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S. A. Saved[a]; T. M. Sami[b]; A. A. Abd El Tawab[b]
[a] DEPARTMENT OF CHEMISTRY FACULTY OF SCIENCE, HELWAN UNIVERSITY, CAIRO, EGYPT
[b] DEPARTMENT OF NON FERROUS METALS, TABBIN INSTITUTE OF METALLURGICAL STUDIES, CAIRO, EGYPT

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Synergistic Extraction of Some Rare Earths(III) from Nitrate Media by Thenoyltrifluoroacetone and Tri-*n*-octylamine

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S. A. SAYED*
DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
HELWAN UNIVERSITY
CAIRO, EGYPT

T. M. SAMI and A. A. ABD EL TAWAB
DEPARTMENT OF NON FERROUS METALS
TABBIN INSTITUTE OF METALLURGICAL STUDIES
CAIRO, EGYPT

ABSTRACT

The synergistic action of tri-*n*-octylamine (TOA) in the selective extraction of the rare earths La, Nd, Tm, Lu, and Y with thenoyltrifluoroacetone (HTTA) was studied in a nitrate media (0.6 M HNO_3 + 11.6 g/L CaO). The synergism enhances the REE extraction and separation. The [HTTA], [TOA], diluent, complexing agents, and calcium ion effects were also studied.

INTRODUCTION

The greatest developments in extractive metallurgy have arisen from the use of chelating acidic reagents. The ability to use concepts of coordination chemistry, like the hard and soft acid-base theory and formation (stability) constants, to design selective reagents has interested chemists for many years (1). Solvent extraction is now a commonly used technique in industrial processes for the separation of lanthanides and yttrium (2). The choice of extracting agent depends on the raw materials and the pur-

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* To whom correspondence should be addressed.

pose of extraction. HDEHP gives higher separation factors than does TBP, but the dilution required with HDEHP decreases its capacity. TBP requires large amounts of HNO_3. At low acidity it preferably extracts the lighter, usually more abundant elements. The presence of Ca^{2+} has been found to enhance extraction (3, 4). Use of amines to extract lanthanides from nitrate solution showed that tertiary amines were relatively ineffective except in the presence of a high nitrate ion concentration ($LiNO_3$ 500 g/L, Amine 30%, pH1) (5, 6). Exhaustive data are reported in the literature on synergistic extraction of metal ions, where simple adducts of metal β-diketonates with neutral or basic donors are responsible for synergism (7–9). Mathur et al. (10) also studied the synergistic extraction of some lanthanides(III) with a mixture of thenoyltrifluoroacetone (HTTA) and tri-*n*-octylamine (TOA) from nitrate media. They showed the formation of synergistic species: $M(TTA)_3 \cdot TOA$, $M(TTA)_3 \cdot TOA \cdot HNO_3$, as well as $M(TTA)_3 \cdot TOA \cdot HTTA$ in the organic phase.

In the present study, mixtures of solutions of thenoyltrifluoroacetone and tri-*n*-octylamine in ternary solvents were examined for the selective extraction of some rare earth elements from a nitrate solution containing calcium ions.

EXPERIMENTAL

Chemicals

2-Thenoyltrifluoroacetone (HTTA) was A.R. grade and supplied by Aldrich. Tri-*n*-octylamine (TOA) was A.R. grade and supplied by Sigma. All other chemicals and materials used were also of A.R. purity grade and obtained from B.D.H (England).

Extraction Procedure

In all cases the organic phase was preequilibrated with an aqueous medium containing 0.01 M HNO_3. The aqueous phase was made by dissolution of 11.2 g/L CaO in 0.6 M HNO_3, which is similar to the aqueous solution produced on dissolution of calcium-REE-oxalate in 0.6 M HNO_3 (11). REE solution was added to the aqueous phase to be 2×10^{-3} M; the pH was adjusted to 2.6 by LiOH solution. Partition investigations were carried out using 10 cm^3 volumes of the preequilibrated organic and aqueous phases. Equilibrium was achieved by vigorous mechanical shaking for 15 minutes at ambient temperature (25 ± 1°C). After phase separation by centrifugation, the REE concentration was determined spectrophotometrically at 655 nm with an error of 3% as described before. The distribution ratio of each rare earth ion between the aqueous and the organic phases was determined as follows:

