1} and $NaHCO_3$ 0.3 × 10^{-3} mol L^{-1} and the anions were detected by conductimetry.

Results and discussion

Preliminary tests were performed in order to compare the extraction of Se(VI) and Cr(VI) using L as its chloride form and other ammonium salts such as Aliquat 336 ($(C_8H_{17})_3(CH_3)N^+$,Cl^-) and dodecylamine, p-*tert*-butyl-tetra(2-aminobutoxy)calix[4]arene (L^1) and 4-*tert*-butylphenyl(4-amino)butyl ether (L^2) under protonated form.

Extractions of Se(VI) or Cr(VI), 5 × 10^{-5} mol L^{-1} in a 0.01 mol L^{-1} NaCl solution were carried out at pH 2.6 and 25 °C using the five different ligands, 5 × 10^{-4} mol L^{-1} in chloroform, except for Aliquat 336 whose concentration was 10^{-3} mol L^{-1} in chloroform. Results are summarized in Table 1.

From these data, it seems that the preorganization of the ammonium functions induced by the calixarene platform allows a better extraction of anions, especially for Se(VI). The extraction by the calixarene L^1 is however greatly affected by its partition into water under these conditions; partition coefficients of L and L^1 between chloroform and water at pH 2.6 were measured and found to be infinite and 0.10 ± 0.01, respectively.

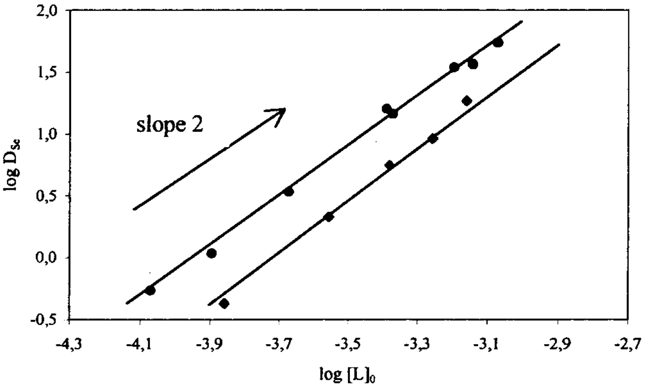

Figure 2. Extraction of Se(VI) 5 × 10^{-5} mol L^{-1} from a 0.01 mol L^{-1} NaCl solution at pH 2.6 (●) or 4.5 (♦) by (LH_2^{2+}, $2Cl^-$) in $CHCl_3$ at 25 °C.

Mathematical treatment

All data were analyzed using the classical slope analysis method.

Assuming the extraction of an anion X^{n-} by the anion exchanger (B^+, Cl^-) according to the following equilibrium:

$$n(B^+,\ Cl^-)_{org} + X^{n-}_{aq} \overset{K_{ex}}{\rightleftharpoons} ((B^+)_n, X^{n-})_{org} + nCl^-_{aq},$$

the extraction constant K_{ex} is then defined by:

$$K_{ex} = \frac{[(B^+)_n, X^{n-}]_{org}[Cl^-]^n_{aq}}{[X^{n-}]_{aq}[(B^+, Cl^-)]^n_{org}}. \tag{1}$$

Equation (1) can be re-written

$$\log D = \log K_{ex} + n \log[B^+, Cl^-]_{org} - n \log[Cl^-]_{aq},$$

where D_X is defined as the ratio of the analytical concentration of the anion X^{n-} in both phases: $D_X = [X]_{org}/[X]_{aq}$.

Consequently, plots of $\log D_X$ vs $\log[B^+, Cl^-]_{org}$ may lead to a straightline whose slope n allows access to the stoichiometry of the extracted species.

Influence of pH

The influence of the aqueous phase pH was investigated in $CHCl_3$/water systems. The formation of a third phase was observed but this phase was shown to have a low Se(VI) or Cr(VI) content as errors in mass balances did not exceed 5%.

Figure 2 represents the extraction of Se(VI), expressed as $\log D_{Se}$, as a function of the logarithm of the (LH_2^{2+}, $2Cl^-$) initial concentration in $CHCl_3$ for pH 2.6 and 4.5.

The obtained plots are straight lines whose slopes are close to 2, which might be attributed to the extraction of a species of 2:1 (ligand/metal) stoichiometry.

