

Dynamic light scattering study on the aggregation behaviour of *N,N,N',N'*-tetraoctyl diglycolamide (TODGA) and its correlation with the extraction behaviour of metal ions

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ABSTRACT

Dynamic light scattering (DLS) studies were carried out to investigate the aggregation behaviour of *N,N,N',N'*-tetraoctyl diglycolamide (TODGA) in *n*-dodecane and 1-octanol. The effect of the nature and concentration of different acids such as HCl, HNO₃ and HClO₄ on aggregation behaviour was investigated. The aggregation tendency of TODGA in different acids followed the order: HClO₄ > HNO₃ > HCl, which is similar to the extraction pattern of trivalent actinides/lanthanides in these acids. A direct correlation was observed between the extraction behaviour of Am(III) and the aggregation behaviour of TODGA in the presence of these acids. The aggregation of TODGA increased with increasing concentration of HNO₃, HCl and HClO₄. However, the aggregation tendency of TODGA was independent of its concentration at fixed acidity. The presence of Eu(III) ions facilitated the aggregation of TODGA. The aggregation studies revealed that about 2 nm aggregate size of ligand was the critical size required for efficient extraction of trivalent actinide and lanthanide ions.

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1. Introduction

The presence of long-lived alpha emitting minor actinides (e.g. ²⁴¹Am, ²⁴³Am, ²⁴⁵Cm, ²³⁷Np) along with the residual plutonium in the high level waste (HLW) is of great environmental concern. In this context, the strategy of P&T (partitioning of long-lived radionuclides followed by transmutation) is under extensive evaluation by several countries across the world [1]. For the partitioning of actinides, pentaalkyl substituted malonamides, viz. *N,N,N',N'*-dimethyldibutyl tetradecyl malonamide (DMDBDMA) and *N,N'*-dimethyl-*N,N'*-dioctylhexaethoxy malonamide (DMDO-HEMA) have received considerable attention amongst European countries under EUROPAT programme [1,2]. This class of extractants displays excellent radiolytic stability and back extraction of the metal ions (actinides/lanthanides). In addition, the amide ligands are completely incinerable, which implies that the amount of secondary waste generated in nuclear waste treatment could be reduced significantly [3]. However, forward extraction of actinide(III)/lanthanide(III) from nitric acid (3–4 M) is quite moderate and it is recommended to use upto 1 M ligand concentration. In this context, recently developed tridentate diglycolamide class of extractants (containing ether linkage between two amide groups) have been found very interesting in view of their unique ability

to extract trivalent cations at much lower concentration of ligand (~0.1 M) [4,5].

Amongst the long chain derivatives of diglycolamides, *N,N,N',N'*-tetraoctyl diglycolamide (TODGA) was found to be the most promising extractant for actinide partitioning and has been extensively studied in our laboratory as well as elsewhere [4–11]. However, the studies of metal–TODGA complexes in the organic solvents show unusual interesting features that are difficult to reconcile within the framework of the traditional coordination chemistry interpretations. Measurements based on simple extraction thermodynamics suggest the participation of four TODGA molecules in the extraction of actinide(III) ions from nitric acid medium [4,5]. Considering the tridentate nature of TODGA and the coordination number of actinide(III) (which is barely 9), the number of TODGA molecules appears to be more than that can be reasonably accommodated in the inner co-ordination sphere of these cations. Subsequent studies have suggested that the extraction of trivalent actinides takes place by TODGA aggregates (tetramers) where only two TODGA molecules are coordinated directly to the metal ions and remaining molecules are present in the outer sphere of the complex [12–14]. Small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS) studies have confirmed the formation of tetrameric reverse-micelles (aggregates) of TODGA when equilibrated with acid solutions [13,14]. The study suggests a transition from a mixture of TODGA monomers and dimers at low acidities (<0.5 M HNO₃) to tetramers at high acidities (>0.7 M HNO₃).

