Experimental report

15/12/2020

Proposal: 9-10-1637 **Council:** 10/2019

Title: Understanding of extraction mechanisms of uranium by tertiary amines in sulfuric environment

Research area: Chemistry

This proposal is a new proposal

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Samples: Tridecylamine, 5% 1-octanol, natural uranium, deuterated dodecane
Triisooctylamine, 5% deuterated 1-octanol, natural uranium, deuterated dodecane
Trihexylamine, 5% deuterated 1-octanol, natural uranium, deuterated dodecane
Tridecylamine, 5% deuterated 1-octanol, natural uranium, deuterated dodecane
Trioctylamine, 5% deuterated 1-octanol, natural uranium, deuterated dodecane
Trinonylamine, 5% 1-octanol, natural uranium, deuterated dodecane
Triisooctylamine, 5% deuterated 1-octanol
Triheptylamine, 5% 1-octanol, natural uranium, deuterated dodecane
Triheptylamine, 5% deuterated 1-octanol, natural uranium, deuterated dodecane
Trioctylamine, 5% 1-octanol, natural uranium, deuterated dodecane
Trinonylamine, 5% deuterated 1-octanol, natural uranium, deuterated dodecane
Tris(2-ethylhexyl)amine, 5% 1-octanol, natural uranium, deuterated dodecane
Tris(2-ethylhexyl)amine, 5% deuterated 1-octanol, natural uranium, deuterated dodecane

Instrument	Requested days	Allocated days	From	To
D16	3	2	22/01/2020	24/01/2020

Abstract:

Amine Extraction (AMEX) process uses tertiary amines as selective extracting agent, which enables the selective extraction of uranyl cations from sulfuric acid leach liquors. Despites its extensive application, the AMEX process is still facing several problems. In this context, this project has the objective to test different tertiary amines molecules, with alkyl chains of different lengths or branching. Coupled SAXS and SANS measurements are necessary as they will provide us the core and aggregates radius of the formed aggregates. SANS measurements will indeed provide a complementary contrast of the aggregates, and allow performing a simultaneous fit of SAXS and of SANS, which is necessary to recover the exact microstructure of the reverse micellar aggregates.

Understanding of extraction mechanisms of uranium by tertiary amines in sulfuric environment

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Background

Solvent extraction is the most widely used chemical separation method at the industrial scale. Amine Extraction (AMEX) process uses tertiary amines as selective extracting agent, which enables the selective extraction of uranyl cations from sulfuric acid leach liquors. Despites its extensive application, the AMEX process is still facing several problems: 1/The selectivity of uranium towards zirconium is not ideal;[1] 2/It requires a phase modifier to prevent third phase formation, and the poor solubility of molydebnum complex with tertiary amine in conventional aliphatic diluent makes the third phase appearing more easily;[2] 3/The degradation problem of tertiary amines because of the presence of V(V) and phase modifier.[3, 4] Although the process presents several inconveniences, few studies have been dedicated to the optimization of uranium extraction in sulfuric solution. Therefore, the AMEX process needs to be understood in more details for optimization.

Objectives

In this context, this project has the objective to test different tertiary amines molecules, with alkyl chains of different lengths or branching. The extraction performance of uranium and its selectivity towards competitive metal ions have been evaluated by ICP-OES. To explain their extraction properties, structural characterization have been performed. As the main difference between these systems is the structure of their alkyl chains, SANS measurements are thus necessary to analyze the effect of the various extractants alkyl chains structure and branching on their extraction properties. Through this study in ILL, we are able not only to acquire the exact microstructure of the reverse micellar aggregates, but also to confirm CAC measurements which are difficult to derive properly for this kind of systems with surface tension. Information obtained from SANS fitting allowed moreover to establish a thermodynamic analysis to decompose the uranium free energy of transfer into different contributions as complexation, micellisation and the bending energies.

Results

The main results of this experiment are summarized in Figure 1 and Figure 2. Effect of linear alkyl chains lengths and of alkyl chains branching on the aggregation properties are analyzed thanks to SANS data. Clear aggregation signals can be identified in Figure 1 for the 5 tested amines having linear alkyl chains. Adopting a sticky hard sphere structure factor, we found out that the attractive interactions between the aggregates become less important as the alkyl chains get longer, which is in agreement with the fact that less third phase was observed for amines with longer alkyl chains.

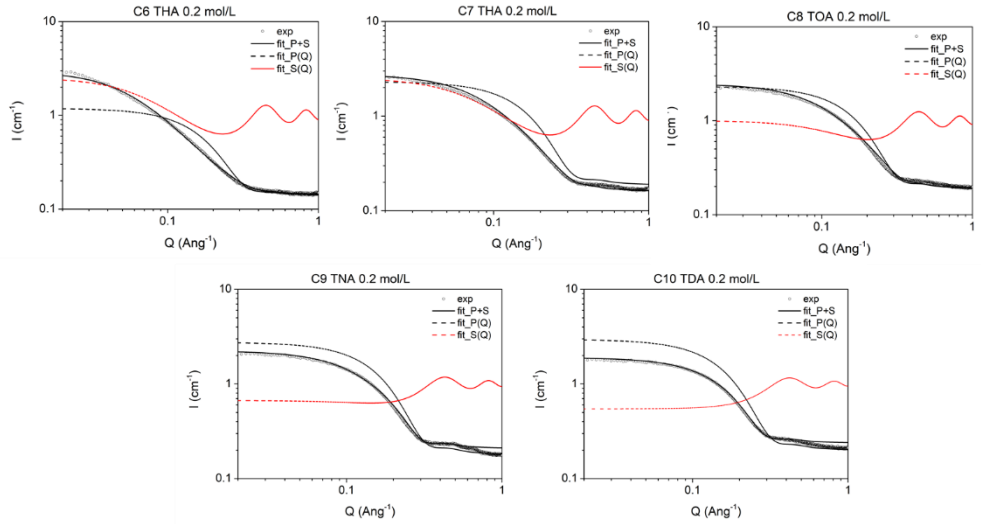

Figure 1 SANS spectra (experiment and fit) of tertiary amines (linear alkyl chains with different carbon numbers) in dodecane after contact with sulfuric solution containing 2500 ppm U(VI)

