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Understanding the complexation of the Eu^{3+} ion with TODGA, CMPO, TOPO and DMDBTDMA: Extraction, luminescence and theoretical investigation

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ABSTRACT

A comparative study was carried out to understand the complexation behavior of the Eu^{3+} ion with important reagents, namely TODGA (N,N,N′,N′ tetraoctyl diglycolamide), CMPO (octyl (phenyl)-N, N-diisobutyl carbamoyl methyl phosphine oxide), DMDBTDMA (dimethyl dibutyl tetradecyl malonamide) and TOPO (tri-n-octyl phosphine oxide) in dodecane, used for the separation of actinides and lanthanides from lab and nuclear high-level wastes, by experimental (extraction and luminescent) and theoretical means. A solvent extraction study revealed the metal–ligand stoichiometry as 1:3 for all the systems with the extraction efficiency TOPO > CMPO > TODGA > DMDBTDMA at 1 M HNO_3, while TODGA > CMPO > DMDBTDMA > TOPO at 3 M HNO_3. A luminescence investigation revealed the presence of single species in the extracted complex for all the systems, with no inner sphere water molecules for all the systems except for DMDBTDMA which had one inner sphere water molecule. The high intensity of the $^5D_0$–$^7F_2$ transition revealed the presence of Eu^{3+} ions in an asymmetric environment with the local point group symmetry C_{3v} for the TODGA and DMDBTDMA complexes, compared to C_{3h} symmetry for the CMPO and TOPO complexes. Judd–Offelt parameters, radiative, non-radiative lifetimes, branching ratio, transition probabilities and quantum efficiencies for all the complexes were estimated and compared. Three O-donor atoms from each TODGA molecule coordinated to the Eu^{3+} ion in the first coordination sphere, while three CMPO units were found to be coordinated in a monodentate fashion. For the Eu-TOPO complex, three O donor atoms from each of the three TOPO molecules and six O donor atoms from three nitrate ions were coordinated. Out of three DMDBTDMA ligands, one was found to be coordinated in a bidentate mode, whereas two were in a monodentate mode, along with three nitrate ligands bonding in a monodentate fashion.

1. Introduction

Nuclear energy is one of the viable options to fulfill the ever increasing world-wide energy demand in the future [1,2]. The success of nuclear technology strongly depends on the safe management of highly radioactive waste [3–5]. Partitioning and transmutation is one of the proposed strategies to address the issue of safe management of radioactive waste obtained after the PUREX (Plutonium Uranium Reduction Extraction) process of spent nuclear fuel [6,7]. The actinide partitioning envisages to separate high neutron absorbing lanthanides from actinides by first co-extraction of lanthanides and minor actinides [8–10] together, followed by their mutual separation [11–13]. Several classes of compounds, such as phosphine oxides, carbamoyl methyl phosphine oxides, malonamides and diglycolamides, have been investigated for the extraction of minor actinides from radioactive waste solutions [14,15], which eventually co-extract lanthanides too. All the above classes of extractants contain hard O-donors and it is not expected to achieve high separation factors from these for actinides from lanthanides. Of these, octyl (phenyl)-N, N-diisobutyl carbamoyl methyl phosphine oxide (CMPO) was proposed to be used in the TRUEX process (TRans Uranium EXtraction) [16,17], while N,N′-dimethyl-N,N′-dibutyl tetradecyl malonamide (DMDBTDMA) was one of the most tested reagents for the proposed DIAMEX process (DiAmide EXtraction) [18–22]. Out of several phosphine oxides investigated, tri-n-octyl phosphine oxide (TOPO) was one of the first few phosphine oxides which showed