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Solvent extraction studies of Am(III) using TODGA from HCl, HNO₃ and HClO₄ medium provided some interesting observations [6]. The distribution ratio of Am (D_{Am}) increased in the order: HCl < HNO₃ < HClO₄. This extraction behaviour is difficult to be explained by simple solvent extraction principles, where acid anions are extracted as counter ions during extraction of metal ions by neutral ligands. Perchlorate ions being weaker complexing, one may expect minimum extraction of Am(III) in HClO₄ medium. However, if the extraction of metal ions takes place by TODGA aggregates/reverse micelles (as suggested by SANS studies [14]), then it will be interesting to investigate the aggregation behaviour of TODGA in various acid solutions. Aggregation behaviour of TODGA will help in understanding its unusual extraction behaviour of Am(III) in HClO₄ medium. In this context, dynamic light scattering (DLS) technique was employed for the first time to study the aggregation behaviour of TODGA in different acid solutions. The data obtained in the present work has been used to explain the interaction of reverse micelles (aggregates) of TODGA with metal ions. These observations have been corroborated with the SANS study on the aggregation behaviour of TODGA.

2. Experimental

2.1. Materials and methods

N,N,N',N'-tetraoctyl diglycolamide (TODGA, Fig. 1) was synthesised in our laboratory as per the reported method [6]. Diluent *n*-dodecane was procured from Lancaster and was used without any further purification. Deionized water from a milli-Q water purification system (millipore) of resistivity 18.2 M cm was used for all dilutions. Suprapure HNO₃, HCl and HClO₄ (Merck, Germany) were used for all studies. Stock solution of Eu(III) was prepared by dissolving high purity Eu₂O₃ (spectroscopy grade) in concentrated nitric acid solutions and diluted to desired acidity. The samples for DLS measurements were prepared by equilibrating the organic phase (TODGA/*n*-dodecane) with the aqueous phase of required acidity for 60 min. This time was found sufficient to reach the equilibrium condition for the formation of reverse micelle. The aggregate size measurements in the organic phase were performed using Zetasizer-3000 DLS spectrometer (Malvern Instrument Company, UK) with a 10 mW He–Ne laser beam at a wavelength of 488 nm. All the measurements were performed at a scattering angle of 90° in a cell of 4 mm path length at room temperature (25 ± 1 °C). The instrument was calibrated using standard colloidal suspension (polystyrene, latex) before the size measurement of the actual samples. Each measurement was repeated at least five times to check the reproducibility of data. The error bars shown on the measured data are the standard deviation of these measurements.

2.2. Theory of DLS measurements

The colloidal particles (reverse micelle in the present case) suspended in a liquid are under constant Brownian motion due to random collisions with the molecules of the liquid that surrounds the particles. When a monochromatic and coherent beam of light falls

on such a suspension, the scattered light photons carry information about the size of the particles. DLS technique measures the fluctuation, in the intensity of the scattered photons, which occur over short time intervals due to scattering of the particles undergoing Brownian motion in the solution. The behaviour of these fluctuations is described quantitatively by the intensity of the autocorrelation function, $C(\tau)$ of scattered intensity as follows:

$$C(\tau) = A \left(1 + \beta \int_0^\infty P(\Gamma) \exp(-\Gamma\tau) d\Gamma \right) \quad (1)$$

where A is the baseline value, β is an instrumental constant and Γ is the characteristic line width of the distribution function $P(\Gamma)$ and is related to the diffusion coefficient (D) of the species by the following expression:

$$\Gamma = Dq^2 \quad (2)$$

where q is the scattering vector which is constant for a given observation angle and wavelength of the incident light. Assuming the scattering species as hard sphere, the apparent hydrodynamic radius (r_h) of the species can be calculated by Stokes–Einstein equation:

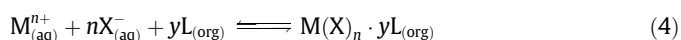
$$r_h = k_B T / (6\pi\eta D) \quad (3)$$

where k_B is Boltzmann constant, T is the absolute temperature and η is the viscosity of the dispersion medium. It is worth mentioning here that the DLS data obtained in the present work provides a gross size of the TODGA species (monomer, dimer and tetramer) in the organic phase.

