

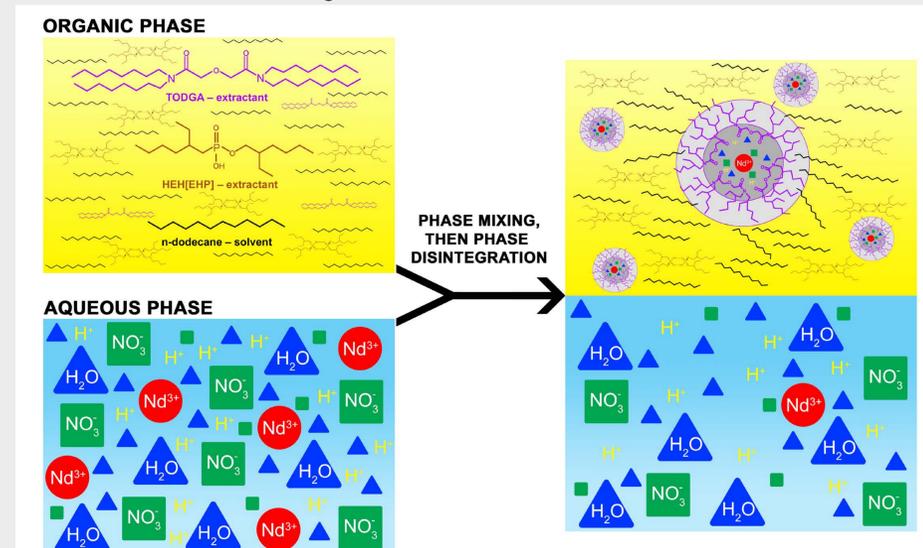
INTRODUCTION

- Potential impact.** Achievements in the field of reprocessing of used nuclear fuel have led to increasing competitiveness of nuclear energy in comparison with other energy sources. From this point of view, the liquid-liquid extraction, or solvent extraction (SX), is of great importance for achieving closed nuclear fuel cycle. One of the current worldwide priorities stemming from the need of nuclear fuel reprocessing is the partitioning of high-level radioactive waste, which requires development of a cost-effective method to separate the trivalent actinides (An^{3+} , such as Am^{3+} and Cm^{3+}) from the trivalent lanthanides (Ln^{3+}) in the PUREX raffinate.
- Problem Overview.** In the majority of the SX processes investigated for this purpose metals are extracted from aqueous phase, which consists of selective extractants in diluent, most frequently aliphatic hydrocarbons. In the recently developed Actinide Lanthanide Separation Process (ALSEP), a mixed solvent extraction system under current development, combinations of HEH[EHP] with TODGA and T2EDGA showed extraction behavior close to ideal, i.e. efficient Ln/An separations¹. On the other hand, mixture of these DGAs with other phosphonic acid derivatives, such as HDEHP, showed less Ln/An selectivity at any significant DGA concentration.
- Overarching goal.** The inter-ligand interactions were investigated to better understand and to possibly predict the extraction and stripping behavior of An/Ln in mixtures of solvating and cation exchange ligands. The goal was achieved through establishment of relationship between the stoichiometry of extracted complexes and extractability upon variation of aqueous phase conditions.

