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Zijun Lu, Sandrine Dourdain, Bruno Demé, Jean-François Dufrêche, Thomas Zemb, et al.. Effect of alkyl chain configuration of tertiary amines on uranium extraction and phase stability – Part I: Evaluation of phase stability, extraction, and aggregation properties. Journal of Molecular Liquids, 2022, 349, pp.118409. 10.1016/j.molliq.2021.118409 . hal-03633060

HAL Id: hal-03633060

https://hal.umontpellier.fr/hal-03633060v1

Submitted on 22 Jul 2024

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Manuscript_bd7a6df55446317fe37a9f8467689911

Effect of alkyl chain configuration of tertiary amines on uranium extraction and phase stability – Part I: Evaluation of phase stability, extraction, and aggregation properties

Zijun Lu[1], Sandrine Dourdain[1], Bruno Demé,[2] Jean-François Dufrêche,[1] Thomas Zemb[1] and Stéphane Pellet-Rostaing[1]

[1] ICSM, Univ. Montpellier, CEA, CNRS, ENSCM, Marcoule, France
[2] Inst. Laue Langevin, Grenoble, France

Abstract

Amine-based extraction processes are broadly exploited for the selective extraction of uranium from sulfuric leaching liquors. The molecular forces (that is, the enthalpy associated with the multi-scale structuration of tertiary amines) are balanced by entropic effects that have not yet been identified. This first part in a series of reports describes the effects of the alkyl chain configuration on the phase stability and aggregation properties of tertiary amines. It is demonstrated that tertiary amines with longer or slightly branched alkyl chains provide better phase stability and enable constant extraction of uranium. In comparison, more branching of the alkyl chains hinders the formation of a highly curved interfacial layer, thus preventing efficient extraction. Combined small-angle scattering determination of the nanostructures in the organic phase and oil-water surface tension measurements revealed that the alkyl chains effects on the efficiency of the extraction process and phase stability are associated with reverse aggregates with smaller polar core volumes and less co-extracted water, suggesting that packing of the alkyl chains has a direct impact on the extraction efficiency of the solvent extraction system.

Introduction

Solvent extraction is one of the most widely used methods of uranium production. Currently, nearly 80% of U is extracted from sulfuric acid leach liquors using the AMEX process (short for AMine EXtraction), which utilizes mixtures of trialkyl-amines as extractants.[1] [2]

Despite its extensive application, this economically efficient process presents several drawbacks, including degradation of the extractants and crud formation leading to high solvent loss, and the frequent formation of a “third phase” due to splitting of the organic phase into heavier and lighter phases, leading to dramatic failure of the extraction process. The latter requires the addition of a phase modifier, which in turn induces extractant degradation problems in the AMEX process.[3,4] Hence, a suitable solvent extraction process would be beneficial for optimizing the yield, safety, and effluent volumes. Optimisation and

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simplification of the process can be achieved by exhaustive experimental designs if the molecular forces governing the extraction process are understood.[5]

“Alamine 336”, the extractant of choice in the industrial AMEX process, comprises a mixture of tertiary and secondary amines. Even in the absence of fully documented comparative studies, this mixture is reputed to be more resistant toward performance degradation that its congeners.

The effects of the alkyl chain configuration have been studied in the case of diamides. The distribution coefficient of lanthanides was shown to vary by four orders of magnitude depending on the hydrocarbon chain volume and by two orders depending on branching of the hydrocarbon chain [6]. Since the 1960s, scattered studies have also been published on the effect of the alkyl chain configuration on the selective extraction of uranium. Coleman *et al.*[7] reported that uranium extraction by tertiary amines was reduced when the branching group was too close to the central nitrogen. The effect of the chain length and branching was also investigated in different diluents: tri-*n*-octylamine has a lower D_U value than tris(tridecyl) amine in kerosene, but higher efficiency in benzene or chloroform.[8] Later, the same author further observed that tertiary amines with longer alkyl chains also presented better zirconium distribution ratios, which were reduced when the alkyl chains were branched.[8] These studies consistently agree that the **alkyl chain configuration has a significant effect on selective extraction. However, there are no clear parametric or structural studies to aid in understanding and predicting this effect.**

Another challenge faced by the industry is the serious degradation of tertiary amines. Degradation into a large number of secondary amines was shown to induce a decrease in the loading capacity and uranium separation factor owing to the higher co-extraction of impurities. The phase modifier was shown to be involved in the extractant degradation mechanisms; thus, employing more stable phase modifiers or amines was proposed as a means of avoiding degradation problems and maintaining high extraction.[9,10] However, systematic studies on the structural effect of the alkyl chain configuration **on the degradation of tertiary amines** are still lacking. Similarly, **the effect of the amine structure on the stability of the oil phase** is also poorly studied. Due to the low solubility of complexes of Mo(VI) with tertiary amines in aliphatic diluents, a third phase and green-yellow crud are observed at high molybdenum concentrations.[11,12] To solve this problem, heavier and more branched tertiary amines, such as alamine 304 (tri-lauryl-amine), have been proposed.[11,12] Moyer *et al.*[13,14] also showed that amines with longer alkyl chains or branched methyl groups formed less of the third phase. In Sato's study, the third phase was observed for primary amines, but was absent for secondary and tertiary amines.[15] Overall, these empirical studies suggest that smaller apolar volumes of tertiary amines lead to greater phase instability. A **key parameter for improving the phase stability of the AMEX process is an extraction system with bulkier extractants, requiring less phase modifier**.