3. Results and discussion

3.1. Effect of diluent on interaction of TODGA aggregates

In general, the two phase equilibrium representing the extraction of metal ions from acidic medium with neutral ligands like TODGA (L) can be represented as,



where the subscripts (aq) and (org) represent the aqueous and the organic phases, respectively. Solvent extraction studies with TODGA suggested that Am(III) ions are predominantly extracted as tetra-solvated species in non-polar diluents like *n*-dodecane, i.e. Am(NO₃)₃·4TODGA (Table 1). The coordination number of Am(III) has been found to be barely 9 [15] and TODGA has been found to be tridentate ligand [12,16]. Therefore, coordination of four tridentate molecules of TODGA with Am(III)-nitrate appears more than that can be reasonably accommodated in the inner co-ordination sphere of trivalent actinide ions. Small-angle neutron scattering (SANS) studies on 0.1 M TODGA/*n*-dodecane solution equilibrated with >0.7 M HNO₃ have shown the presence of monomers, dimers, trimers and small reverse micelles of TODGA tetramers [14]. However, no such species were observed in free TODGA/*n*-dodecane solution as the interparticle attractions are negligible. After the extraction of sufficient acid and water molecules, the interparticle attraction becomes strong enough to facilitate the formation of dif-

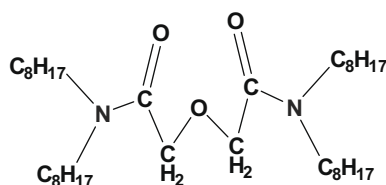


Fig. 1. Structural formulae of TODGA.

Table 1

Distribution ratio data and stoichiometry of the extracted species of Am(III) obtained in dodecane and in octanol; extractant: 0.1 M TODGA; [HNO₃] = 1 M; temperature: 25 °C.

Diluents	Dielectric constant	D_{Am}	Stoichiometry ^a
<i>n</i> -Dodecane	2.01	28 ± 1	3.8 ± 0.1
1-Octanol	10.3	68 ± 2	2.3 ± 0.1

^a Number of ligand molecules coordinated with Am(III).

ferent aggregates of TODGA. The micellar TODGA tetramers rapidly become dominant species in the organic phase when the equilibrium aqueous acidity exceeds 1 M HNO_3 . The existence of tetramers in TODGA/alkane solution determines the nature of the extracted complex. In other words, unusual extracted species of TODGA–Am–nitrate complex can be explained only if we consider the interaction of TODGA aggregates with the metal ions. The aggregation behaviour of TODGA in non-polar diluent (*n*-dodecane) has been confirmed in the present DLS measurements as shown in Table 2. A typical aggregate size of TODGA in *n*-dodecane pre-equilibrated with acid solutions is shown in Fig. 2. It appears that out of TODGA aggregates only two TODGA molecules are directly interacting with the metal ions along with nitrate ions. The remaining TODGA molecules in the aggregates are not coordinating directly to the metal ions, but are showing intermolecular interaction with the aggregates. EXAFS studies have also confirmed that only two TODGA molecules are present in the inner-sphere of the lanthanide ions and other TODGA molecules are present in the outer-sphere [16]. On the basis of present work and available literature data, it can be said that in non-polar diluents like *n*-dodecane, which facilitates amphiphilic aggregation and micellization, the extraction of metal ions takes place by TODGA aggregates.