$$D = \frac{{}^{C}\mathrm{M}_{\mathrm{total}} - {}^{C}\mathrm{M}_{\mathrm{aq}}}{{}^{C}\mathrm{M}_{\mathrm{aq}}}$$

and the extraction efficiency percent:

$$E = \frac{D}{D + (V_{\mathrm{aq}}/V_{\mathrm{org}})} \times 100$$

where C = concentration
D = distribution ratio
E = extraction efficiency
M = rare-earth element.
V_{aq} = volume of aqueous phase
V_{org} = volume of organic phase

RESULTS AND DISCUSSION

The Synergistic Effect in the HTTA + TOA System

Extraction of metal by HTTA alone can be represented by

$$\mathrm{M}^{3+}_{\mathrm{aq}} + 3\mathrm{HTTA}_{\mathrm{org}} \rightleftharpoons \mathrm{M(TTA)}_{3\,\mathrm{org}} + 3\mathrm{H}^{+} \qquad (1)$$

The synergistic effect in the HTTA + TOA system arises from the following organic phase reactions:

$$\mathrm{M(TTA)_3} + \mathrm{R_3N{\cdot}HNO_3} \rightleftharpoons \mathrm{M(TTA)_3{\cdot}R_3N{\cdot}HNO_3} \qquad (2)$$

$$\mathrm{M(TTA)_3} + \mathrm{R_3N{\cdot}HTTA} \rightleftharpoons \mathrm{M(TTA)_3{\cdot}R_3N{\cdot}HTTA} \qquad (3)$$

$$\mathrm{M(TTA)_3} + \mathrm{R_3N{\cdot}NHO_3{\cdot}HTTA} \rightleftharpoons \mathrm{M(TTA)_3{\cdot}R_3N{\cdot}HNO_3{\cdot}HTTA} \qquad (4)$$

The formation constant for each of these reactions was found to be the same for a particular metal ion (10).

The primary cause for synergism is generally accepted to be an increase in hydrophobic character of the extracted metal complex upon addition of the adduct, although proposed mechanisms involve replacement of the metal ion-water molecule by the adduct molecule or expansion of the coordination sphere of the metal ion upon the addition of the adduct molecule. In $\mathrm{Ln(TTA)_3}$ the TTA molecules occupy only six positions of the coordination sphere, there are also three water molecules in the coordination sphere, and the order of increasing the adduct formation constant (K_{ad}) is dependent on the basicity of the donor molecules (12).

Figure 1 illustrates the synergistic extraction of the REE–TTA complex from nitrate media (0.6 M $\mathrm{HNO_3}$, in the presence of 11.6 g/L CaO) into benzene. At the left vertical axes of the figure the free coordination sites