When the search is broadened to other types of extractants beyond tertiary amines, we find that a few groups have evaluated the impact of the structure of the alkyl chain of the extractant on actinide extraction. Suresh *et al.* studied the effect of the alkyl chain structure of trialkyl phosphates on the extraction properties of the phosphates.[16–19] They also showed that increasing the chain length and branching on the first carbon of the alkyl groups of trialkyl phosphates decreased the formation of the third phase.[16,20] The extraction of Th(IV) and U(IV) was not significantly affected by elongation of the alkyl chain or by introducing branched chains away from the P=O group. However, branching on the first carbon atom of the alkyl groups increased the extraction of U(VI) and decreased the extraction of Th(IV), which favoured the selective separation of U/Th.[17,18]

The studies listed above only consider empirical observations of the alkyl chain effect. Investigation of the mechanistic origin often relies on considerations at the molecular scale (influence on complexation and speciation, etc.). Berger *et al.* evaluated a new family of extractants containing a carbamide function, and reported that the alkyl chain length did not significantly influence U(VI) extraction, but had a strong impact on Pu(VI) extraction.[21] Further spectroscopic results confirmed that the coordination sphere of uranyl was not modified, whereas the speciation of Pu(VI) depended on the alkyl chain length of the extractant.[22]

Very recently, Stamberga *et al*. [6] demonstrated that subtle changes in the alkyl chain had marked effects on the extraction and selectivity trends in lanthanide separation, attributed to electrostatic interactions beyond the first coordination sphere of the extracted metals. In a review, Narita *et al.*[23] discussed extraction concepts based on specific interactions at the outer sphere of a metal complex in the organic phase.

The effect of the alkyl chains of the extractant on supramolecular organisation of the molecules is rarely considered in mechanistic studies. To identify the molecular forces responsible for various extraction properties or phase stability when the alkyl chains of the extractant are modified, the supramolecular aggregation of extractants must be taken into account. In 1991, Osseo-Asare suggested that the amphiphilic properties of extractant molecules and their ability to self-assemble in organic solutions have a strong influence on their extraction properties.[24] The morphology of the “reverse micelle” water-in-oil (w/o) aggregates formed by the extractants were further compared with that of w/o or bicontinuous surfactant microemulsions.[25–27] Based on the IUPAC definition, microemulsions are formed by two fluids separated by an interfacial layer without long-range order, while micelles are dispersed in pseudo-phases: all molecules in the core of w/o “reverse micelles” are bound to the head group; there is no detectable fast moving free aqueous microphase in reverse micelles, while the polar core moves faster than the layer formed in microemulsions. Taking into account these definitions, we use the term aggregate, in this study, to describe the association of several extractants that may correspond either to the complex itself or to larger aggregates of extractants that are packed through weak interactions around a polar core. To the best of our knowledge, no microemulsion of amines or tertiary amines has been designed for the extraction of metals.[28] In comparison, branched chains present in the highly studied sulfosuccinate AOT [29] were shown to favour the formation of microemulsions that are much more efficient than micelles for amino acid, peptide, and protein extraction.[30–33]

Experimental observation of the aggregation of extractant molecules in a highly curved thick layer [34] allows determination of the aggregation numbers through structural studies, where the stoichiometry of complexation can be determined by “slope analysis”. This has allowed us to understand the molecular origin of various phenomena, such as the effect of the diluent on the efficacy of the extraction process,[35–37] effect of acids on formation of the third phase,[25,38,39] as well as the synergistic extraction of different extractants.[40,41]

For example, Berthon *et al.* evaluated the role of the alkyl chains and demonstrated that the phase stability of the extractant and diluent is ruled by the universal “chain penetration”, as initially evidenced by Chen, Evans, and Ninham in the case of synthetic lipids,[42–44] where decreasing the chain length of the diluent or increasing that of the extractant improved the phase stability.[35] The shorter and branched chains of the diluent were shown to penetrate more easily in the bottle-brush structure made by the chains of the extractant.[45] Steric stabilization can therefore be improved either by using longer extractant chains or shorter (or branched) diluent chains. We also proposed, in a recent study, that such long-range interactions should be considered in explaining the difference in the selectivities obtained with two bifunctional extractants that differed only by an alkyl chain.[46] It was shown that the packing parameter of the extractant can markedly affect the aggregate size and therefore the selectivity.

As proposed in the "ienaic" approach in 2015, the relevant parameters for quantifying the effect of the alkyl chains of the extractant on the extraction process and phase stability are the free energy of transfer of an anion (defined as a function of the distribution coefficient *D*),[47,48] the free energy of aggregate formation (defined as a function of the critical aggregation concentration, CAC),[49] the curvature free energy of the aggregates, and the effective attractive potential between the aggregates (as determined from small angle scattering experiments).[35,50,51]

In this study, we investigate the effect of various tertiary amine alkyl chain configurations on the extraction efficiency and phase stability by considering organisation of the amines into reverse micellar aggregates. This study is divided into two parts: we describe the experimental results obtained with various alkyl chain branching and lengths on amine extraction, phase stability, and the aggregation properties. The second part provides a thermodynamic analysis of these results via the "ienaic" approach to understand the mechanisms by which aggregation of the extractants influences the extraction and phase stability.

The present study focuses on two groups of tertiary amines with various alkyl chain lengths and branching. The phase stability and uranium, water, and acid extraction are analysed via inductively coupled plasma-atomic emission spectroscopy/mass spectrometry (ICP-AES/MS) and titration techniques. The organic phases are further characterised by X-ray and neutron scattering and surface tension measurements for detailed analysis of the effects of the alkyl chain configuration on the aggregation properties of tertiary amines.

Materials and methods

Reagents

Extraction systems

Tertiary amines (0.05–0.4 mol/L) were first diluted in *n*-dodecane and 1-octanol (5 vol.%.) The obtained organic solutions were further contacted with equal volumes of aqueous solutions containing 2500 ppm $UO_2(NO_3)_2$ (10.5 mmol/L), 1 mol/L $(NH_4)_2SO_4$, and 0.1 mol/L H_2SO_4 (pH = 1). After mixing at 500 rpm and 20 °C for 1 h, the organic and aqueous phases were centrifuged at 11000 rpm and 20 °C for 0.5 h. The organic reagents (tertiary amines), *n*-dodecane, and 1-octanol were purchased from Sigma-Aldrich. The chemical products used for the small-angle neutron scattering (SANS) experiments (deuterated dodecane, deuterated 1-octanol, D_2O, and 96% D_2SO_4) were purchased from Eurisotope.

Experimental methods

Extraction analysis

The aqueous phase with an initial concentration of 2500 mg/L uranium was diluted and analysed before and after extraction by inductively coupled plasma atomic emission spectrophotometry and mass spectrometry (ICP-AES and ICP-MS).

Titrations

Karl Fischer titration was used to determine the concentration of water extracted into the organic phase after mixing and centrifugation. The extracted sulfuric acid was analysed by acid-base titration of the aqueous phase before and after extraction. An 809 Metrohm Titrando titrator was used in these experiments.

