Extraction of Dy(III) and Sm(III) with 
$N,N'$-dimethyl-$N,N'$-dioctylsuccinamide

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Abstract: This work was focused on the applicability of a new diamide $N,N'$-dimethyl-$N,N'$-dioctylsuccinamide (DMDOSA) employing cyclohexane as the diluent to extract Dy(III) and Sm(III) from nitric acid solutions. The extraction from HNO$_3$ was investigated by distribution measurements. The stoichiometry of the predominant adducts of DMDOSA with HNO$_3$ is 1:1 (HNO$_3$.DMDOSA) under the studied conditions. The effect of the concentrations of nitric acid, lithium nitrate and extractant on the distribution ratio was investigated. An IR spectral study was also made of the extracted species.

Keywords: $N,N'$-dimethyl-$N,N'$-dioctylsuccinamide, synthesis, extraction, Dy(III), Sm(III).

INTRODUCTION

There has been significant interest in recent years in the study of amides as alternative extractants to organophosphorus compounds, e.g., tributylphosphate (TBP), for actinide separation, because the products of radiolytic and hydrolytic degradation of amides are less detrimental to the separation processes than those of organophosphorus compounds. In addition, the amide ligands are completely incinerable, which implies that the amount of secondary wastes generated in nuclear waste treatment could be significantly reduced.

To partition the minor actinides (Np, Am, Cm) from the high level waste (HLW) it is essential to study the extraction behavior with diamidic extractants from nitrate media. Diamides were selected for the investigations because they show higher degrees of extraction than amides owing to their chelating ability. The selection of the substituents on the nitrogen atoms (R and R’) in diamides is very important to facilitate metal-ion co-ordination and to allow the solubility of the diamide and its adducts in the organic phase. In order to attain both objectives,

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R and R’ should have different sizes. If R is a small group (typically methyl) and R’ a bigger one, both criteria are satisfied: the stereochemical hindrance around the carbonyl oxygen atoms is kept to minimum and both oxygen atoms can co-ordinate to a metal ion and the lipophilic character of the ligands is attained by the presence of a higher chain-alkyl or aryl groups-at R’.

DMDOSA, the structure of which is presented in Fig. 1, was chosen for this research. In this molecule the aforementioned criteria for the selection of R and R’ are satisfied. This paper presented the extraction of Dy(III) and Sm(III) from nitric acid solution with DMDOSA.

EXPERIMENTAL

Reagents

DMDOSA was synthesized in our laboratory and the pruity of final products was controlled by elemental analysis, IR and 1HNMR and found to be higher than 98%. The other chemicals employed in this work were all of A.R. grade purity.

Preparation of the Dy(III) and Sm(III) solution

1.8652 g Dy₂O₃ were dissolved in 20 ml of 12.80 mol dm⁻³ HNO₃ solution, and the solution was then evaporated carefully at lower temperatures (no higher than 60 °C) to dry. The residue was dissolved in 26.42 ml of 7.57 mol dm⁻³ nitric acid solution and diluted to 200 ml. The obtained solution contained 5.00×10⁻³ mol dm⁻³ Dy³⁺ and 1.00 mol dm⁻³ HNO₃. A series of 5.00×10⁻³ mol dm⁻³ Dy³⁺ solutions was then prepared by quantitative dilution. The Sm(III) solution was prepared in a similar manner as above.

Extraction of HNO₃ with DMDOSA

The aqueous phase and the organic DMDOSA were shaken together for five minutes. After separation by centrifugation, aliquots of each phase were sampled for analysis. The acidities were measured by NaOH titration in aqueous or ethanolic media for the aqueous and organic solutions, respectively.

Extraction of Dy(III) and Sm(III) with DMDOSA

In the studies of the distribution of Dy(III) and Sm(III) solutions of the desired concentration of DMDOSA in cyclohexane were employed after pre-equilibration at the respective acidities. Equal volumes of organic and aqueous phases were agitated for 40 min (enough for equilibrium) at 25 °C under the desired experimental conditions. The two phases were then centrifuged and assayed by taking known aliquots (0.05–0.1 mL) from the aqueous phases. The concentrations of Dy(III) and Sm(III) in the sample were determined by Arsenazo-III visible spectrophotometric analysis and that in organic phase was obtained by subtracting the aqueous concentrations from the total initial aqueous concentration of Dy(III) and Sm(III). The distribution ratio (D) was calculated as the ratio of the concentration of Dy(III) and Sm(III) in the organic phase to that in the aqueous phase.