SUPRAMOLECULAR CHEMISTRY UNDER THE ACTINIDE-LANTHANIDE SEPARATION CONCEPT

Formation of aggregates and interligand adducts in the ALSEP

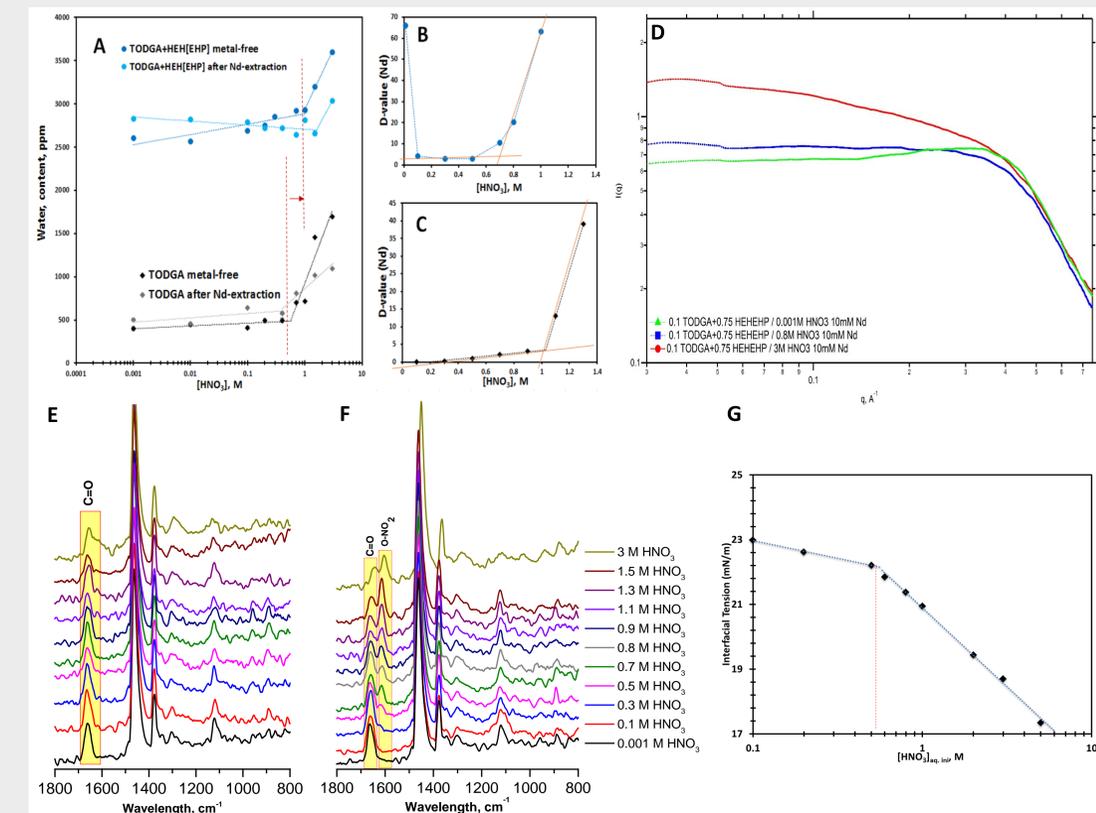
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Materials and methodology. HEH[EHP] obtained from Alfa Aesar was purified to >99% purity by the Cu-precipitation method² as confirmed by ³¹P NMR. TODGA and T2EDGA (from Eichrom) were used as received. Before all extraction experiments preequilibration step was performed by vigorously mixing organic phase with nitric acid at 3:1 volumetric ratio for 10 min. 10 mM solutions of $Nd(NO_3)_3$ in nitric acid of different concentrations were used as aqueous phase for extraction. The total volumes of samples were in the range of 6-8 mL. IR spectra were collected on a Nicolet 6700 FTIR Spectrometer using an attenuated total reflectance (ATR) diamond plate attachment. Water concentration in the organic phases was determined by volumetric Karl Fischer titrations on a Mettler Toledo DL58 auto titrator.

KEY FINDINGS

- Both TODGA and TODGA+HEH[EHP] organic phases behave as classical amphiphilic surfactant systems forming heterogeneous self-assemblies. These assemblies consist of a hydrophilic core of water, metal ions, and nitric acid surrounded by extractant molecules. The tendency to form reverse micelles, the shape and composition of micelles is regulated by nitric acid concentration in the contacting aqueous phase.
- The critical micelle concentration was found to be around 0.8 M HNO_3 for systems after preequilibration step and it decreases to 0.6 M HNO_3 after following neodymium extraction.
- Micelle formation is corroborated by the increase in amount of water and nitric acid quenched in organic phase after phase mixing and phase disintegration. The systems with reverse micelles extract considerably more water and nitric acid than the ones without them, i.e. prior to critical micelle concentration.
- SAXS studies revealed spherical aggregates formed by only HEH[EHP] at low nitric acid concentrations which in HEH[EHP]+TODGA system at high concentrations of nitric acid are transformed into bigger elongated micelles formed by TODGA and HEH[EHP] together.



SUPPORTING DATA

Figure A - Water concentration in the equilibrium TODGA/n-dodecane extraction solutions as a function of nitric acid concentration in aqueous phase. The intercepts of two asymptotes give the concentrations, above which the reversed micelles are formed (critical micelle concentration).

Figure B – Neodymium extraction by 0.1 M TODGA + 0.75 M HEH[EHP] in n-dodecane after contact with 0-1.5 M HNO_3 .

Figure C - Neodymium extraction by 0.1 M TODGA in n-dodecane after contact with 0-1.5 M HNO_3 .

Figure D - Scattered intensity $I(q)$ versus momentum transfer q measured via SAXS for a fixed TODGA and HEHEHP concentration of 0.1 M and 0.75 M, respectively. The nitric acid initial concentration of the aqueous phase contacted with the organic phase: 0.001M (green ▲), 0.8 M (blue ■), 3 M (red ●).

Figure E - FTIR spectra of 0.1 M TODGA in n-dodecane after contact with 0-1.5 M HNO_3 .

Figure F - FTIR spectra of 0.1 M TODGA in n-dodecane after contact with 0-1.5 M HNO_3 + 9.8 mM Nd^{3+} .

Figure G - Interfacial Tension of 0.1 M TODGA in n-dodecane versus concentration of HNO_3 in the initial aqueous phase.



References:

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- Partridge, J. A.; Jensen, R. C. "Purification of Di-(2-Ethylhexyl)Phosphoric Acid by Precipitation of Copper(II) Di-(2-Ethylhexyl)Phosphate," *Journal of Inorganic and Nuclear Chemistry*, 31, 2587-2589, 1969



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