Small-Angle Scattering

The organic phase containing 0.2 mol/L tertiary amine was diluted in *n*-dodecane and 1-octanol (5 vol.%). The solution was characterised by small-angle X-ray scattering (SAXS) and SANS experiments after contact with the aqueous phase, as described in the section above.

- Small-Angle X-ray Scattering

SAXS experiments were performed using a home-built SAXS camera at the Institut de Chimie Séparative de Marcoule (ICSM). The setup involves a molybdenum source delivering a 1 mm circular beam of energy at 17.4 keV. A monochromatic beam was obtained by using a Fox-2D multishell mirror, and collimation of the beam was achieved using 2 sets of "scatterless" slits, which are crucial for the quantification of weak scattering near the beam-stop, together with precise monitoring of the transmission of the sample and solvents used as the reference. The scattering pattern was recorded using a MAR345 two-dimensional imaging plate, with a typical duration of 1 h. The measurements were performed in transmission geometry using 2 mm glass capillaries. The experimental resolution was set to $\Delta q/q = 0.05$. The detector count was normalised to the differential cross-section per unit volume (in cm^{-1}) with either a 2.36 mm thick high-density polyethylene sample (from Goodfellow®) ($I_{max} = 5.9\ cm^{-1}$) or 3 mm water for which the level of scattering at low q is known ($1.64 \times 10^{-2}\ cm^{-1}$). Data pre-analysis was performed using FIT2D software, taking into account the electronic background of the detector (where the flat-field response was homogeneous), transmission measurements (using a photodiode that can be inserted upstream of the sample), and empty cell subtraction. The scattering intensities are expressed as a function of the magnitude of the scattering vector.

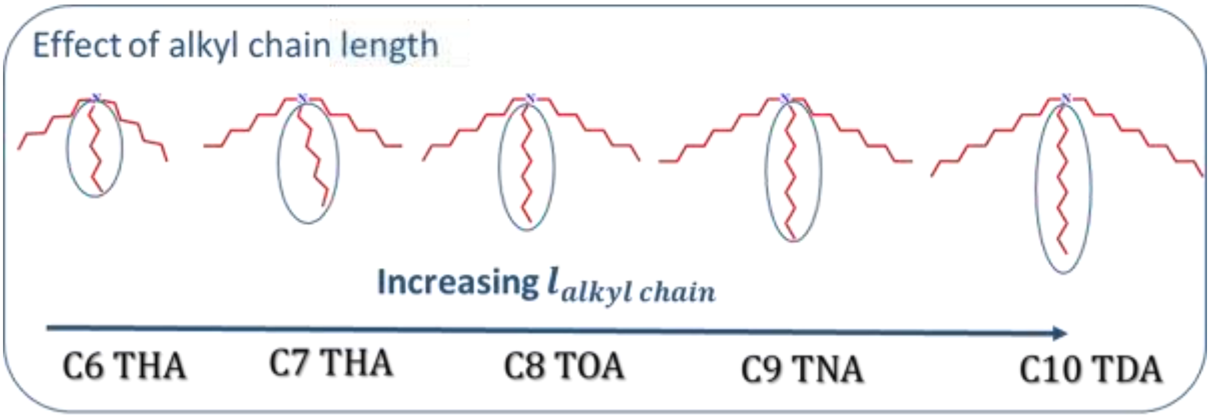
- Small-Angle Neutron Scattering

SANS measurements were carried out on the D16 instrument at the Institut Laue-Langevin (ILL) in Grenoble (France), set in pinhole geometry for SANS/WANS data collection. A pyrolitic graphite monochromator was used, giving a working wavelength of $\lambda = 4.48$ Å and $(\Delta\lambda/\lambda) = 0.01$. Two pairs of motorised slits in the casemate and at the sample were used to collimate the beam, with openings of 20 mm × 20 mm and 9 mm × 9 mm, respectively, followed by a 6 mm circular aperture in front of the sample. The diffracted neutrons were measured over an angle range of 2–10°, corresponding to a q range of 0.02–0.3 Å^{-1}. The detector pixel efficiency and solid angle were calibrated using the flat incoherent signal of water for calibration, and the scattered intensities were normalised in absolute units (cm^{-1}).

Results and discussion

Herein, focus was placed on the influence of the configurations of the alkyl chain of tertiary amines on the extraction and aggregation properties of the amines. To investigate the effect of chain length and branching, two groups of tertiary amines were tested:

- The first group contains five molecules with linear alkyl chains but different chain lengths: trihexylamine (C6 THA), tri-heptylamine (C7 THA), tri-octylamine (C8 TOA), tri-nonylamine (C9 TNA), and tri-*n*-decylamine (C10 TDA).
- The second group includes three molecules with the same carbon number on the alkyl chains but different branching conformations: trioctylamine (C8 TOA), tri-isooctylamine (C8 TIOA), and tris(2-ethylhexyl)amine (C8 TEHA). The molecular configurations are shown in Figure 1.



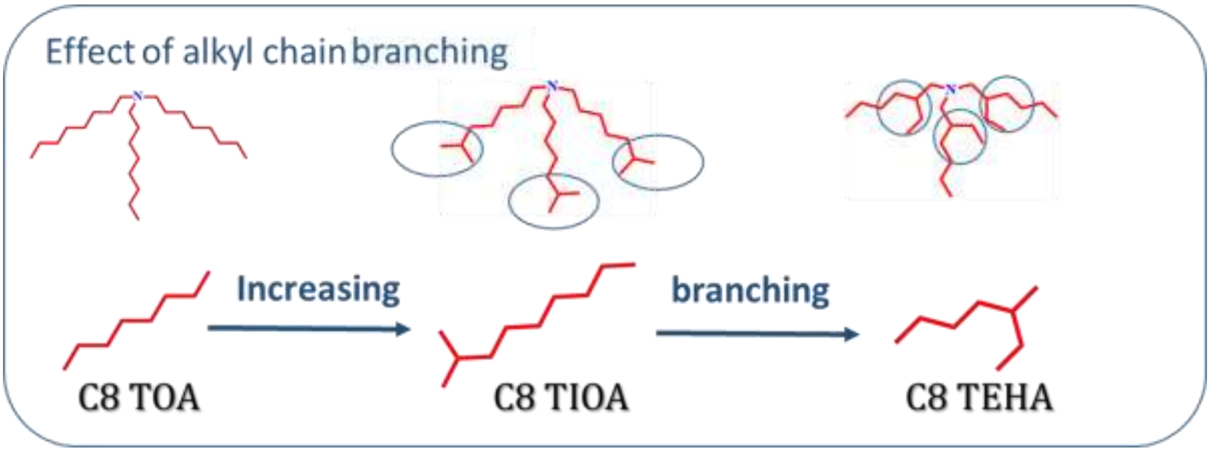


Figure 1. Molecular structures of tertiary amines with linear and branched alkyl chains studied in this work.