Concerning amines with branched chains, Figure 2 shows a clear signal of aggregation at small angles for the more branched molecules (TOA and TIOA) while for TEHA, signal is much less intense. These behaviors indicate that TOA and TIOA aggregates in dodecane while TEHA, shows no sign of aggregation. This

observation is also consistent with the poor extraction properties of TEHA observed in our extraction experiments.

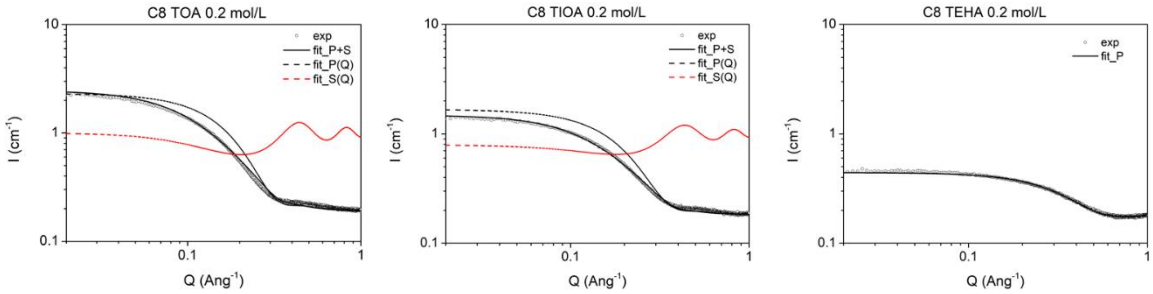

Figure 2 SANS spectra (experiment and fit) of tertiary amines (branched alkyl chains with same carbon number) in dodecane after contact with sulfuric solution containing 2500 ppm U(VI)

A complete fit of the SANS data also allowed us to evaluate quantitatively the radius of polar core r_{core}, the thickness of the apolar shell Δt_{shell} of the aggregates, as well as the number of extractant per aggregate N_{agg}. With these parameters, we estimated the main thermodynamic driving force as introduced in the ienaic approach to account for the ion transfer in solvent extraction. [5, 6]

$$\Delta G_{transfer} = \Delta G_{complexation} + \Delta G_{bulk} + \Delta G_{micellisation} + \Delta G_{chain}$$

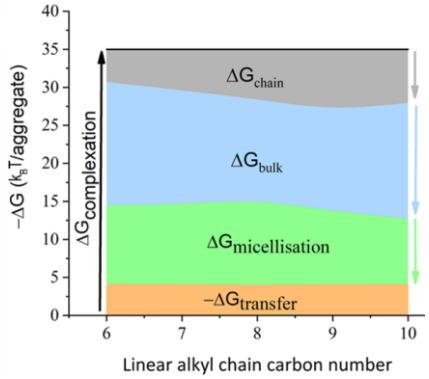

Figure 3 The main contributions are summed to illustrate their influence on the transfer energy.

It was found that the effect of alkyl chains length is not significant on the bulk and micellization free energies, which are the two most important inhibitors of the uranium transfer. Assuming a constant complexation energy, the chain free energy was shown to increase with increasing chains length and the bending constant of the amines with different alkyl chains lengths was further deduced. All these contributions allow reproducing the quasi-constant transfer free energy for tertiary amines with different alkyl chains length.

On the contrary, alkyl chains branching was shown to have a significant influence on the transfer energy. When the branched group of alkyl chains becomes larger and closer to the polar head, the chain free energy becomes a major inhibitor. It almost counter balances the complexation free energy and results in a huge drop of extraction efficiency towards water, acid and uranium.

These results were exploited for one of the chapter of Zijun LU's PhD thesis, and will be submitted for publication in Langmuir.

References:

[1] Sato T, Watanabe H. The Extraction of Zirconium(Iv) from Sulfuric-Acid-Solutions by Long-Chain Alkyl Quaternary Ammonium Compound. Sep Sci Technol. 1982;17:625-34.

[2] Sato T, Watanabe H, Suzuki H. Liquid-Liquid-Extraction of Molybdenum(Vi) from Aqueous Acid-Solutions by High-Molecular-Weight Amines. Solvent Extr Ion Exc. 1986;4:987-98.

[3] Chagnes A, Courtaud B, Thiry J, Bayardon J, Juge S, Cote G. Influence of Phase Modifiers on the Degradation of Tri-N-Octylamine/Dodecane Extracting Mixture by an Acidic Solution of Vanadium (V). Solvent Extr Ion Exc. 2012;30:67-76.

[4] Chagnes A, Cote G. Chemical Degradation of aMixture of tri-n-Octylamine and 1-Tridecanol in the Presence of Chromium(VI) in Acidic Sulfate Media. Metals-Basel. 2018;8.

[5] Rey J, Bley M, Dufreche JF, Gourdin S, Pellet-Rostaing S, Zemb T, et al. Thermodynamic Description of Synergy in Solvent Extraction: II Thermodynamic Balance of Driving Forces Implied in Synergistic Extraction. Langmuir. 2017;33:13168-79.

[6] Dufrêche JF, Zemb T. Effect of long-range interactions on ion equilibria in liquid–liquid extraction. Chem Phys Lett. 2015;622:45-9.