

Summary

The work described in this Thesis deals with the synthesis of new cavitand- and tripodand-based ligands, their extraction properties, and their potentiometric response towards different cations, among them Am^{3+} and Eu^{3+} . A general introduction is given in Chapter 1. In addition, the contents of the Thesis are summarized.

Nuclear fission energy generation gives rise to highly radioactive waste due to the presence of plutonium and minor actinides. Chapter 2 deals with the different processes that are under investigation for the reduction of the highly radioactive waste. Special attention has been paid to the hydrochemical process (PUREX), which recovers uranium and plutonium. The different processes involved in the coextraction of actinides and lanthanides from the waste are reported. It is important, for the final conversion of the actinides into their short live isotopes, its separation from lanthanides. Therefore Chapter 2 also describes the selective extractants that are under investigation. In addition, an overview is given of known ligands that specifically bind actinides and/or lanthanides.

In Chapter 3 the preparation of different carbamoylmethylphosphonate (CMP), -phosphine oxide CMPO, and *N*-acyl(thio)urea-tetrafunctionalized cavitands is described. Liquid-liquid extractions were performed from aqueous nitric acid into dichloromethane or *o*-nitrophenyl hexyl ether (NPHE). The extraction of Am^{3+} and Eu^{3+} was studied in both the absence and presence of the hexabrominated cobalt bis(dicarbollide) anion ($\text{Br}_6\text{-COSAN}$) as a synergist. *N*-acyl(thio)urea cavitands are less effective extractants than the corresponding CMP(O) derivatives. However, they present an interesting selectivity for Am^{3+} over Eu^{3+} in the presence of $\text{Br}_6\text{-COSAN}$. Higher extraction efficiencies were achieved with the ionophores that have a propyl chain between the cavitand platform and the chelating groups.

Chapter 4 describes the results of the binding properties towards different cations of the CMP(O)- and *N*-acyl(thio)urea tetrafunctionalized cavitands as obtained from metal picrate extractions and the incorporation of the ionophores in ion selective electrodes (ISEs). Picrate extractions showed that there is more than a 40% increase of the Ag^+

extraction for *N*-acylthiourea cavitand derivatives in comparison with the single *N*-benzoyl-*N'*-benzylthiourea. This shows that the attachment of four *N*-acylthiourea moieties to a molecular platform improves the complexation behavior. The complexation behavior of cavitands functionalized with CMP(O) moieties or *N*-acyl(thio)urea moieties in ion selective electrodes was studied. The complex formation constants for these ionophores were obtained via potentiometric sandwich membrane measurements. CMP(O)-cavitands form very stable and stronger complexes than the *N*-acyl(thio)urea-tetrafunctionalized cavitands, which can be explained by the different nature of the chelating groups (CMP(O) vs *N*-acyl(thio)urea). The selectivity coefficients obtained with ion selective electrodes correlate well with the complex stability constants; CMP(O) cavitands are very selective for UO_2^{2+} and Pb^{2+} cations, whereas *N*-acyl(thio)urea cavitands have the highest selectivity for Ag^+ . The correlation between the potentiometric selectivity and the ability of examined cavitands to form metal-ligand complexes is discussed.

Chapter 5 deals with the extraction properties for Am^{3+} and Eu^{3+} of appropriately functionalized cavitands substituted at the upper or lower rim with cobalt bis(dicarbollide) anions (COSAN). A comparative study showed that COSAN-containing cavitands functionalized at the upper rim with CMPO, *N*-acylthiourea, or picolinamide moieties have higher distribution coefficients than the corresponding reference cavitands, that do not contain COSAN. Two different spacers were used for the linkage of COSAN to the cavitand, an ethyleneglycol chain or a methyl spacer. It was found that long and flexible spacers result in an improvement of the extraction properties. COSAN-containing *N*-acylthiourea cavitand, which has a long and flexible spacer between the COSAN and the cavitand, has about 6000 times higher distribution coefficients than reference *N*-acylthiourea cavitand. Contrary to this result, COSAN-containing CMPO cavitand, which has a methoxy group as a spacer, has only 2 times higher distribution coefficients than the reference CMPO cavitand.

Chapter 6 deals with the synthesis, extraction and sensing behavior of trimethylolpropane-based tripodal ionophores with *N*-acyl(thio)urea and picolin(thio)amide as chelating units. The *N*-acylurea derivative has high separation factors at very low nitric

acid concentrations for $\text{Am}^{3+}/\text{Eu}^{3+}$ separation, although the distribution coefficients are low. In the presence of $\text{Br}_6\text{-COSAN}$ as a synergist the distribution coefficients were increased considerably, especially in the case of the picolinamide derivative (>1000). It is also a very good ionophore for the extraction of Hg^{2+} , however, it forms so strong complexes that it cannot be used as ionophore in ion selective electrodes.

Chapter 7 deals with a study of two CMP(O) tripodands. All the techniques employed in the other Chapters have been used in order to investigate the behavior of these ionophores towards different cations, paying special attention to Am^{3+} and Eu^{3+} . The last part of the chapter deals with solid-liquid extractions of Am^{3+} and Eu^{3+} performed with magnetica silica particles functionalized with CMP(O) tripodands. Particles with CMPO tripodand have about 10 times higher distribution coefficients than particles with CMP tripodand. The high distribution coefficients reached at low HNO_3 concentration makes of the CMPO tripodand bearing particle a promising system for an industrial development.