All of the amine samples had the same complexing site; the only difference was the alkyl chain configuration. Because C8 TOA is the main extractant used in the AMEX process, it was considered as the reference extractant. In the following text, the effects of the alkyl chains on formation of the third phase, the extraction performance (uranium, water, and acid), and on aggregate formation in dodecane are evaluated.

Influence on third phase formation

The effect of the alkyl chain length and branching on formation of the third phase was studied using amine-dodecane-sulfuric acid extraction systems. For this purpose, the extractant concentration compatible with a two-phase regime (aqueous phase and one organic phase only, separated by a meniscus) was increased stepwise until phase instability could be visually detected (see concentrations in Table SI-1). Recall here that a phase modifier such as 1-octanol is industrially added to prevent formation of the third phase. To observe the formation of a third phase with all the extractants tested, the 1-octanol concentration was also varied. The composition of the aqueous phase was fixed for all tested amines, while the concentration of the added 1-octanol was varied from 1 to 5 vol% (0.064 to 0.318 mol/L).

A generic phase diagram with points relevant to all extractants tested is presented in Figure 2 to show the location of the biphasic region and the third phase regime. Between the two regimes, the oil phase appeared unstable in some cases, and the formation of a thick interphase was observed at the interface. The meniscus between the interphase and water was still an optically thin meniscus, but there was no clear meniscus inside the oil phase. In the case of TODGA (tetraoctyl diglycolamide), the thickness and viscosity of the interphase could be characterised, and the interphase was found to be formed when the metal concentration in aqueous phase reached half of the limit concentration at which the complete separation into three phases takes place.[52]

The tested concentration range of the extractants ranged from 0.05 to 0.4 mol/L. The corresponding range of the total volume fraction of the polar head of the extractant and polar species extracted into the organic solution was calculated to be approximately 0–3.3% (see values in Table SI1).

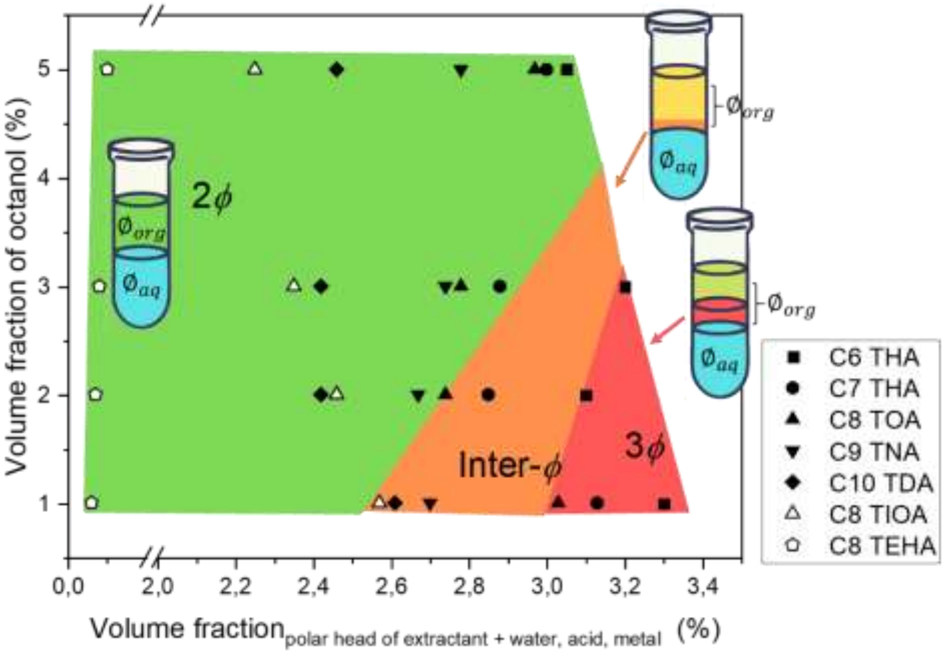


Figure 2. Third phase boundary illustrated for volume fraction of octanol versus total volume fraction of extractant polar head + polar species in organic solution for tertiary amine-dodecane solutions after equilibration with acidic aqueous solutions. The aqueous solutions contained 2500 ppm $UO_2(NO_3)_2$ (10.5 mmol/L), 1 mol/L $(NH_4)_2SO_4$, and 0.1 mol/L H_2SO_4 (pH = 1). The biphasic region, inter-phase, and third phase are presented in yellow, orange and red respectively, while the domains in the phase diagram are represented in green for the two phases (Winsor II), orange for the interphase regime and red for the Winsor I II regime).

Formation of the third phase refers to the phenomenon where the organic phase splits into one denser phase containing most of the extracted species and extractant molecules, while the upper lighter phase usually consists mostly of diluent molecules. ‘Interphase’ refers to the intermediate state observed after equilibration. Unlike the case of the third phase, in the interphase, some extractant molecules can still be found in the supernatant of the organic phase; here phase separation is incomplete and the process is classified as a surface-induced phase transition.