Considering the investigated range of ligand concentrations, corrections cannot be neglected as the free ligand concentration at equilibrium can no longer be the same as

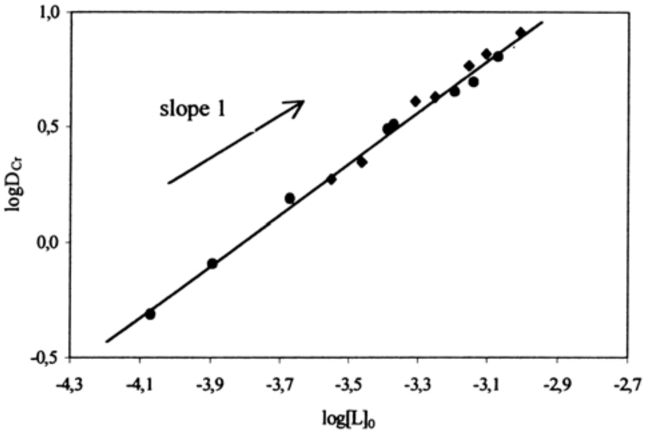

Figure 3. Extraction of Cr(VI) 5×10^{-5} mol L^{-1} from a 0.01 mol L^{-1} NaCl solution at pH 2.6 (●) or 4.5 (◆) by (LH_2^{2+}, $2Cl^-$) in $CHCl_3$ at 25 °C.

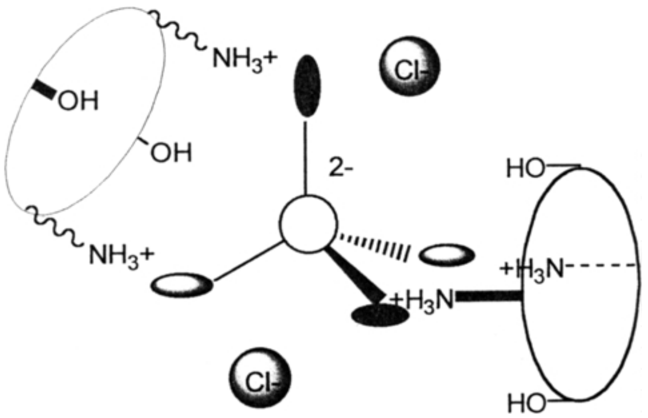

Figure 4. Assumption of the extracted species involving SeO_4^{2-} and 2 molecules of (LH_2^{2+}, $2Cl^-$).

its initial concentration. In these conditions, the slope of the $\log D_{Se}$ vs. $\log[LH_2^{2+}, 2Cl^-]_{org}$ straight line was found to be 1.7 at pH 2.6. This was attributed to the presence of the following equilibrium:

$$HSeO_4^- \rightleftharpoons SeO_4^{2-} + H^+$$

and allowed us to consider the simultaneous extraction of 2:1 and 1:1 complexes, according to the following equilibria:

$$(LH_2^{2+}, 2Cl^-)_{org} + HSeO^-_{4\,aq} \overset{K_{11}}{\rightleftharpoons} (LH_2^{2+}, Cl^-, HSeO_4^-)_{org} + Cl^-_{aq} \tag{2}$$

$$2(LH_2^{2+}, 2Cl^-)_{org} + SeO^{2-}_{4\,aq} \overset{K_{21}}{\rightleftharpoons} ((LH_2^{2+})_2, 2Cl^-, SeO_4^{2-})_{org} + 2Cl^-_{aq}. \tag{3}$$

According to these assumptions conditional constants were calculated from experimental data and found to be $\log K_{11} = 2.6 \pm 0.2$ and $\log K_{21} = 4.1 \pm 0.1$.

At pH 4.5, the expected slope of $\log D_{Se}$ vs. $\log[LH_2^{2+}, 2Cl^-]_{org}$ should be 2 as $HSeO_4^-$ is negligible. The experimental straight line exhibits a slope of 2 but the extraction was less than expected by calculation, considering K_2 as the extraction constant. This is likely due to the deprotonation of (LH_2^{2+}, $2Cl^-$) which may play a significant role at this pH, a role which is obvious in the case of a total deprotonation of the ligand.

A similar experiment was conducted with Cr(VI). Figure 3 represents the extraction of Cr(VI), expressed as $\log D_{Cr}$ as a function of $\log[LH_2^{2+}, 2Cl^-]_0$ in $CHCl_3$ for the same pH values.

For both pH values, $HCrO_4^-$ is the only anionic form of Cr(VI) in solution and slopes close to 1 were obtained. This would indicate that the presence of the monoprotonated form of the ligand, (LH^+, Cl^-), at pH 4.5 does not affect the extraction of $HCrO_4^-$. It then seems that the two following equilibria coexist:

$$(LH_2^{2+}, 2Cl^-)_{org} + HCrO^-_{4\,aq} \overset{K_{11}}{\rightleftharpoons} (LH_2^{2+}, Cl^-, HCrO_4^-)_{org} + Cl^-_{aq} \tag{4}$$

$$(LH^+, Cl^-)_{org} + HCrO^-_{4\,aq} \overset{K'_{11}}{\rightleftharpoons} (LH^+, HCrO_4^-)_{org} + Cl^-_{aq}, \tag{5}$$

with similar K_{11} and K'_{11} values. Calculations of these constant values lead to $\log K_{11} = \log K'_{11} = 1.9 \pm 0.1$.