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favorable extraction of trivalent f-elements [23–25] at low acidities, whereas N,N,N′,N′ tetraoctyl diglycolamide (TODGA) was considered as the most promising extractant in the class of diglycolamides [26–31]. All the above main extracting agents, with phase modifiers such as TBP (tri-n-butyl phosphate), DHOA (di-n-hexyl octanamide) etc., display different extraction efficiencies for trivalent actinide/lanthanide ions, attributed to different basicities, reverse micellar properties etc. All of the agents have common O-donors present in various numbers and functional groups with mono, bi and tri denticities. For example, TOPO, which has one functional P═O group, is expected to be monodentate while CMPO, having two functional groups, namely C═O and P═O, was shown to be both mono and bidentate, depending on the conditions, and was insensitive to the aqueous phase acidity when extracting Am^{3+} or Eu^{3+}. The other two extractants came to the fore, based on the C, H, O, N principle, essentially as alternatives to the phosphorus based systems. DMDBTDMA has two amidic (—C═O—NR_2) groups and is expected to lead to higher extraction of Am^{3+}/Eu^{3+} with obvious bidenticity, while TODGA, possessing two amidic groups and one ethereal oxygen atom, i.e. three O-donors, is expected to be tridentate, which would extract a trivalent f-element to a relatively much larger extent. Thus, with a common O-donor present in different numbers and environments in these extractants, it is really puzzling and interesting to know the common features responsible for their different extraction capabilities. Of course, it is to be mentioned here that for avoiding a third phase, CMPO and TODGA need certain polar molecules such as TBP and DHOA as phase modifiers, respectively, which eventually were shown to have no role to play and are not responsible for the high extraction of trivalent actinide vis-à-vis lanthanide ions. Reports on the comparison of organophosphorus (TOPO, CMPO etc.) and amidic extractants (TODGA and DMDBTDMA), to our knowledge, are rather scarce and not available in the literature. So, there is a need for a comparative study on the complexation of these reagents with trivalent lanthanides or actinides, both by experimental and computational means. The present paper describes the investigations carried out to understand the complexation of Eu^{3+} (taken as a representative actinide/lanthanide ion) with the above ligand molecules by extraction, photoluminescence and computational methods.

2. Experimental

2.1. Materials

TBP and DHOA were procured from Koch-Light Laboratories, USA. TODGA was synthesized by a previously reported method and its purity was determined by ^{1}H NMR spectroscopy, elemental analysis and distribution coefficient measurements of Am^{3+} and UO_2^{2+} [32,33] (Supplementary Table S1). CMPO and DMDBTDMA were also synthesized by the reported methods and their purities were checked by their distribution behaviour towards Am^{3+} [34–37]. All the other chemicals used for the present investigation were of analytical reagent grade. The radioactive tracer ^{152,154}Eu was procured from the Board of Radiation and Isotope Technology (BRIT), India. The structures of CMPO, TODGA, DMDBTDMA and TOPO are shown in Fig. 1.

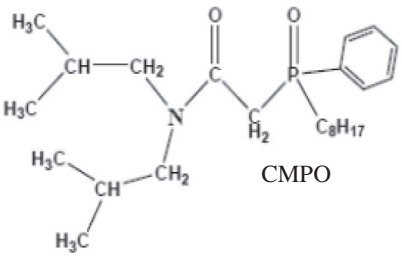
2.1.1. Solvent extraction experiments

The general procedure for the extraction of Eu^{3+} with an organic phase, like 0.1 M TODGA + 0.5 M DHOA, 0.2 M CMPO + 1.2 M TBP, 1.1 M TOPO and 1 M DMDBTDMA in dodecane, is given as follows. For the batch studies, aqueous solutions of nitric acid traced with the radioactive tracer (^{152,154}Eu) was equilibrated with an equal volume of the organic phase in a thermostated water bath at 25 ± 0.1 °C for 30 min. This time was found to be sufficient for attainment of an equilibrium. The phases were centrifuged and aliquoted for radioassay. The D_{Eu} values were calculated as the ratio of the activity of the organic phase to that of the aqueous phase. The material balance was >95% and the error was within 5%.

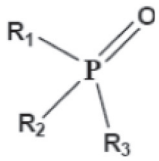
For luminescence investigations, the extracted organic phase employing the above extractants was used, taking an inactive 2 mM $Eu(NO_3)_3$ (99.9% Eu_2O_3-Merck, Darmstadt, Germany) solution in nitric acid medium as the aqueous phase.

2.2. Instrumentation

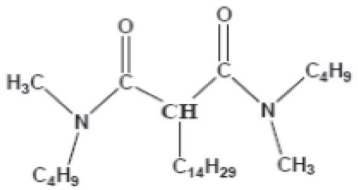
Emission profiles were recorded on an Edinburgh F-900 Fluorescence spectrometer in the 200–750 nm region with a Xe lamp as the excitation source, M-300 monochromators and a Peltier cooled photo multiplier tube as the detector. The acquisition and



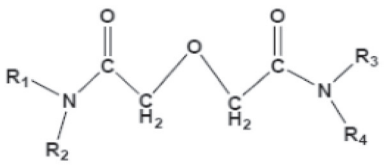
CMPO



TOPO (R_1, R_2, and R_3 = *n*-octyl)



DMDBTDMA



TODGA (R_1, R_2, R_3 and R_4 = *n*-octyl)

Fig. 1. The structures of the ligands CMPO, TOPO, DMDBTDMA and TODGA.