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Electrochemical Behavior of Cerium (IV) Species in n-TriButylPhosphate

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ABSTRACT

This work investigates the electrochemical behavior of Ce(IV) complexes extracted in n-tributylphosphate (TBP) from nitric aqueous solutions as an entry to the direct electrochemical characterization of plutonium in organic extractants related to nuclear fuel reprocessing. Ce(IV) complexes displayed a reversible electrochemical reduction wave in TBP, which could be observed only at glassy carbon electrodes. At slow scan rates, that reduction wave showed a Nernstian dependence on the logarithm of both nitric acid and TBP concentrations in the organic phase, featuring the exchange of nitrates and TBP upon reduction to Ce(III). The presence of increasing amounts of a common degradation product of TBP, such as hydrodibutyl phosphate (HDBP) resulted in a shift of the Ce(IV) reduction wave towards more negative potential values, a behavior consistent with the formation of HDBP-Ce (IV) complexes.

1. Introduction

The control of the concentration of actinides at each step of nuclear fuel reprocessing is a crucial issue for the safety and sustainability of nuclear energy [1]. The plutonium content of spent fuel is particularly scrutinized with respect to the long-term radiotoxicity of Pu. The production of mixed U/Pu fuel (MOX), aimed at re-introducing Pu in a new fission cycle in power plants, relies on the capacity to achieve selective separation and purification steps on spent nuclear fuels. In that context, PUREX (for Plutonium Uranium Refining by EXtraction) is the most widespread U/Pu recovery process, featuring the extraction of U^{VI} and Pu^{IV} from the original aqueous nitric solution to an organic phase composed of tributyl phosphate TBP (coordinating phase/agent) and an alkane diluent [2]. The real-time monitoring of actinide concentration in the organic phase has not been extensively described. Considering that TBP is the end-phase of the extraction step, the characterization of both the distribution of the complexes extracted and their relative concentration is of interest in the context of the traceability of actinides all along the refining process. Actually, the speciation in the TBP phase is complex since it involves extracted water, nitric acid, cations (mostly actinides (IV) and (VI)) and a TBP degradation product HDBP [2]. Moreover, few techniques allow simple, fast, and nondestructive determination of the concentration of metallic cations and complexes present in solution. The electrochemical determination of concentrations in solutions can be performed on micrometer range electrodes and volumes, namely upon implementation within microfluidic systems [3–7]. Therefore, the development of electroanalytical methods aimed at probing the concentration of reprocessed actinides directly in the TBP phase is of interest, viz. through the derivation and analysis of small aliquots of the bulk organic phase, thus significantly lowering the exposure of people and equipment to radiations. This consideration is especially true for the TBP phase which speciation of the elements of interest (actinides and extractible fission products) is not well-known, due to the low conductivity of the medium.

In this work we report our investigation of the electrochemical behavior of cerium(IV) species in TBP. Cerium has been selected as a model radio-inactive element since it mimics both the valence IV and the coordinating properties of plutonium(IV). To our knowledge, the electrochemical behavior of Ce(IV)/Ce(III) in TBP solutions was only reported by Pletcher and Valdes in dichloromethane as solvent [8]. In TBP, the predominant extracted solvates

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reported for tri- and tetravalent metal cations are respectively M$(NO_3)_3 \cdot 3TBP$ and $M(NO_3)_4 \cdot 2TBP$ [9]. Therefore, the expected electrochemical reduction of Ce(IV) to Ce(III) may be written as:

$$Ce(NO_3)_4 \cdot 2TBP + e^- + TBP \Leftrightarrow Ce(NO_3)_3 \cdot 3TBP + NO_3^- \qquad (1)$$

We have investigated the effect of nitrate and TBP concentration on the electrochemical behavior of the Ce(IV)/Ce(III) couple, probing the dependence of the potential value of the reduction wave of Ce(IV) on the logarithm of nitrate and TBP concentration. Finally, the influence of a common and highly coordinating PUREX degradation product hydrodibutyl phosphate (HDBP) [10–13] on the electrochemical behavior of Ce (IV)/Ce (III) has been explored. The structures of TBP and HDBP are shown in Scheme 1.

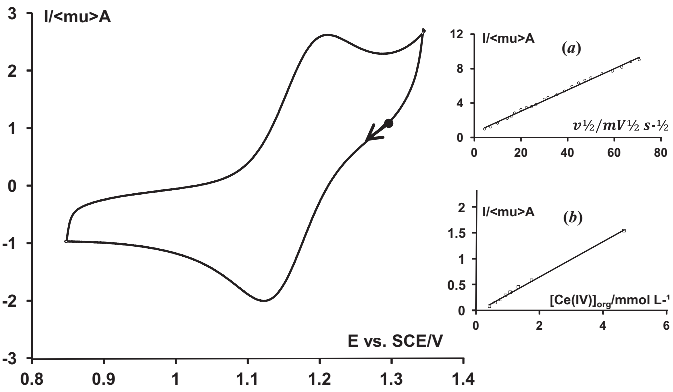


Fig. 1. *Left: CV of Ce (IV) 4.66×10^{-3} mol.L^{-1} in TBP extracted from a HNO_3 5 mol.L^{-1} aqueous solution at a GCE (area 0.007 cm^2). Scan rate 100 mV.s^{-1}. Right: (**a**) Reduction peak current of Ce (IV) as a function of, (**b**) Reduction peak current of Ce (IV) as a function of the concentration of Ce (IV) in organic phase.*