Solvent extraction data of Am(III) by TODGA in polar diluents like 1-octanol shows the extraction of bi-solvated species, i.e. $\text{Am}(\text{NO}_3)_3 \cdot 2\text{TODGA}$ (Table 1). DLS data summarised in Table 2 also confirmed the absence of any TODGA aggregate in 1-octanol medium. It suggests that the TODGA molecules are present only in inner-sphere of the metal–ligand complex. It appears that the polar solvents like 1-octanol does not allow the formation of TODGA aggregates due to dipole–dipole interaction of diluent and ligand molecules and hence 1:2 metal–ligand complex is formed. This behaviour was subsequently confirmed by recording IR spectrum where $\sim 30 \text{ cm}^{-1}$ down shift in the $\text{C}=\text{O}$ stretching frequency of TODGA was observed in 1-octanol solution. Such shift was not observed when *n*-dodecane was used as the diluent.

3.2. Effect of acidity on aggregation of TODGA

The distribution studies of Am(III) from HCl, HNO_3 and HClO_4 medium shown that for a given concentration of TODGA, the distribution values of Am(III) vary in the order: $\text{HCl} < \text{HNO}_3 < \text{HClO}_4$ (Fig. 3). In case of HNO_3 , the D_{Am} values increased sharply with nitric acid concentration upto 3 M, beyond which a plateau was observed. On the other hand, D_{Am} value observed in HCl medium did not show any significant change upto 2 M HCl, but increased sharply beyond 4 M HCl. Lower distribution value in HCl medium was ascribed to the weaker aqueous complexation of Am(III) with Cl^- ion as compared to that with NO_3^- ion (equilibrium reaction (4)). However, relatively large distribution ratio of Am(III) in HClO_4 medium is difficult to be explained on the basis of complexation of perchlorate ion with Am(III) as former is a weak complexing ion. If we believe that the extraction of Am(III) takes place by TODGA aggregates (as described earlier), then it is worth to investigate the aggregation behaviour of TODGA in above three acid solutions

Table 2

Effect of diluent and acid on the aggregation behaviour of TODGA; ligand: 0.1 M TODGA; temperature: 25 °C.

Acid	Aggregate size (nm)	
	<i>n</i> -Dodecane	1-Octanol
6 M HCl	2.15 ± 0.51	2.13 ± 0.54
6 M HNO_3	8.70 ± 1.01	1.50 ± 0.32^a
6 M HClO_4	7.88 ± 1.33	1.24 ± 0.23

^a 4 M HNO_3 .

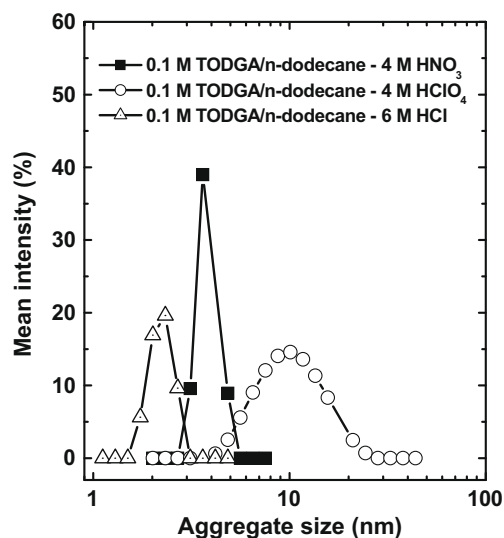


Fig. 2. Typical aggregate size of TODGA pre-equilibrated with different acid solutions; organic phase: 0.1 M TODGA in *n*-dodecane; temperature: 25 °C.

