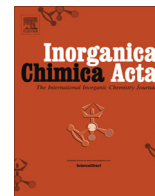




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Research paper

Acid-switched Eu(III) coordination inside reverse aggregates: Insights into a synergistic liquid-liquid extraction system

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ABSTRACT

Determining the structure of complex solutions bearing metal ions is challenging, but crucial for developing important technologies such as liquid-liquid extraction for metal refining and separation purposes. Herein, the structure of an organic Eu(III) solution consisting a binary mixture of lipophilic ligands di-2-ethylhexyl phosphoric acid (HDEHP) and tetraoctyl diglycolamide (TODGA) in dodecane is studied using synchrotron small angle X-ray scattering (SAXS) and X-ray absorption fine structure spectroscopy (EXAFS). This system is of technological importance in f-element separation for nuclear fuel cycle applications, where extraction is controlled by varying nitric acid concentration. Extraction is promoted at low and high concentration, but is retarded at intermediate concentration, leading to a U-shaped function; the structural origins of which we investigate. At the nanoscale, the solution is apparently comprised of reverse micelles with polar cores of approximately 1 nm in size, and these remain virtually unchanged as acid concentration is varied. Inside the polar cores, the coordination environment of Eu(III) switches from a 9-coordinate $[\text{Eu}(\text{TODGA})_3]^{3+}$ motif at high acid, to a 6-coordinate HDEHP-dominated complex resembling $\text{Eu}(\text{HDEHP}\cdot\text{DEHP})_3$ at low acid. The results show that extraction is controlled within the coordination sphere, where it is promoted under conditions that favor coordination of either one of the two organic ligands, but is retarded under conditions that encourage mixed complexes. Our results link solution structure with ion transport properties in a technologically-important liquid-liquid ion extraction system.

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Uncovering the structure and interactions around ions in solution is key to understanding solvation [1]. Most systems of natural or technologic importance that hinge on ion chemistry operate in the solution state, where the inherent dynamics facilitate transformations, such as protein folding around Fe(III), to liquid-liquid ion transport for industrial metal refining [2]. Fundamental to these applications is the coordination structure of metal ions inside the wider nanoscale solution structure, and how this relates to conditions (e.g. pH) and ion transport/solvation. It is crucial, therefore, to conduct studies that probe solution structure directly, despite the dynamics and rotational averaging inherent to solutions that makes experimental structural studies extremely challenging.

The present study is concerned with the structure of a metal-foamphiphile-alkane solution. Metal ions are dissolved as lipophilic complexes by binding to the amphiphile headgroups; a phenomenon that underpins liquid-liquid ion separations for nuclear fuel reprocessing as well as metal refining processes. In these systems, metal ions are transported from an aqueous phase and into the hydrocarbon solution as they interact with the coordi-

nating amphiphilic species (known as “extractants”) within the oil. The organic solution is notoriously prone to micellization, where the self-assembly of extractant amphiphiles into aggregates provides a nanoscale solvation environment encapsulating the target ion [3]. The competitive solvation of ions between the immiscible aqueous and organic solutions dictates the performance of the process. Recent research has shown that ion solvation in the organic phase is influenced by both the nanoscale structure of the reverse micelle, as well as the local coordination interactions between the lipophilic donors and metal center [4]. Therefore, in order to understand the structural origins of liquid-liquid extraction behaviors, it is important to investigate the solution at both the supramolecular and molecular scales.

Synchrotron small angle X-ray scattering (SAXS) and X-ray absorption fine structure spectroscopy (EXAFS) techniques are employed herein to simultaneously probe the supramolecular structure and coordination environment inside a Eu(III) liquid-liquid extraction organic phase. The subject system involves the extraction of Eu(III) from nitric acid into n-dodecane oil using a binary mixture of an acidic and a neutral extractant. The extractants in question are di-2-ethylhexyl phosphoric acid (HDEHP)

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and tetraoctyl diglycolamide (TODGA) (shown in Fig. 1 a,b). When dissolved in a water-immiscible hydrocarbon oil, these extractants are used in a process to separate f-block elements from aqueous solutions via liquid-liquid extraction for next-generation nuclear fuel recycling [5]. This process was designed to operate at 0.05 M TODGA and 0.75 M HDEHP concentrations, and f-element extraction can be controlled by varying the concentration of nitric acid in the aqueous phase. Binary mixtures of extractants are often used in liquid-liquid ion separation processes because they can behave synergistically and yield useful extractive properties [6]. However, such complex solution mixtures can yield complex extractive properties, particularly with regard to acidity (see Fig. 1c and the discussion below).

It is important to understand the fundamental structural origins of metal ion extraction behaviors in order to better predict and control the process. Muller et al. have shown recently that acid-induced changes in synergistic properties of binary extractant mixtures may be related to changes in ion complexation [7]. Rey et al. have shown that synergism is also related to changes in the nanoscale reverse micelle structure [8]. Therefore, to understand the acid dependence observed in the present HDEHP-TODGA-Eu(III) system, both the coordination and supramolecular solution structures must be investigated. Using synchrotron X-ray techniques, I thus address the fundamental question: *how are coordination and micellar solution structures related to acid-induced changes in Eu(III) extraction behaviors in the TODGA-HDEHP liquid-liquid extraction system?* My findings give new insight into the effects of acid on synergistic liquid-liquid extraction in particular, as well as structured rare earth organic solutions, in general.

