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Dynamic light scattering studies on the aggregation behavior of tributyl phosphate and straight chain dialkyl amides during thorium extraction

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ABSTRACT

Dynamic light scattering (DLS) studies were carried out to investigate the aggregation behavior of 1.1 M solutions of tributyl phosphate (TBP), *N*,*N*-dihexyl octanamide (DHOA) and of *N*,*N*-dihexyl decanamide (DHDA) in *n*-dodecane equilibrated with varying concentrations of nitric acid (0.1–6 M) and of Th (10–200 g/L). There was a gradual increase in thorium extraction with increased aqueous phase acidities. A significant enhancement in the aggregate sizes was observed with increasing concentration of thorium in the organic phase. The effect of 1-octanol as phase modifier was also investigated on the aggregation behavior of extracted species for TBP system.

1. Introduction

During solvent extraction experiments, the term "*third-phase*" refers to a situation wherein the organic phase splits in to two phases viz. (a) diluent rich, and (b) extractant rich containing the metal solvate. Third-phase formation behavior of any extractant for a particular metal ion or even an acid under a specified condition is expressed in terms of Limiting Organic Concentration (LOC). This refers to the concentration of the metal ion/acid concentration in the organic phase beyond which the organic phase splits in to two phases [1]. Conventionally, PUREX and THOREX processes have been proposed for the reprocessing of U and Th based spent fuels employing tributyl phosphate (TBP, Fig. 1(a)) as the extractant [2]. However, it has a tendency to form third-phase during the extraction of tetravalent metal ions such as Th((IV) (*relevant for Th fuel cycle*) and Pu(IV) (*relevant for fast reactor fuel reprocessing*) [3]. Therefore, extensive studies have been performed on the evaluation of several organophosphorous extractants toward third-phase formation during the extraction of metal ions [4–12]. It was observed that third-phase formation is almost instantaneous in trialkyl phosphates and in amine systems. By contrast, Gasparini noted slow third-phase formation kinetics in the case of dialkyl amides [13,14]. These extractants offer several advantages over organophosphorous compounds especially with respect to the (i) innocuous nature of their degradation products, viz. carboxylic acids/amines; and (ii) the possibility to incinerate the used solvent leading to reduced volume of secondary waste [15–21]. Detailed studies have demonstrated that the physico-chemical properties of this class of ligands can be tuned by the judicious choice of alkyl groups. In the last decade, many investigations have been conducted on the improvement of amide structures in order to secure the best extracting properties.

At Bhabha Atomic Research Centre, Advanced Heavy Water Reactor (AHWR) is being developed to achieve large-scale use of thorium for the generation of commercial nuclear power [22]. Initially, the AHWR fuel-assembly is proposed to have mixed oxides of (^{233}U,Th)O_2 and (Pu,Th)O_2 in fuel-pins. The (Pu,Th)O_2 pins will require a three stream reprocessing i.e. separation of thorium, uranium and plutonium. This suggests that additional provisions would be required in the reprocessing plants wherein the integration of PUREX and THOREX processes can be realized. A process flow sheet has been proposed for the reprocessing of AHWR spent fuels employing straight chain *N*,*N*-dihexyl octanamide (DHOA, Fig. 1(b)) as an alternative of TBP for the recovery of ^{233}U and Pu from (Pu,Th)O_2 spent fuels as the extractant [23–26]. The reprocessing is currently focused mainly on the recovery of ^{233}U and Pu from the spent fuels leaving bulk of Th ($\sim$100 g/L) in the High Level Waste (HLW) solutions. No systematic attempts have been made so far to identify suitable solvents for the recovery of thorium from AHWR-HLW solutions. However, this is a difficult problem in view of the third-phase formation tendency of different extractants during the extraction of large concentrations of Th(IV)

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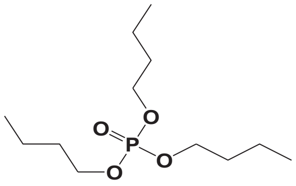
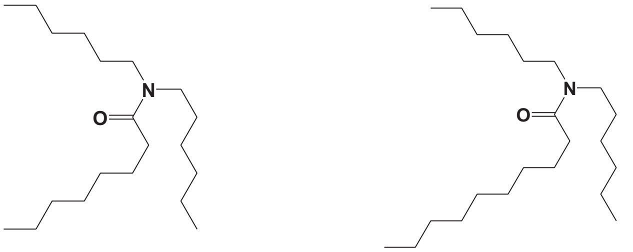