Figure 2 shows that under the given experimental conditions, all tertiary amine extraction systems required the addition of 1-octanol to prevent formation of the third phase, and that the third phase was formed more easily for amines with shorter alkyl chains. Increasing the alkyl chain length extends the composition at which phase stability is ensured, which is in agreement with the results reported in the literature.[15]

Regarding the effect of alkyl chain branching on formation of the third phase, Figure 2 shows that the third phase is formed earlier for less branched molecules: TOA < TIOA < TEHA. Compared to the reference extractant TOA, the molecules TIOA and TEHA have the same number of carbons in their alkyl chains, but TIOA has a branched methyl group at the end of each alkyl chain and TEHA is branched with an ethyl group that is located closer to the nitrogen atom (Figure 2) . Better phase stability was observed for the intermediate branched molecule TIOA: no third phase appearance was observed with octanol above 2%. For the more branched molecule TEHA, no phase splitting was observed under any circumstance.

These results confirm the reported trends: extractants with longer or bulkier alkyl chain lengths enhance the phase stability during solvent extraction.

When the octanol content was increased, the phase stability was enhanced, and no phase splitting was observed above 4 vol.% octanol. To ensure that no third phase was formed in the following extraction and scattering experiments, and for the sake of homogeneity, 5 vol.% octanol was added to all samples.

Influence on extraction properties

In the following section, the influence of the amine alkyl chain length and branching on the extraction properties of the amines is investigated.

Extraction tests were performed with 0.2 mol/L extractant diluted in *n*-dodecane and 5 vol.% octanol. The extraction properties were interpreted in terms of the distribution coefficient of uranium (D_U) and the concentrations of co-extracted water ($[H_2O]_{org}$) and acid ($[H_2SO_4]_{org}$), as plotted in Figure 3. The distribution coefficient of uranium can be defined using the following equation:

$$D_U = \frac{[U]_{org,eq}}{[U]_{aq,eq}}$$

(a) (b) (c)

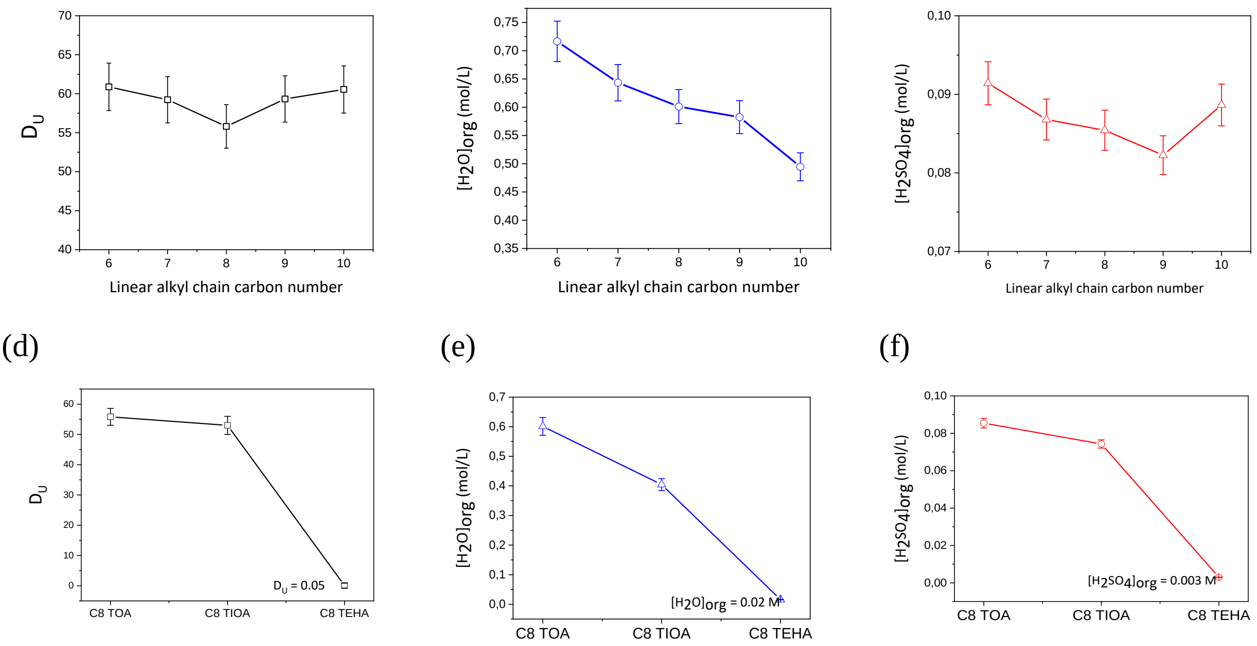


Figure 3. Distribution ratio of uranium, extracted water concentration, and extracted acid concentration for tertiary amines with linear alkyl chains (a, b, and c) and with branched alkyl chains (d, e, and f). Concentration of tertiary amines was 0.2 mol/L. Aqueous solutions contained 2500 ppm $UO_2(NO_3)_2$ *(10.5 mmol/L), 1 mol/L* $(NH_4)_2SO_4$*, and 0.1 mol/L* H_2SO_4 *(pH = 1). The volume ratio between the aqueous phase and organic phase A/O was fixed to 1.*

As shown in Figure 3(a), the five amines presented high extraction efficiency for uranium (more than 98% of uranium was extracted). Although the plot of D_U reached minimal value for C8 TOA, this inflexion was not considered significant, as the difference in the D_U values was in the range of the experimental error.

Figure 3(b) shows that the co-extracted water decreased as the length of the linear alkyl chain increased. Importantly, the ratio of co-extracted water decreased from 3.5 to 2, and thus, the volume of the polar core decreased with the volume of the chains. The extracted concentration of acid also decreased linearly in moving from C6 THA to C9 TNA, but increased slightly with C10 TDA (Figure 3(c)).

Regarding the effect of alkyl chain branching on extraction, the values of D_U, $[H_2O]_{org}$, and $[H_2SO_4]_{org}$ are presented in Figure 3(d–f) for TOA, TIOA, and TEHA.

Figure 3(d) shows that TIOA has a slightly lower D_U value than TOA. In comparison, the D_U value of TEHA declined to almost to 0, which indicates that TEHA extracted almost no uranyl from the aqueous phase. A clear decrease in $[H_2O]_{org}$ and $[H_2SO_4]_{org}$ is observed in Figure 3(e) and (f) in moving from TOA to TIOA, and finally to TEHA. The most “branched” extractant among these three amines (TEHA) extracted almost no water or acid.

