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Extraction behavior of trivalent lanthanides from nitric acid medium by selected structurally related diglycolamides as novel extractants

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ABSTRACT

The extraction affinity of trivalent lanthanides, Ln(III), from nitric acid medium has been explored using a series of ten structurally related synthesized diglycolamides (DGA) diluted with toluene. The structure-reactivity relationship with extraction of trivalent lanthanides as well as their atomic number was investigated. The extraction of nitric acid and selected lanthanide ions by N,N,N′,N′-tetradodeceyldiglycolamide (TDDGA), from nitric acid medium was studied in details. Distribution ratio of the trivalent lanthanide ions has been studied as a function of aqueous HNO_3 concentrations, DGA concentration, and temperature. The stoichiometry of La(III), Nd(III), and Eu(III) was determined at different nitric acid concentrations by slope analysis of extraction data, and enthalpy change accompanied by extraction was also determined and reported in this work.

1. Introduction

Developing the valuable extractants is an important task in the application of innovative chemical separation techniques to the efficient recovery and separation of metal ions from raw materials and industrial waste as well as partitioning of the high level radioactive liquid [1,2]. Radiolytic and hydrolytic degradation of extractants, phase modifiers, and diluents are integral parts of hydrometallurgical processing of radioactive materials [3–7]. Study of the solvent extraction of lanthanides and actinides elements using monoamides and diamides has continued over the last 20 years [5–9]. The principal advantage of amides over organophosphorus compounds is their complete incincerability and the fact that the formed degradation products can be easily removed [3–9]. Within this context, studies relating to the utilization of a number of diamides for actinides and lanthanides extraction from aqueous nitrate media have been carried out over a number of years [10–12]. Malonamides are one of the favorable bidentate diamide ligands for actinides extraction [13–15]. A judicious choice of alkyl groups enhanced the selectivity of malonamides [12–15].

Mowafy et al. [12,15–17], reported on the extraction of actinides and lanthanides from nitrate media by several synthesized monoamides and diamides. Several malonamides substituted with oxyalkyl group at the central methelene carbon showed a higher affinity to extract different metal ions than alkyl group-substituted or non-substituted malonamides at a central carbon atom [18–19]. This behavior was related to the basic character of these malonamides. On search of new extractant, diglycolamides, Fig. 1, was recently introduced. Diglycolamides contain three oxygen atoms that can vigorously capture the metal ions, and act as tridentate ligands. This produces a very stable complex through the bonding of the extractant with the actinides. These attractive features make them good candidates for further investigations to assess their possible use in nuclear waste management. Studies with some diglycolamides derivatives [20–22] showed that theses new class of diamides were successfully used as extractants for selected metal ions from nitrate media and worthy for further investigation. Narita et al. [23,24] investigated the tridentate coordination of diglycolamide having two phenyl group in chloroform to the lanthanides by XRD and EXAFS analysis. The influence of the nature and concentration of different acids such as HCl, HNO_3 and $HClO_4$ extraction on the aggregation properties of diglycolamides such as TODGA in n-octane, 1-octanol or n-dodecane was investigated by several authors [25–28]. They found that the aggregation of TODGA increased with acid concentration of equilibrating solutions. However, the aggregation tendency was independent on TODGA concentration at fixed acidity. Although, diglycolamides have been extensively studied for the extraction of actinide and lanthanide ions, only a very few work is available to understand the effect of diglycolamides structure on the metal extraction behavior.

In our previous works [29,30], we reported on the synthesis of a number of novel structurally related diglycolamide compounds by

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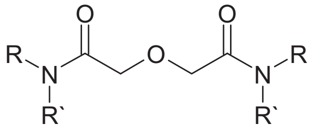

Fig. 1. Chemical structure of diglycolamide (DGA).

a modified efficient method. These compounds were applied to the extraction of selected actinides, lanthanides, and alkaline earth metals under various conditions. The main goal of the present work was to establish the correlation between the structure of diglycolamide compounds under investigations toward lanthanides. A systematic investigation of the extraction behavior of lanthanides in HNO_3 with TDDGA were also carried out. In addition, to define the influence of the individual substituents (alkyl or aryl) on the extraction ability of diglycolamides, we have synthesized ten structurally related diglycolamides (DGA), Fig. 1, and grouped into four series for comparison:

(i) N,N,N′,N′-tetrabutyldiglycolamide (TBDGA), N,N,N′,N′-tetrahexyldiglycolamide (THDGA), N,N,N′,N′-tetraoctyldiglycolamide (TODGA), and N,N,N′,N′-tetradodeceyldiglycolamide (TDDGA), where (R = R′, symmetrical) the length of the linear carbon chain on the nitrogen atom changes;
(ii) N,N,N′,N′-tetraisobutyldiglycolamide (TIBDGA) and N,N,N′,N′-tetra (2-ethylhexyl) diglycolamide (T2EHDGA), where (R = R′, symmetrical) the branched alkyl group on the nitrogen atom changes;
(iii) N,N′-dimetyl-N,N′-diphenyldiglycolamide (DMDPhDGA), N,N′-dimethyl-N,N′-dioctyldiglcolamides (DMDODGA), where (R ≠ R′, unsymmetrical) the length of the carbon chain on the nitrogen atom has different size, R is a small group (typically methyl) and R′ a bigger one and change (alkyl or aryl);
(iv) N,N′-di(isobutyl)-N,N′-dioctyldiglycolamides (DIBDODGA), N,N′-di(2-ethylhexyl)-N,N′-dioctyldiglycolamides (D2EHDODGA), where (R ≠ R′, unsymmetrical), had the same R group (R = octyl) and various in R′ group (branched alkyl substituent).