(a): Tri-*n*-butyl phosphate



(b): *N,N*-dihexyl octanamide

(c): *N,N*-dihexyl decanamide

Fig. 1. Structures of different extractants.

from nitric acid solutions. We have evaluated two straight chain dialkyl amides such as DHOA, and *N,N*-dihexyl decanamide (DHDA, Fig. 1(c)) vis-à-vis TBP for the recovery of the thorium from AHWR-HLW solutions [27]. The choice of these dialkyl amides was based on their third-phase formation behavior during the extraction of Th(IV) from nitric acid medium [28,29]. Generally, there is an increase in the Th-LOC values with the total number of carbon atoms and the carbon chain length on the carbonyl group.

At 4 M HNO_3 and 25 °C, typical Th(IV)-LOC (g/L) values for 1.1 M DHOA, 1.1 M DHDA and 1.1 M TBP solutions in *n*-dodecane were 33, 50, 35 g/L, respectively [28].

Recently, some interesting efforts have been made to understand the structure and morphology of the organic phase species using different techniques such as Spectrophotometry, Small-angle neutron scattering (SANS), Small-angle X-ray scattering (SAXS), vapour pressure osmometry (VPO), tensiometry and conductivity etc. [30–37]. Chemical analyses of the organic phase obtained during Th extraction studies from nitric acid medium have shown the existence of a trisolvate $Th(NO_3)_4{\cdot}(TBP)_3$ species. In addition, the third-phase also contains HNO_3 (though small amount) through hydrogen-bonding to the trisolvated complex. These studies have shown that the formation of the heavy phase is a result of the attractive interactions of small reverse micelle-like aggregates of 3–4 TBP molecules per metal nitrate complex. The formation of large ellipsoidal aggregates has been found to be responsible for the appearance of third-phase during extraction studies. Dynamic light scattering (DLS) has also been used to determine the hydrodynamic diameters of supramolecular associates, aggregation behavior during different extraction processes [38–41].

This paper employs DLS technique to understand the third-phase formation/aggregation behavior of two straight chain amides DHOA, DHDA vis-à-vis TBP dissolved in *n*-dodecane during the extraction of Th(IV) from nitric acid medium. This work has been focused on the measurement of the aggregate sizes formed under different experimental conditions. The data obtained in the present work has been used to explain the third-phase formation behavior of these extractants under the conditions of this work.

2. Experimental

2.1. Materials and methods

Both the dialkyl amides viz. DHOA and DHDA used in this work were synthesized in our laboratory as per the reported method [21]. Diluent *n*-dodecane was procured from Lancaster and used without any further purification. Deionized water from a milli-Q purification system (Millipore) of resistivity 18.2 MΩ cm was used for all dilutions. The organic phases to be used for extraction studies were prepared by dissolving required weights of DHOA, DHDA and TBP to yield 1.1 M solutions in *n*-dodecane. Stock solutions of Th(IV) (10–200 g/L) at different acidities (1–6 M HNO_3) were prepared by dissolving required weights of $Th(NO_3)_4{\cdot}5H_2O$ in suitable nitric acid medium and adjusting to the desired acidity. The concentration of Th(IV) was determined by EDTA (ethylenediaminetetraacetic acid) complexometric titration using xylenol orange as indicator. Nitric acid concentration was determined by alkalimetry employing phenolphthalein as the indicator.

2.2. Sample preparation and DLS measurements

The samples for DLS measurements were prepared by equilibrating the organic phases (1.1 M solutions of TBP/DHOA/DHDA in *n*-dodecane) with desired aqueous phases for about 60 min (sufficient for attaining equilibrium condition). 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 of 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 points are the standard deviations of multiple measurements.

3. Theory of DLS measurements

The aggregates (reverse micelles in this study) 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 fluctuations 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. These fluctuations are described quantitatively by the intensity of the autocorrelation function, $C(\tau)$ of scattered intensity as follows:

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

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:

$$\Gamma = Dq^2 \tag{2}$$

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 through Stokes–Einstein equation:

$$r_h = \frac{k_B T}{6\pi\eta D} \tag{3}$$

where, k_B is the Boltzmann constant, T is the absolute temperature and η is the viscosity of the dispersion medium. It is important to