These extraction properties show that even though the alkyl chain length has an insignificant influence on uranium extraction, tuning the chain configuration (either length or branching) strongly affects the extraction of hydrophilic species such as water and acid. Uranium extraction is also strongly reduced when branching is introduced closer to the nitrogen atom.

The tested amines share the same complexing site, which suggests that the differences in the extraction properties of the amines are due to different supramolecular organisations in the organic diluent. The efficiency of uranyl extraction depends not only on the ability of the amines to complex uranyl, but also on their aggregation properties in the organic diluent. Thus, a supramolecular approach was exploited in the following section to evaluate the structure of the aggregates formed by these tertiary amines.

Influence of structure on aggregation properties

Aggregation properties have been exploited to explain phenomena such as phase instability and selective extraction in different extractant systems. The nature of the diluent and the apolar chains of the extractant have been shown to be an important parameters influencing the phase stability of the extractant system.[53]

Penetration of the diluent into the shell of the aggregates is considered to be an important factor for aggregate stabilization [35] as the diluent induces strong variation in the bending energy of the reverse micelle-like aggregates, consequently limiting their swelling or perturbing metal complexation.[37] Studies have connected the efficient coordination of lanthanide cations with supramolecular ordering in the organic phase.[54,55]. By changing the diluent, the supramolecular ordering in the organic phase can be modified, which, in some cases, alters the extraction efficiency.[36,56] These studies reinforce the interest in determining the aggregation properties of amines bearing various alkyl chains. For this purpose, the organic phases were characterised by small-angle scattering experiments, and the critical aggregation concentration (CAC) was determined by surface tension measurements.

Scattering methods (SAXS and SANS)

SAXS experiments were performed on organic solutions containing 0.2 mol/L of tertiary amines diluted in *n*-dodecane, in contact with aqueous solutions containing 2500 ppm $UO_2(NO_3)_2$ (10.5 mmol/L), 1 mol/L $(NH_4)_2SO_4$, and 0.1 mol/L H_2SO_4 (pH = 1). SANS experiments were performed under the same conditions, but with deuterated octanol, dodecane, acid, and water to reduce incoherent signals from protons.

The absolute-scaled SAXS and SANS spectra obtained with different tertiary amines are shown in Figure 4.

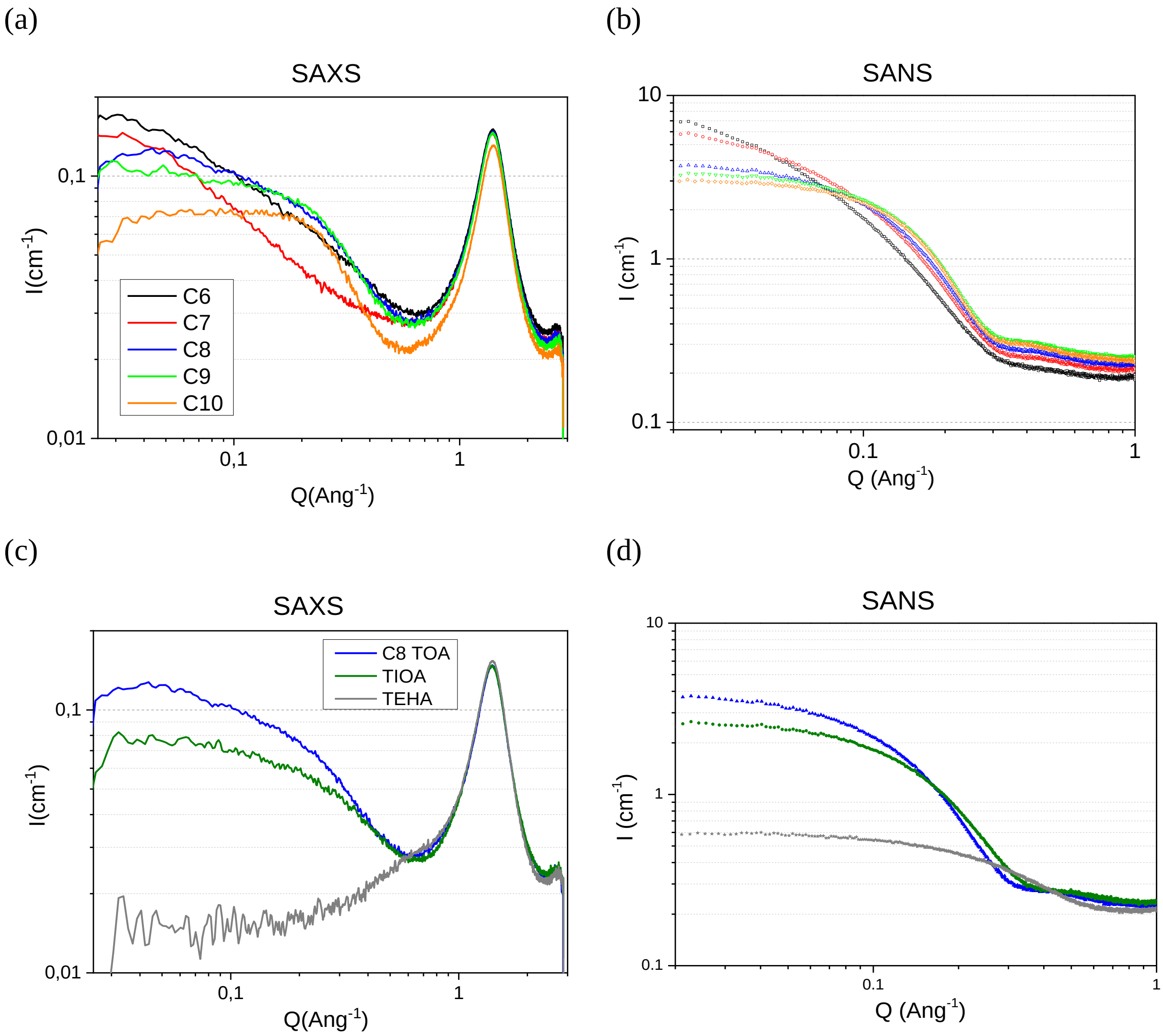


Figure 4. SAXS and SANS spectra of tertiary amines with linear alkyl chains (a) and (b), and with branched alkyl chains (c) and (d).