Preparation and characterization of the extracted species

The extracted species were prepared. A DMDOSA solution was shaken with a saturated solution of Dy(NO₃)₃ and Sm(NO₃)₃, centrifuged and the organic phase separated. The organic sol-
vent was removed and FTIR spectrum of the residue was recorded using an FTS-165 Spectrometer in the range 400–4000 cm\(^{-1}\). The samples were measured between potassium bromide windows. The scan time and the resolution were 60 and 2 cm\(^{-1}\), respectively.

RESULTS AND DISCUSSION

Extraction of HNO\(_3\) with DMDOSA

The effect of DMDOSA concentration on the extraction of HNO\(_3\) in the presence of LiNO\(_3\) was examined and the plots of log \(D_{\text{HNO}_3}\), as a function of log \(c_{\text{DMDOSA}}\) are shown in Fig. 2. The slope of the line is about 1.2, which shows that the stoichiometry of the predominant adducts of DMDOSA with HNO\(_3\) is 1:1 (HNO\(_3\)·DMDOSA) under the studied conditions. Thus, the extraction of HNO\(_3\) can be expressed as:

\[
\text{HNO}_3 + \text{DMDOSA}(o) = \text{HNO}_3 \cdot \text{DMDOSA}(o) \quad (1)
\]

where the subscript \((o)\) represents the organic phase. The extraction equilibrium (1) is characterized by the constant \(K_{\text{HNO}_3}\)

\[
K_{\text{HNO}_3} = \frac{[\text{HNO}_3 \cdot \text{DMDOSA}]_{(o)}}{\gamma_{\pm}^2 [\text{H}^+][\text{NO}_3^-] [\text{DMDOSA}]_{(o)}} \quad (2)
\]

in which \(\gamma_{\pm}\) is the mean activity coefficient of nitric acid and is equal to 1.755 calculated by MK (Meisser–Kusik) method.\(^8\) The value of \(K_{\text{HNO}_3}\), calculated using Eq. (2), is 0.83 mol\(^{-2}\) dm\(^6\).

Effect of nitric acid concentration on the extraction of Dy(III) and Sm(III)

The extractions of Dy(III) and Sm(III) nitrate solutions containing 5.00 mol dm\(^{-3}\) LiNO\(_3\) and nitric acid in solutions in the range of 0.10–3.20 mol dm\(^{-3}\) at 298 K were investigated (Fig. 3). The results show that the extractability is very poor at
high HNO₃ concentrations, which may be due to the extraction of HNO₃. In the further experiments, the aqueous HNO₃ concentration was fixed at 0.10 mol dm⁻³ to avoid hydrolysis of the metal ions experiments.

**Effect of lithium nitrate concentration on the extraction of Dy(III) and Sm(III)**

The effect of the lithium nitrate concentration on the extraction distribution ratio of Dy(III) and Sm(III) is shown in Fig. 4. The distribution ratio of Dy(III) and Sm(III) increased significantly with increasing LiNO₃ concentration in which the co-ion effect plays a crucial role. This is in agreement with the results of Cuillerdier.⁸

**Effect of the extractant concentration on the extraction of Dy(III) and Sm(III)**

The variations of the distribution ratio of Dy(III) and Sm(III) with DMDOSA in cyclohexane are given in Fig. 5. The log–log plots of the distribution ratio vs. the initial DMDOSA concentration show that the lines have a slope of nearly 3. This
implies that the stoichiometries of the extracted species in cyclohexane were \( \text{Dy(NO}_3\text{)}_3\cdot3\text{DMDOSA} \) and \( \text{Sm(NO}_3\text{)}_3\cdot3\text{DMDOSA} \). These results are consistent with the observation of Sun et al. for the extraction of Dy(III) with tetrabutylmalonamide.\(^3\)