2. Experimental

2.1. Chemicals

All chemicals used were of analytical reagent grade purity and used without further purification.

2.2. Synthesis of diglycolamides

The ten different diglycolamides investigated in this study were synthesized and purified in our laboratory by using the modified method (three- step method) reported in our previous work [29,30]. The purity of final products was controlled by different tools such as elemental analysis, IR and H NMR which is found to be higher than 98%.

2.3. General extraction procedure

Prior to the extraction studies, the solvents were pre-equilibrated with aqueous phases containing the same nitrate concentrations as the aqueous phase under study in order to prevent the co-extraction of HNO_3, which could be occurred during the distribution of metal ions. Liquid-liquid extractions were carried out by shaking equal volumes of aqueous and organic phases for about 15 min (equilibrium) in a thermostated water bath adjusted to the desired temperatures (15–55 ± 0.5 °C). The two phases were then centrifuged and assayed by taking know aliquots from the aqueous phase. Unless otherwise stated toluene was used as diluent for the ten diglycolamides used.

In all cases aqueous feed contained 5×10^{-3} M of metal nitrate in HNO_3 solutions. The concentration of trivalent lanthanides in the aqueous phases was analyzed before and after extraction by both atomic absorption spectrometry (AAS, Perkin Elmer-400) and spectrophotometry (Labmed, INC., model-UVD-2950) using the Arsenazo-III method [31]. The distribution ratio (D) was measured, as the ratio between the concentration of an element in the organic and aqueous phases. For each sample, three aliquots were considered and the results were critically treated. The amount of metal ion in the organic phase was obtained by subtracting the aqueous concentration from the initial aqueous concentration of the investigated metal ions. For acid extraction, the diglycolamide solutions of concentration 0.03–0.5 M in toluene were equilibrated with 1 M HNO_3 for 30 min. After phase separation, the acidity in the aqueous and organic phase was determined as previously reported [29].

3. Results and discussion

The optimum conditions for the extraction of trivalent lanthanides ions were established by varying the experimental parameters, such as HNO_3 concentration, extractant concentration, and the equilibration time. Toluene was chosen as the diluent for the investigated diglycolamides. For all extractants no third phase formation was observed after extraction; good and fast phase separation were also attained for all the extraction experiments that were conducted.

Diamides derivatives, named oxapentanediamide, diglycolamides, generally expressed as $(RR'–NCO–CH_2)_2–O$, are of high interest due to their desirable coordination properties of oxygen donors to metal ions. It has been found that nitrogen or sulfur donor's ligands have higher coordination affinities for trivalent actinide compared to trivalent lanthanide ions [32–35]. Within this merits, diglycolamides with three oxygen donors and 2 N atoms might have different extraction properties for actinides and lanthanides. The extraction efficiency of the diglycolamides is thought to be related to both the electro-inductive effects as well as the steric hindrances around the binding site. Therefore, the structure of the diglycolamides derivatives used in the present work has been chosen following their different size in nitrogen substituents.

3.1. Influence of structure

The nature of N substituent (R and R′ groups) plays an important role on the extraction ability of the diamides. The diglycolamides considered were synthesized with different substituting groups. The use of a group such as methyl allows the minimization of the stereochemical hindrance around the carbonyl groups. On the other hand, the presence of branched alkyl groups (isobutyl, ethylhexyl), long chain alkyl groups (butyl, hexyl, octyl or dodecyl) or bulk group (phenyl) bonded to the nitrogen atoms act as electron donating, thus giving the molecular structure a more basic character. This series allow a systematic determination of the role of structure on the extraction of lanthanide ions. The extraction of La(III), Nd(III), Sm(III), Eu(III), Gd(III), Dy(III), Er(III) and Lu(III) from 1.5 M HNO_3 solution by 0.1 M of the different four groups of diglycolamides in toluene has been studied, Table 1. Except for La(III) and Sm(III), the extracting power of the first group (TBDGA, THDGA, TODGA, TDDGA) for the investigated trivalent lanthanides was found to increase slightly when increasing the carbon chain length R and R′ from C_4H_9 to C_6H_{13} (R = R′). On the other hand, the extraction of the investigated trivalent lanthanides was found to suffer a notable decrease when increasing in the alkyl chain