The strong increase in the SAXS/SANS intensity at low Q indicates the presence of aggregates in all organic phases. The slight oscillation observed on the SANS data at 0.6Å^{-1} can be interpreted as an oscillation of the form factor of the aggregates or might be due to interactions between octanol or alkyl amines molecules.[57] The absence of a medium-range common peak in the SANS and SAXS profiles excludes the presence of bicontinuous mesostructures.[28] A slight shoulder can be observed at $Q = 0.6$ Å^{-1} in Figure 4c, similar to a previous study, and is assigned to inter-or intra-correlations of the diluent alkyl chains.[58] The spectra of the amines with linear chains show interesting evolution in terms of the shapes and intensity in the low-Q region. In the SAXS and SANS spectra in Figure 4(a) and (b), respectively, the scattering intensity increased at low-Q for the three amines (C6, C7, and C8). For the other two amines (C9 and C10), a plateau was observed in the low-Q region. As the alkyl chain length of the extractants increased, the scattering intensity decreased, and the plateau became lower in the higher-Q region (0.02 to 0.3 Å^{-1}). This indicates either that the aggregates have **different size distributions** or **that they present a significant variation in the inter-aggregate attraction**, or both.

The absolute-scaled SAXS and SANS spectra of the three tertiary amines with branched chains are shown in Figure 4(c) and (d). The spectra show a clear increase in the scattering intensity at small angles for TOA and TIOA. For TEHA, this strong increase is absent, and the flat scattering at low Q confirms the absence of aggregation. These behaviours indicate that TOA and TIOA form aggregates in dodecane, whereas TEHA shows no sign of aggregation.

Evolution of SAXS intensity and hydrophilic species in organic phases

If the interactions between two aggregates can be neglected when Q tends to zero, the classical equation of scattering can be expressed as follows:

$$I_{SAXS}(Q \to 0) = \frac{N_A(C - CAC)}{N_{agg}} \left(V_{core}\Delta\rho_{core} + V_{agg}\Delta\rho_{agg}\right)^2$$

where N_A is Avogadro's number, C is the total concentration of ligands, CAC is the critical aggregation concentration, N_{agg} is the aggregation number, which is equal to the average number of ligands in each aggregate, V_{core} and V_{agg} are the core and aggregate volumes; $\Delta\rho_{core} = \rho_{core} - \rho_{shell}$ and $\Delta\rho_{agg} = \rho_{shell} - \rho_{agg}$ are the scattering length density contrasts. SAXS is sensitive to electron density contrast; thus, the SAXS signal is mainly due to scattering from the core of the aggregates, which is richer in electrons. As shown in the above equation, the SAXS intensity is proportional to the square of the aggregate volume. Thus, the evolution of the SAXS signal is a good indicator of the evolution of the size of the polar cores of the aggregates, and consequently, of the volumes of the hydrophilic species that are extracted by the tertiary amines.

Considering that all extracted hydrophilic species, including metallic ions, water, and acid molecules, are confined in the polar core of the aggregates, the total volume can be compared to the trend of the SAXS intensity at low Q. The total volume of extracted hydrophilic species was calculated according to the following equation and compared with the SAXS intensity when Q tends to zero (Figure 5).

$$V_{species\ in\ org} = [species]_{org} \times N_A \times V_{mol,species}$$

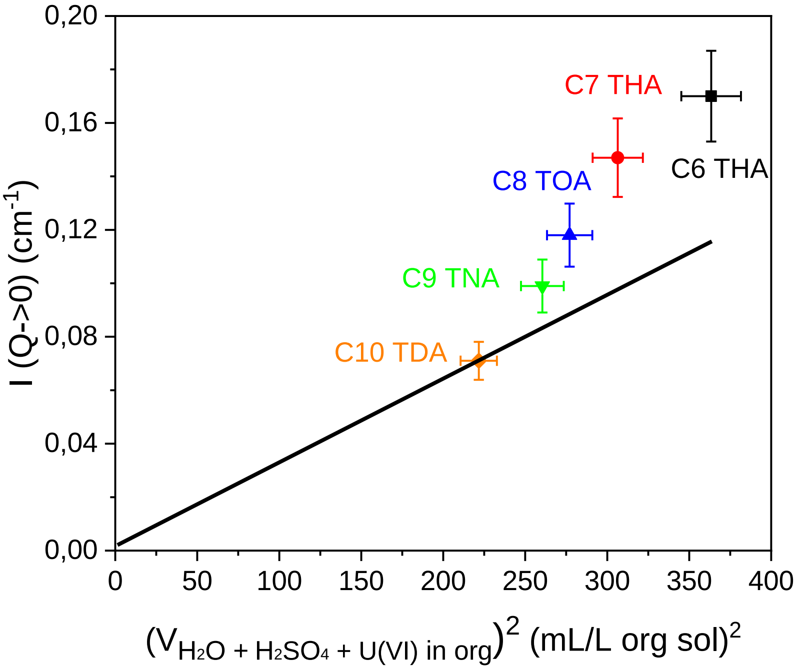


Figure 5. SAXS intensity when Q tends to nil versus square of total volume of hydrophilic species extracted in organic solution containing tertiary amines with linear alkyl chains. The solid black line indicates the linear trend expected for the scattered intensity at low Q if Q is proportional to V_{core}^2.

The total volume of the hydrophilic species extracted in the organic solution ($V_{H_2O+H_2SO_4+U(VI)}$) decreased as the alkyl chains became longer or more branched (Figure 5). This suggests that tertiary amines form aggregates with smaller polar cores. Figure 5 also shows that for the two amines with long alkyl chains (C9 TNA and C10 TDA), the SAXS intensity ($I_{SAXS}(Q \rightarrow 0)$) is proportional to V_{core}^2, while for the other three amines, the SAXS intensity deviates from linearity when Q tends to 0. This observation suggests that the size difference of the polar core of the aggregates is not sufficient to explain the scattering trend for the different amines. This discrepancy with the evolution of the SAXS intensity at low Q can be assigned to the evolution of the interactions between the aggregates, indicating that the structure factor for a sticky hard sphere, which is generally employed for systems forming third phases, should be selected to fit the data. Although this preliminary analysis shows that the alkyl chain configuration of tertiary amines strongly impacts their extraction properties as well as their aggregation and phase stability, a complete fit of the scattering data is necessary to obtain quantitative results such as the size evolution of the aggregates and the attractive interactions between aggregates. These experiments will be undertaken in the second part of this study.