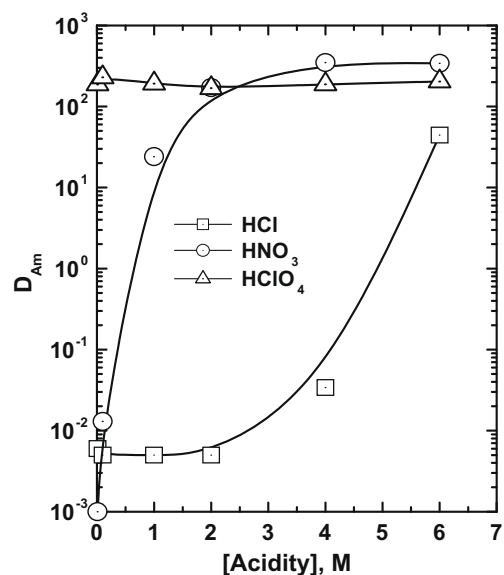


Fig. 3. Variation of D_{Am} with aqueous phase acidity; extractant: 0.1 M TODGA in *n*-dodecane; temperature: 25 °C.

(HNO_3 , HCl and HClO_4). Fig. 4 shows the variation in the size of TODGA aggregates in different acid solutions. For all the acid solutions, the size of the aggregates increased with the acidity of the equilibrating solution. However, in case of perchloric acid, a maxima was observed at 4 M HClO_4 , the reason for which could not be assigned. Increased in the size of the aggregates was attributed to the increased extraction of water and acid in the organic phase. The aggregation for different acids varied in the order: $\text{HCl} < \text{HNO}_3 < \text{HClO}_4$. It is interesting to note that in the case of perchloric acid, the aggregate size was $>2 \text{ nm}$ even at 0.1 M HClO_4 . On the other hand, in HCl medium, this size reached only after 4 M HCl. It is evident from Figs. 3 and 4 that efficient extraction of metal ions takes place only when the aggregate size of TODGA reaches $>2 \text{ nm}$. It has been shown that the presence of acid and water in the organic phase plays an important role in the aggregation of TODGA as their presence helps in the formation of reverse micelle [14]. The extraction of water in the organic phase follows the

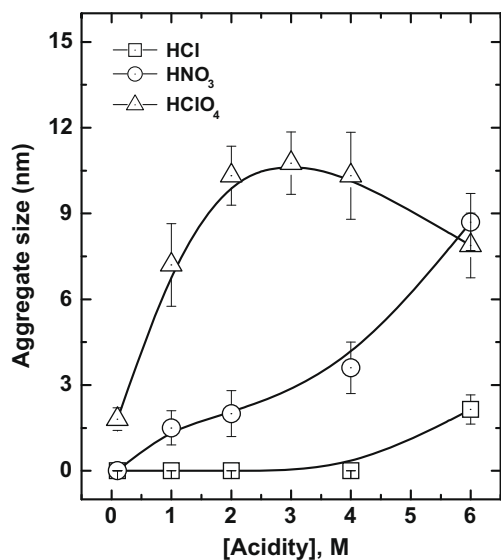


Fig. 4. Effect of different acid concentrations on the aggregation of TODGA; organic phase: 0.1 M TODGA in *n*-dodecane; temperature: 25 °C.

order: $\text{HClO}_4 > \text{HNO}_3 > \text{HCl}$, which is consistent with the aggregate size obtained by DLS measurements. Higher extraction of water in case of perchloric acid helps in the formation of aggregate even at lower acidity, thereby showing higher extraction of Am(III) by TODGA. In contrast, extraction of Am(III) increases only after 6 M HCl when sufficient amount of water and acid is extracted which leads to the formation of TODGA aggregates. It may be noted that though the aggregate size increased with increased acid concentration in the aqueous phase, the extraction of Am(III) did not increase further. This observation suggests that about 2 nm aggregate size is the critical size required for the efficient extraction of metal ions. It appears that beyond critical aggregate size, the size of the aggregate does not play any role in the extraction.