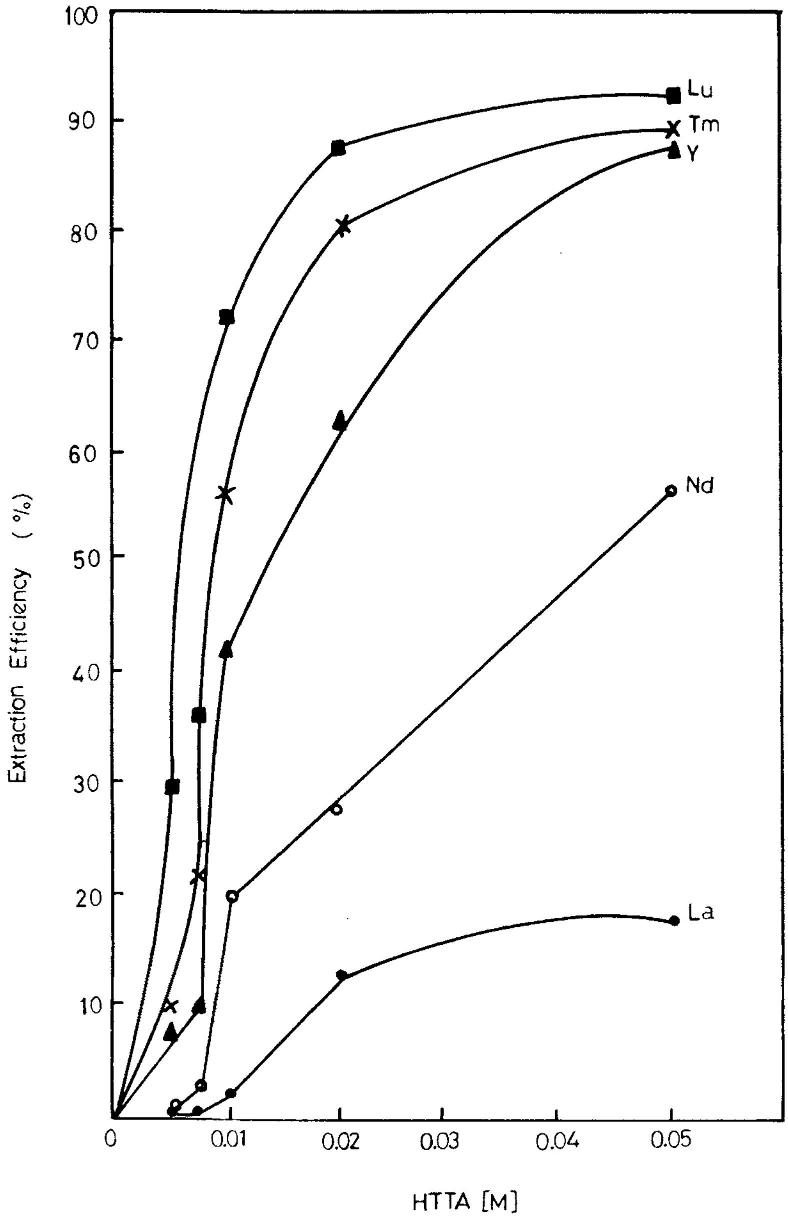

FIG. 1 The synergistic extraction of the REE–TTA complex from nitrate media (11.6 g/L CaO in 0.6 M HNO_3) at 1% TOA.

of the rare earth ions are occupied by water or NO_3^- only, and the REE–TTA complexes are poorly extracted by tri-*n*-octylamine (TOA) alone as a negatively charged complex (5, 6).

When thenoyltrifluoroacetone (HTTA) is added gradually, from 5×10^{-3} to 5×10^{-2} M $M(TTA)_3$ is formed at an [L]/[M] ratio ≅ 3.0 a gradual increase in complex stability and extraction constant with an increase of atomic number of lanthanide elements (13) are observed as an increase of the extraction percent values at constant TOA concentration which served as an adduct. This region in the curve (0.0–0.01 M), [HTTA] could be represented by Eq. (2), with the formation of synergistic adducts as $M(TTA)_3 \cdot TOA \cdot HNO_3$.

In the presence of an excess concentration of HTTA, the extraction percent is also increased, which is in accordance with Eqs. (3) and (4), with the formation of synergistic adducts as $M(TTA)_3R_3N \cdot HTTA$ or $M(TTA)_3R_3N \cdot HNO_3 \cdot HTTA$.

The selectivity observed in the present work as high extraction of the trivalent ions Y, Tm, and Lu over La and Nd, may be explained by the presence of calcium ions in our working solution, which could form an unextracted complex with HTTA in benzene, and be able to be exchanged with ions having comparable radii and extraction constants, especially as La and Nd ions (radius of hydrated ions; Ca = 0.100 nm, La = 0.105 nm, Nd = 0.098 nm) (12) (log K_e MTTA; Ca = −12.0, La = −10.31, Nd = −8.58) (13) that result in masking these ions in a low concentration of HTTA which could be consumed in calcium–TTA complex formation, then in a high concentration of HTTA. Exchange with Ca is pronounced. $La(TTA)_3$ and $Nd(TTA)_3$ are formed and enhanced extraction is observed.