Experimental determination of critical aggregation concentration (CAC)

Because the "aggregated" and monomeric forms of any surface-active molecule in a solvent are pseudo-phases in dynamic equilibrium, quantifying the monomers in any sample provides a direct measure of the free energy cost of formation of aggregates. The CAC versus temperature relationship can be used to classify micellization as an enthalpy-or entropy-dominated phenomenon.[59][60] The critical aggregation concentration of the extractants was determined experimentally from the interfacial tension and SANS for all the amines compared in this study (Figure 6).

The principle of CAC determination by SANS is similar to the tensiometry method, which uses the inflexion point of the surface tension, when aggregates start to form. In the case of scattering, a break in the slope is also expected when the scattered intensity at low *Q* is plotted as a function of the extractant concentration. All extractant molecules induced weak and "flat" scattering at low concentrations. Above the CAC, that is, when w/o aggregates are formed, the contribution of each molecule to the scattering corresponds to the square of the volume of the aggregates.[61]

SANS experiments were performed on organic solutions with amine concentrations ranging from 0.01 mol/L to 0.2 mol/L. The evolution of the SANS intensity is plotted in the Supporting Information, together with the surface tension data.

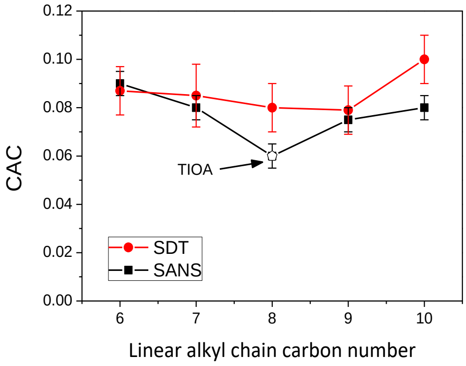


Figure 6. CAC values for tertiary amines tested in this work.

For the amines with different chain lengths, evaluation of the CACs obtained by the two methods shows that tertiary amines start forming aggregates from 0.06 mol/L to 0.09 mol/L. The two techniques produce relatively large errors, but consistently yield CACs of *ca.* 0.07±0.02 mol/L for all chain lengths. Using SANS, a slight inflexion was observed for the

C8 alkyl chains. However, considering the large uncertainties and the low CAC variations, the CAC is thought to remain quasi-constant as a function of the alkyl chain length.

The CAC values obtained for the branched amines show that TIOA has the same CAC of 0.06 mol/L as TOA, while for TEHA, no break in the slope of the scattering intensity (that can be interpreted as a CAC) was observed. This confirms that the hyperbranched alkyl chain, as proposed by the theories developed by Eastoe et al., can completely quench the micellization and, therefore, deteriorate the extraction efficiency.[62] Notably, this behaviour appears more pronounced when the branched groups are bulkier and closer to the chelation site.

For amines with linear alkyl chains, amines with longer chains tend to form aggregates with smaller polar cores, which are thus unlikely to confine or extract more hydrophilic species inside the aggregates. Concomitantly, the attractive interactions between the aggregates appear to be reduced, and formation of the third phase has a higher free energy cost. However, under the present experimental conditions, the effect of the alkyl chain length did not significantly influence micellization of the tertiary amines.

For amines with branched alkyl chains, the volume and position of the branched groups on the alkyl chains have a remarkable influence on the formation of aggregates. Tertiary amines with small branched groups at the end of their side chains (TIOA) form aggregates with a smaller polar core and extract less water and acid, but it have the same CAC as the linear analogue TOA. As the branched group becomes larger and closer to the polar head, the amine loses the ability to form aggregates and extract water molecules or to solubilise acid in the polar cores of the aggregates. Thus, the tertiary amine (TEHA) was barely protonated. Consequently, no uranyl was extracted with this tertiary amine.

Conclusion

The effects of the configuration of the alkyl chains (alkyl chain length and branching) of tertiary amines on the phase stability, extraction, and aggregation properties of the amines were evaluated using two series of amines.

- Phase stability:

Less 1-octanol is required to prevent formation of the third phase for tertiary amines with longer and branched alkyl chains. In addition, amines with longer and more branched alkyl chains exhibit better phase stability.

- Extraction properties:

For tertiary amines, the uranium extraction efficiency is similar irrespective of the linear alkyl chain length, whereas amines with shorter chains extract more water and acid.

When comparing amines with different branched groups on their alkyl chains, TIOA, which has a methyl group at the end of its alkyl chains, extracts uranium almost as efficiently as TOA. TEHA, having a branched ethyl group closer to the polar head, extracts nearly no uranium. In addition, amines with more branched chains were found to extract less water or acid. The effect of chain branching on the extraction properties is more significant than the effect of the chain length.

- Aggregation properties:

Scattering experiments showed that amines with different chain lengths formed aggregates in dodecane. The scattering spectra show that the size of the polar core of the aggregates decreases for amines with longer alkyl chain lengths, accompanied by less third phase formation.

Tertiary amines branched with a methyl group at the end of their alkyl chains formed aggregates, similar to TOA, whilst no aggregation was observed for TEHA, having a branched group that is larger and closer to the polar head. Compared to linear alkyl chains, amines with branched chains are assumed to have smaller polar cores, with weaker attractive interactions between the aggregates. A complete fit of the SANS data will be performed in the second part of this study to verify this hypothesis.

In conclusion, tertiary amines with longer chains and branched groups on their alkyl chains are more resistant to forming a third phase, while maintaining efficient uranium extraction. The configuration of the alkyl chains has a significant influence on the aggregation of tertiary amines, and can affect their extraction properties to a great extent. To evaluate this influence quantitatively, thermodynamics analysis will be conducted in the second part of this study to evaluate the influence of the alkyl chain configuration on the driving forces governing uranium transfer.

Acknowledgements

This research was financially supported by the NEEDS program and CEA. We thank Beatrice Baus-Lagarde for help with the ICP experiments. We deeply thank ILL for the beam time allocation on D16 (https://doi.ill.fr/10.5291/ILL-DATA.9-10-1637).

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