The effect of ligand concentration on the aggregation behaviour of TODGA was also investigated at 0.5 M, 1 M and 2 M HNO_3 and the results are shown in Fig. 5. It is evident that aggregation depends upon the concentration of the acid in the aqueous phase

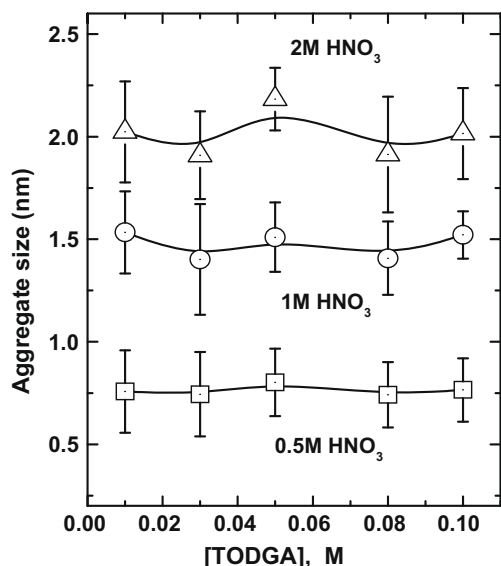


Fig. 5. Effect of ligand concentration on aggregation behaviour of TODGA; aqueous phase: HNO_3 ; diluent: *n*-dodecane; temperature: 25 °C.

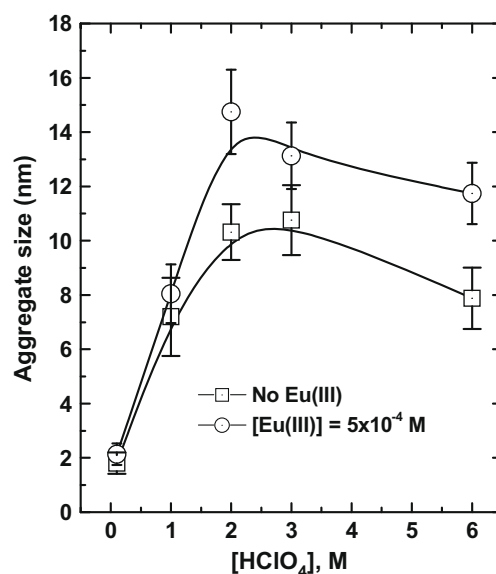


Fig. 6. Effect of Eu(III) ions on aggregation behaviour of TODGA; extractant: 0.1 M TODGA in *n*-dodecane; temperature: 25 °C.

and it is independent of ligand concentration. As described earlier, the aggregation of ligand is only possible when sufficient amount of acid and water is extracted in the organic phase. As the extraction of water as well as acid increases with the aqueous phase acidity, the aggregation of TODGA also increases.

The aggregation behaviour of TODGA was also investigated in the presence of Eu(III) ion. The organic phase was equilibrated with aqueous phase containing 5×10^{-4} M Eu(III) at different acidities (0.1–6 M HClO_4). Fig. 6 shows that presence of Eu(III) in the organic phase enhances the aggregate formation under the conditions of present study. This behaviour can be explained on the basis of increased charge density on the complex due to presence of metal ions in the organic phase which facilitates the dipole–dipole interaction. This observation is, however, in contrast to the previous reported work which shows that the aggregation of TODGA is independent of metal ions presence in the equilibrating solution [14].

4. Summary

The aggregation behaviour of TODGA was studied with dynamic light scattering (DLS) technique. The aggregation tendency of TODGA/*n*-dodecane equilibrated with different acids followed the order: $\text{HClO}_4 > \text{HNO}_3 > \text{HCl}$, which followed the extraction pattern of actinides/lanthanides in these acids. The aggregation of TODGA increased with acid concentration of equilibrating solutions. However, the aggregation tendency was independent of TODGA concentration at fixed acidity. The aggregation studies revealed that about 2 nm aggregate size of ligand is the critical size required for efficient extraction of trivalent actinide and lanthanide ions. The aggregation of TODGA was facilitated in non-polar diluents like *n*-dodecane. Polar diluent like 1-octanol does not allow the formation of TODGA aggregates due to dipole–dipole interaction of diluent and ligand.

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