2. Experimental

2.1. Reagents and solutions

All chemicals and solvents were analytical grade and used without further purification. All aqueous solutions were made with Milli-Q purified water (Millipore). The extractant was tributylphosphate TBP (Acros Organics), the source of cerium (IV) was ceric ammonium nitrate (Alfa Aesar). Suprapure grade. 69% nitric acid was purchased from VWR.

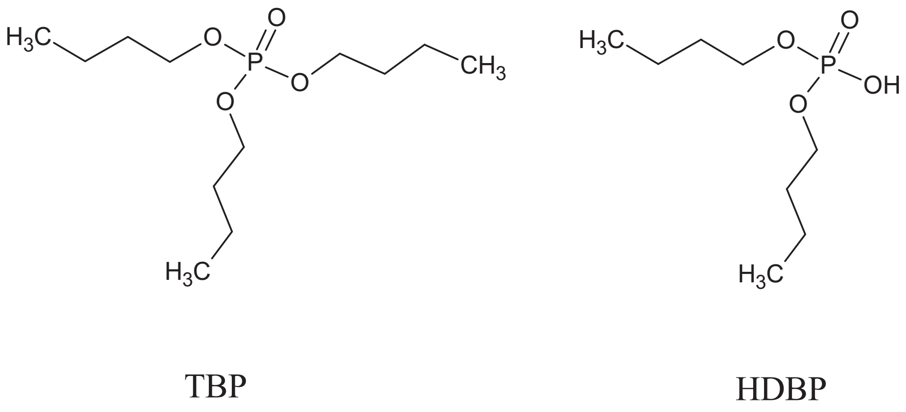
2.2. Instrumentation

Electrochemical measurements were carried out using a PAR 2273 potentiostat. Cyclic Voltammetry was performed under positive feedback compensation of the ohmic drop. The same potentiostat was used for Electrochemical Impedance Spectroscopy (EIS). All electrochemical experiments were driven using the PowerSuite Software. CV simulation was performed using Digisim® software. The electrochemical cell was a conventional three electrodes-one compartment glass cell filled with 10 mL of TBP, previously equilibrated as depicted below. Homemade glassy carbon electrodes (GCE) were used at the smallest diameter available. They were prepared from glassy carbon rods (1 mm diameter, purchased from Goodfellow) which were embedded in a glass tube sealed with epoxy resin (Loctite Hysol vacuum Sealant Kit purchased from Ted Pella inc.). Prior to each run, the glassy carbon electrode was polished on Struers 4000 paper and rinsed with MilliQ water and ethanol. Platinum gauze was used as counter electrode.

A saturated calomel electrode (SCE) was used as reference electrode for TBP solutions equilibrated with aqueous HNO_3 solutions, its average potential value being -0.450 ± 0.002 V vs Fc^+/Fc (see Supporting Information Fig. 1). A platinum / polypyrrole quasi-reference electrode (Pt/PPy) was used in highly resistive media (e.g. dodecane / TBP mixtures) in order to minimize the resistance due to junctions. These Pt/PPy quasi-reference electrodes were fabricated according to a procedure adapted from the literature [14]. Briefly, a polypyrrole film was electrochemically deposited on a platinum wire by cyclic voltammetry (50 cycles between 0.6 and 1.4 V vs SCE) in an acetonitrile solution containing 0.01 mol.L^{-1} pyrrole and 0.1 mol.L^{-1} Bu_4NBF_4. The final cycle was stopped at 0.65 V/SCE for 30 s in order to partially oxidize the film. The platinum/ polypyrrole quasi-reference electrode was rinsed with acetonitrile and soaked in acetonitrile for 30 min. The Pt/PPy potential was measured before and after each series of CV experiments versus a SCE. The average potential value of the Pt/PPy quasi-reference was +0.875 ± 0.005 V/SCE. For the sake of simplicity, all potentials in the figures were plotted against the SCE.

The starting potential and the sense were indicated on all voltammograms (Figs. 1–5) by an arrow.

The conductivities of solutions were monitored by a CDM210 conductimeter from Radiometer Analytical equipped with a CDC741 two-pole cell (Radiometer Analytical). The conductimeter was calibrated using standard solutions of KCl (0.1 mol.L^{-1}) in H_2O. The conductivity of TBP solutions was then determined once the conductivity value σ remained stable for 5 min. The value of the resistance R at the GCE was estimated using Newman's expression [15], i.e $R = \frac{1}{4\sigma r}$ (σ being the conductivity of the electrolyte, and r the radius of the disk) and its value used for positive feedback compensation of the ohmic drop.



Scheme 1. Structures of TBP and HDBP.