

A thermodynamic outlook of the extraction mechanism in the TALSPEAK with 0.3 M di-2-ethylhexylphosphoric acid, HDEHP/di-isopropylbenzene) for lanthanide(III)/actinide(III) group separation was developed. The quantitative comparison of free energy of complexation and extraction of Ln(III) and trivalent transplutonium elements (TPE) with DTPA, HDTPA, HL and HDEHP shows that the extraction mechanism is the same for the two groups of elements. Ln(III) and TPE are extracted predominantly as the complexes  $ML^{2+}$  and M(III) solvated with HDEHP anions. The effects of the metal complexation and extraction in the systems HDEHP + HL, HDEHP+ DTPA, HDEHP + HDTPA, HDEHP + HL + DTPA and HDEHP + HL + HDTPA were considered in detail and the extractabilities of Ln(III) and TPE were calculated for every system. In the extraction mechanism both aqueous mixed (MC) complexes  $ML_i DTPA^{-(2+i)}$  and protonated complexes  $MDTPAH^+$  were found to have significant effect on the dissociation of the complex  $MDTPA^{2-}$  and the subsequent extraction of M(III). Our work supports the view that important step in mechanism of TALSPEAK process is based on the synergistic substitution of water molecules for  $L^-$  in  $MDTPA^{2-} \cdot n H_2O$  resulting in MC formation. The 'n' values have been get to be  $1 < n < 2$  for Ln(III) and  $2 < n < 3$  for TPE complexes. The optimal numbers of  $L^-$  in MC which are effective for the extraction mechanism were determined for Ln(III) and TPE. A semi-empirical model for the prediction of stability of complexes  $ML_i DTPA^{-(2+i)}$  and  $MLHDTPA^{2-}$  was presented and the stability constants for  $MC = MDTPA L^3$ ,  $MDTPAL^4_2$  and  $MDTPAL^5_3$  were calculated (M=Ln and TPE). Good quantitative agreement between calculated and experimental values of extractability for Ln(III) and TPE was obtained. The effect of lactic and citric acids (Hcit) in TALSPEAK process have been compared for the Ln(III) group separation. The stability constants of MC (M=Ln) with DTPA and cit have been calculated.

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SOLVENT EXTRACTION SEPARATION OF URANIUM (VI) WITH ACETATECALIX[N]ARENE AND  $\beta$ -DIKETONE (HTTA)

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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 that is, the ligand must discriminate strictly between  $UO_2^{2+}$  and other metal ions present in great excess in sea water. A possibly unique solution to this difficult problem is provide be the unusual coordination structure of  $UO_2^{2+}$  complexes which require either a pseudoplanar pentacoordinate or hexacoordinate structure. This suggest 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). Acetatecalix[n]arene-based uranophiles bearing acetate group on the lower rim have been synthesized and the extractability (%E) and the selectivity towards uranyl ion ( $UO_2^{2+}$ ) estimated in a two phase (acetate - toluene) solvent extraction system. %E for acetatecalix[n]arene/htta increases from pH4 and saturation is reached at around pH 6-7 where more than 90% extractability occurs. Extraction of  $UO_2^{2+}$  from aqueous acetate solution established that the hexaacetatecalix[6]arene/htta in organic phase can compete efficiently with

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Ac<sup>-</sup> ions in the aqueous phase for UO<sub>2</sub><sup>2+</sup> whereas in tetraacetatecalix[4]arene/htta as a uranophile.

We also found that the selectivity of acetatecalix[n]arene/htta is superior top-*tec*-butyl calix[n]arene/htta. The results shown that hexaacetate calix[6]arene/htta serve as an excellent UO<sub>2</sub><sup>2+</sup> selective extraction reagent.

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### PIII-69

#### HOT ELECTRON-INDUCED ELECTROCHEMILUMINESCENCE OF Tb(III) CHELATES AT OPTICALLY TRANSPARENT TUNNEL EMISSION ELECTRODES PREPARED BY ATOMIC LAYER EPITAXY

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Hot electron injection into aqueous electrolyte solution from thin insulating film-coated electrodes provides a means for electrochemical excitation of a wide variety of luminophores usable as labels in bioaffinity assays such as in immunoassays or DNA-probing assays. This provides a possibility to utilize both wavelength or time discrimination in the separation of signals emerging from different label molecules. Thus, the present electrochemiluminescence excitation method allows easily multiparameter assays, or the use of internal standards in assays. The use of internal standard on the basis of wavelength discrimination is most convenient, if both the working electrode and the counter electrode are optically transparent in a two-electrode thin layer cell and inexpensive optical filters can be used. Indium tin oxide (ITO) electrodes are readily usable as anodes in the present application, but they are useless unless the ITO-film is additionally coated with a 2-4 nm thick insulating film.

The present work was carried out by using as working electrodes ITO-glass electrodes covered with a thin Y<sub>2</sub>O<sub>3</sub> layer deposited on top of ITO film by Atomic Layer Epitaxy (ALE), and aromatic Tb(III) chelates as models of electrochemiluminescent labeling molecules. Yttrium oxide thin films were deposited in a commercial flow type hot-wall atomic layer epitaxy (ALE) reactor by using Y(thd)<sub>3</sub> (thd = 2,2,6,6-tetramethylheptadione) and ozone as precursors. The ECL-measurements were carried out in borate buffer at pH 9.2. Linear log-log calibration plots spanning over several orders of magnitude of concentration were obtained for Tb(III) chelates.

### PIII-70

#### SPECTROSCOPY AND MAGNETISM OF POLYNUCLEAR (Sm, Gd) TRI-CHLOROACETATES AND THEIR HETERONUCLEAR (Sm:Cu AND Gd:Cu) ANALOGUES

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Heteronuclear copper lanthanide compounds are widely studied for their unusual structural features, optical and magnetic properties and also because of their potential applications in