1. Experimental

Solvent extraction: >99% purity TODGA was purchased from Technocomm (Scotland). All other reagents were of >99% purity and purchased from Sigma Aldrich (Milwaukee). 1 mL volumes of the organic phase were vortexing in capped plastic test tubes at 23 °C with an equal volume of 10 mM europium nitrate in nitric acid (0.1–3 M). Initial experiments showed that a 30 min vortexing time was sufficient to reach equilibrium. Aliquots of the aqueous phases were withdrawn for analysis after centrifugation and phase separation. The metal concentration in the aqueous phase before and after extraction was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

XAS data collection and analysis: EXAFS data collection and analysis were performed using the same general method as reported in our previous publication [9]. Eu L3-edge spectra were collected in fluorescence mode at beamline 12-BM-B at the

Advanced Photon Source (APS) at Argonne National Laboratory. A multi-element Ge detector (Canberra) was used to collect the fluorescence signal. The incident X-ray energy was calibrated against the inflection point energy of a Eu oxide foil. The solutions were injected into 1 mm Kapton capillaries for data acquisition. Three 1 h scans were averaged for each solution. Analyses of the $k^3\chi(k)$ EXAFS were performed using EXAFSPAK and curve-fitting using theoretical phase and amplitude functions calculated with FEFF8.01.

SAXS data collection: SAXS data were collected at the APS beam-line 12-ID-C. Samples were contained in 1.5 mm diameter quartz capillary tubes (Charles Supper Co., 20-QZ) with incident photon energy of 19.0 keV. 2D scattering profiles were acquired in 0.1 s exposure times with a MAR-CCD-165 detector (MAR USA). The scattering vector, Q , was calibrated using a silver behenate standard and the 2D scattering images were corrected for spatial distortion and detector sensitivity before radial averaging to produce plots $I(Q)$ versus Q . The GIFT method [10] was used to obtain real space functions from the scattering data as described previously [11]. Briefly, GIFT interprets the globular particle system, $I(q) = nP(q)S(q)$, in which n is the number of particles per unit volume, $P(q)$ is the average form factor (corresponding to the shape and size of the scattering particles) and $S(q)$ is the average structure factor (scattering produced from inter-particle interactions). $P(q)$ is the Fourier transformation of its real space counterpart, $p(r)$. Thus, the real space functions are obtained by removing $S(Q)$ and conducting the inverse Fourier transform on the remaining $P(Q)$ function. The selection of the appropriate structure factor model is key to the calculation and the Percus–Yevick (PY) closure relation was used. This has been shown previously to closely approximate the interaction effects of micelles [12].

2. Results and discussion

Four liquid-liquid extraction experiments were performed by mixing a 0.05 M TODGA + 0.75 M HDEHP in dodecane organic solutions with nitric acid aqueous phases (0.1 to 3 M HNO_3) containing Eu(III) (10 mM). These conditions mirror those used in the f-element separation process, and show the characteristic U-shaped acid dependence of Eu(III) extraction observed in previous studies (see Fig. 2) [5]. This dependence is exactly the same as found previously by Gelis et al. with the same HDEHP-TODGA-dodecane mixture [5]. SAXS and Eu L3-edge EXAFS measurements were then collected from all four solutions to probe simultaneously the supramolecular solution structure as well as the coordination environment around Eu(III).

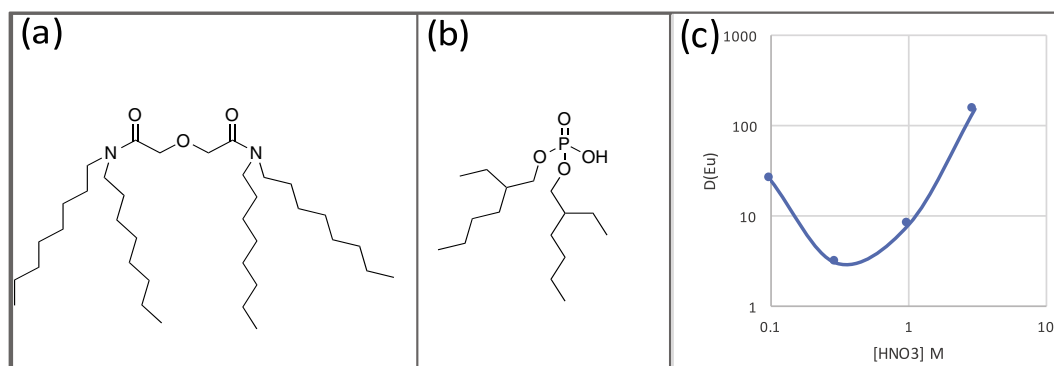


Fig. 1. Depictions showing the molecular structures of (a) neutral extractant TODGA and (b) acidic extractant HDEHP. (c) The extraction dependence of Eu(III) relative to acid concentration. Distribution coefficient (D) is the concentration ratio of Eu in the organic phase over Eu in the aqueous phase against nitric acid concentration in the aqueous phase. Organic phase was 0.05 M TODGA + 0.75 M HDEHP in dodecane.

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