All these experiments lead us to assume that the difference between (LH^+, Cl^-) and (LH_2^{2+}, $2Cl^-$) in their extracting power towards SeO_4^{2-} could be attributed to a peculiar dimer structure of the extracted species, represented schematically in Figure 4.

Influence of diluent

As a third phase formation was observed in the extraction of these anions by (LH_2^{2+}, $2Cl^-$), the addition of decanol as phase modifier was investigated.

Figure 5 represents the results obtained for the extraction of Se(VI) at pH 2.6 by (LH_2^{2+}, $2Cl^-$) in solution in $CHCl_3$ or in mixtures of $CHCl_3$/decanol. No third phase formation was observed but the modifier was shown to decrease dramatically the Se(VI) extraction.

In the presence of decanol, the slopes of the obtained straight lines are closed to 2. Corrections operated on ligand concentrations assuming the involvement of 2 ligands in the extraction of Se(VI) confirm the only extraction of a 2:1 species in the presence of decanol. In the case of extraction of sulfuric acid by trioctylamine (R_3N), Sato *et al.* already reported that an addition of octanol (R′OH) in benzene promotes the extraction of SO_4^{2-}, compared with HSO_4^-, via the formation of $(R_3NH)_2 \cdot SO_4 \cdot 2R'OH$ [12]. Similarly, it can be assumed that decanol favors the extraction of SeO_4^{2-}, compared with $HSeO_4^{2-}$, but the extraction of a complex involving one or more alcohol molecules has not been demonstrated.

The influence of decanol on Cr(VI) extraction was also investigated (Figure 6).

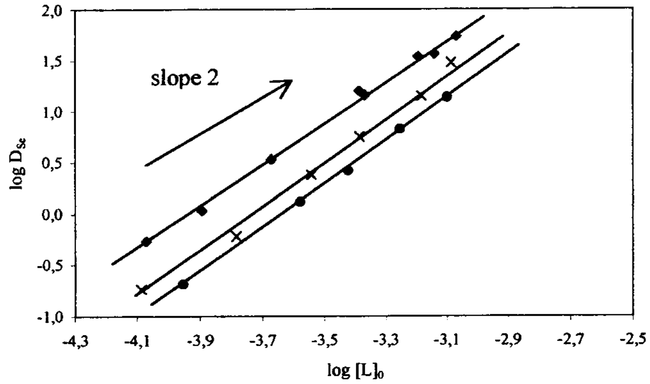

Figure 5. Extraction of Se(VI) 5 × 10^{-5} mol L^{-1} from a 0.01 mol L^{-1} NaCl solution at pH 2.6 by (LH_2^{2+}, $2Cl^-$) in $CHCl_3$ (♦), $CHCl_3$/decanol 95/5 (×) or $CHCl_3$/decanol 90/10 (●) at 25 °C.

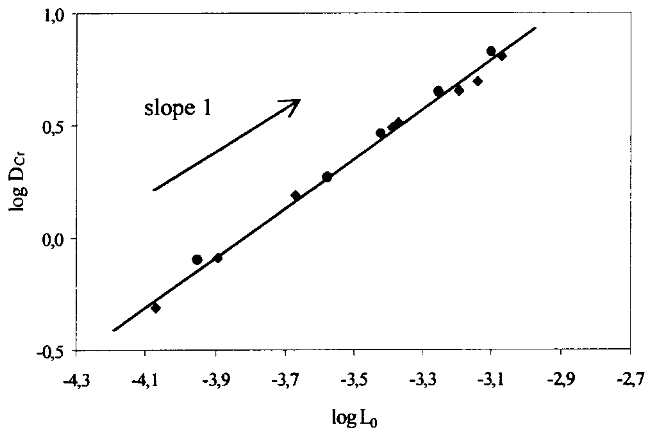

Figure 6. Extraction of Cr(VI) 5 × 10^{-5} mol L^{-1} from a 0.01 mol L^{-1} NaCl solution at pH 2.6 by (LH_2^{2+}, $2Cl^-$) in $CHCl_3$ (♦) or $CHCl_3$/decanol 90/10 (●) at 25 °C.

The results seem to indicate that the extraction of $HCrO_4^-$ is not affected by the presence of a phase modifier.