Hence the equilibrium expressions, written as the solvating reaction of Dy(III) and Sm(III), are as follows:

\[
\begin{align*}
\text{Dy}^{3+} + 3\text{NO}_3^- + 3\text{DMDOSA}^{(o)} & \rightleftharpoons \text{Dy(NO}_3\text{)}_3\cdot3\text{DMDOSA}^{(o)} & (3) \\
\text{Sm}^{3+} + 3\text{NO}_3^- + 3\text{DMDOSA}^{(o)} & \rightleftharpoons \text{Sm(NO}_3\text{)}_3\cdot3\text{DMDOSA}^{(o)} & (4)
\end{align*}
\]

for which the apparent equilibrium constants for Dy(III) and Sm(III), \( K_{\text{ex1}} \) and \( K_{\text{ex2}} \), respectively, are

\[
\begin{align*}
K_{\text{ex1}} &= \frac{[\text{Dy(NO}_3\text{)}_3\cdot3\text{DMDOSA}]^{(o)}}{[\text{Dy}]^{3+} [\text{NO}_3^-]^3 [\text{DMDOSA}]^3^{(o)}} & (5) \\
K_{\text{ex2}} &= \frac{[\text{Sm(NO}_3\text{)}_3\cdot3\text{DMDOSA}]^{(o)}}{[\text{Sm}]^{3+} [\text{NO}_3^-]^3 [\text{DMDOSA}]^3^{(o)}} & (6)
\end{align*}
\]

To obtained the values of \( K_{\text{ex1}} \) and \( K_{\text{ex2}} \), the free DMDOSA concentration must be calculated:

\[
[D\text{MDOSA}]^{(o)}_{\text{free}} = c_{\text{DMDOSA}} - [D\text{MDOSA}]^{(o)}_{\text{bound}} & (7)
\]

where \([D\text{MDOSA}]^{(o)}_{\text{bound}} = [\text{HNO}_3\cdot\text{DMDOSA}]^{(o)}_{(o)} = [\text{H}^+]^{(o)}\). Hence, one obtains

\[
[D\text{MDOSA}]^{(o)}_{\text{free}} = c_{\text{DMDOSA}} - [\text{H}^+]^{(o)} & (8)
\]
From the result of the extraction of nitric acid the values of $K_{\text{ex}_1}$ and $K_{\text{ex}_2}$ can be obtained through Eqs. (5) and (6). The calculated values are $0.44 \pm 0.01 \text{ mol}^{-6} \text{ dm}^{18}$ for Dy(III) and $0.56 \pm 0.01 \text{ mol}^{-6} \text{ dm}^{18}$ for Sm(III). These results show that the extractability of Sm(III) by DMDOSA is higher than that of Dy(III).

**Structural characterization of the extracted species**

The wavelength 1500–1700 cm$^{-1}$ is the region where the stretching bands of the carbonyl groups in DMDOSA are observed (Fig. 6). The adsorption bands around 1650 cm$^{-1}$ could be assigned to the carbonyl stretching modes in free DMDOSA (curve 1). In the presence of Dy(III) and Sm(III) these bands are red-shifted and appear around 1630 cm$^{-1}$ and 1590 cm$^{-1}$ (curve 2 and curve 3), indicating the formation of Dy–DMDOSA and Sm–DMDOSA complexes. These results are consistent with the observation of Byers$^{10}$ for the complexation of La(III) with tetraethylmalonamide, where the C=O stretching mode of the free ligand was at 1645 cm$^{-1}$ but was shifted to 1613 cm$^{-1}$ in the bound ligand. Edwards et al.$^{11}$ also reported similar red-shifts of carbonyl stretching bands when malonamides, succinamides and glutaramides formed bidentate chelates with neodymium, uranium and thorium. Based on the literature information,$^{9,11}$ and observations in the present study, it is concluded that both Dy(III) and Sm(III) form bidentate complexes with DMDOSA through the two carbonyl oxygen atoms and the two coordinate bonds are different due to the appearance of two carbonyl bands in the IR spectra of the complexes. Further studies will be carried out in new equipment in an attempt to understand the effect of the structure of the ligands on the extraction of lanthanides.

**CONCLUSIONS**

Dy(III) and Sm(III) can be extracted effectively with DMDOSA in cyclohexane from nitrate media to form Dy(NO$_3$)$_3$.3DMDOSA and Sm(NO$_3$)$_3$.3DMDOSA. The
apparent equilibrium constants are 0.44 ± 0.01 dm\(^{-6}\) and 0.56 ± 0.01 dm\(^{-6}\) for Dy(III) and Sm(III), respectively. The values of \(D\) decrease with increasing nitric acid concentration. From IR spectroscopy, it can be concluded that DMDOSA forms bidentate complexes with Dy(III) or Sm(III) through its two carbonyl oxygen atoms and that the two coordinated bonds are different.

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