Once again, the difference between the Se(VI) and Cr(VI) behavior could be attributed to the peculiar conformation adopted by the extracted selenium species. As a consequence, the extraction selectivity, defined as $\alpha = \frac{D_{Se}}{D_{Cr}}$, decreases drastically and even reverses when decanol is present as shown in Figure 7.

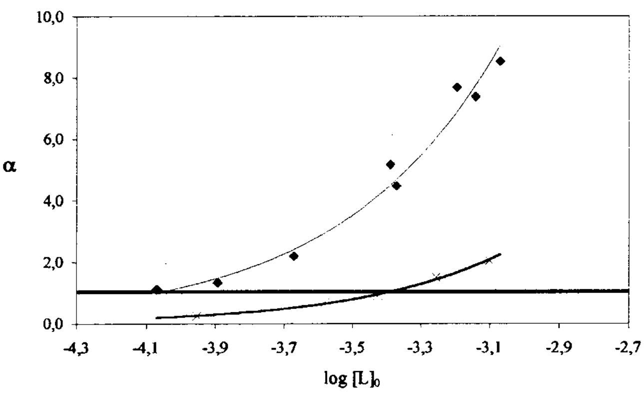

Figure 7. Selectivity α of Se(VI) versus Cr(VI) in their extraction from a 0.01 mol L^{-1} NaCl solution at pH 2.6 by (LH_2^{2+}, $2Cl^-$) in $CHCl_3$ (♦) or $CHCl_3$/decanol 90/10(×) as diluent.

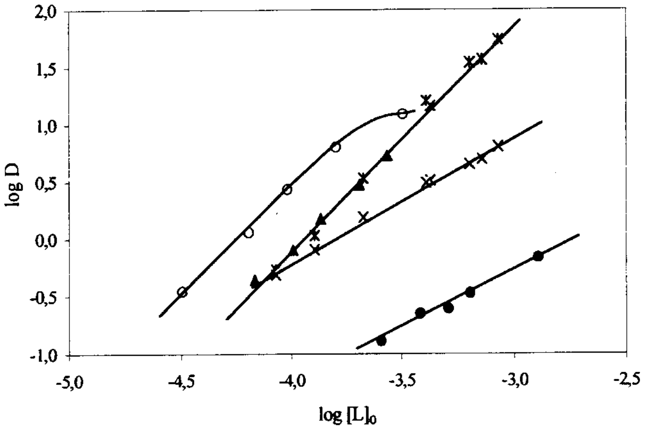

Figure 8. Individual extractions of $S_2O_3^{2-}$(○), SeO_4^{2-}(*), SO_4^{2-}(▲), $HCrO_4^-$(×), 5 × 10^{-5} mol L^{-1} and NO_3^-(●) 10^{-4} mol L^{-1} from a 0.01 mol L^{-1} NaCl solution at pH 2.6 by (LH_2^{2+}, $2Cl^-$) in $CHCl_3$ at 25 °C.

Comparison with the extraction of other oxyanions

Individual extractions of $S_2O_3^{2-}$, SO_4^{2-}, HPO_4^{2-}, $HAsO_4^{2-}$ and SeO_3^{2-} all 5 × 10^{-5} mol L^{-1} and NO_3^- 10^{-4} mol L^{-1} were carried out from a 0.01 mol L^{-1} NaCl solution at pH 2.6 by (LH_2^{2+}, $2Cl^-$) in $CHCl_3$ and compared to SeO_4^{2-} and CrO_4^{2-}. Figure 8 represents the results obtained.

The results show that the extraction of divalent anions is favored compared to monovalent anions. The extraction order is:

$$S_2O_3^{2-} > SeO_4^{2-} \approx SO_4^{2-} > HCrO_4^- > NO_3^-$$

No extraction of $H_2PO_4^-$, $H_2AsO_4^-$ and $HSeO_3^-$ was observed whatever the ligand concentration.

Conclusion

The use of diammoniumcalix[4]arene (LH_2^{2+}, $2Cl^-$) in $CHCl_3$ was demonstrated to lead to an extraction of Se(VI) at pH 2.6 from a NaCl medium with a good selectivity over Cr(VI). This was attributed to the peculiar conformation adopted by the 2:1 extracted species. On the other hand, no discrimination was possible between Se(VI) and its sulfur analog. The formation of a third phase was observed. However, attempts to avoid this phase, e.g., by pH increase or decanol addition, were shown to reduce drastically both the extraction of Se(VI) and the selectivity Se(VI)/Cr(VI).

A future application of solvent extraction using the diaminocalix[4]arene as a preconcentration method for Se(VI) in real samples will require an investigation of the behavior of organic selenium species in such conditions.

Acknowledgement

The authors would like to thank Dr J.-P. Brunette for fruitful discussions and constant support.

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