Figure 2 illustrates the effect of the addition of TOA adduct-forming molecules on the extraction efficiency of the trivalent ions La, Nd, Y, Tm, and Lu, at constant HTTA concentration (0.01 M). A sharp increase in the extraction efficiency of Y, Tm, and Lu was observed with an increase of [TOA] from 0.0 to ~0.02 M, which is proof for the role of TOA as adduct with an increase of its concentration. The extraction doesn't register a notable increase, and this may be recognized by the predominance of the monomer form of TOA below ≅ 250 mmol/L and around or over that concentration. The dimer form is responsible to the small increase of synergism because dimerization may be considered to be self-adduct formation which serves the same purpose of reducing the hydrophilicity of the acid molecule (3). On the other hand, the behavior of La(III) and Nd(III) ions extraction in comparison with Y(III), Tm(III), and Lu(III) is in accordance with a decrease of the basic character of the elements with an increase of atomic number, which may be considered to be a retarding and opposite force for the basic TOA adduct molecules.

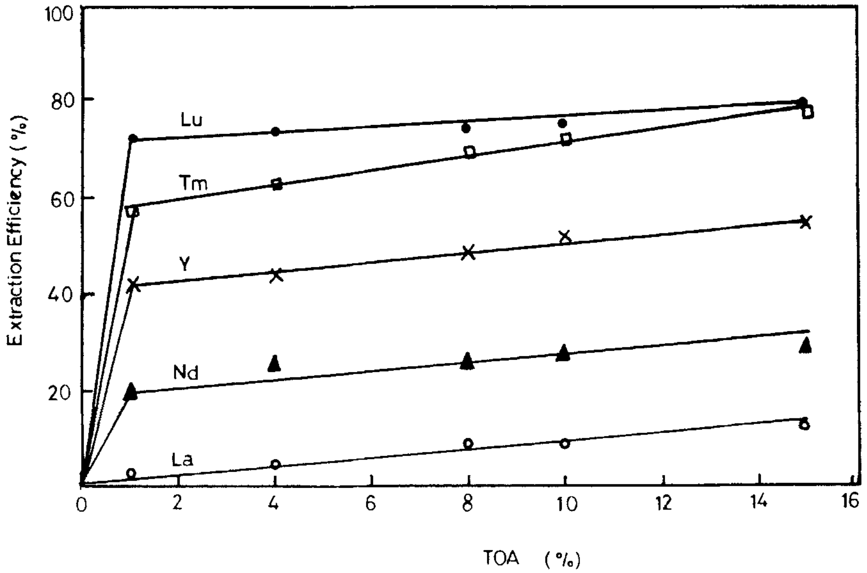

FIG. 2 Effect of TOA addition on the extraction efficiency of REE(III) at 0.01 M HTTA.

Effect of Diluent on the Synergistic Extraction

Diluents have a very large effect on synergistic extraction of trivalent metal ions. The extraction of a particular metal ion in different diluents follows a reverse order of solubility of water in these diluents (14). Among other factors that have been actively considered as responsible are the dielectric constant, the interaction of diluents with neutral donors, and the regular solution theory (15).

It has been observed that the dielectric constants of the diluents have a varying effect on the equilibrium constants for the formation of the synergistic adduct species (16).

Table 1 shows the data obtained on the selective extraction of the aforementioned ions from the working solution by using the synergistic system [HTTA (0.01 M) + TOA (1%)]. There is a decrease in extraction efficiency in toluene and an increase of it in chloroform. This would suggest the calcium ion orients the dipoles of polar solvents by its electric field as a charged solute by formation or disruption of hydrogen bonds or by other interactions. The water solubility of chloroform is more than that of benzene and toluene, which means more orientation force by Ca^{2+} in the same order of water solubility and the enhancement of extraction.

TABLE 1
Effect of Solvent on the Extraction Efficiency at [0.01 M HTTA + 1% TOA] in Benzene

Solvent	Dielectric constant (*E*)	Water in solvent (%)	Solvent in water (%)	La (%)	Nd (%)	Y (%)	Tm (%)	Lu (%)
Benzene	2.28	0.062	0.179	2	20	42.3	56.6	72.4
Toluene	2.38	0.033	0.052	0	0	17.2	26	30.7
Chloroform	4.9	0.090	0.815	60.5	87	92.8	92.3	95

Effect of Chelating Agents

Many solvent extraction processes are indeed ligand displacement reactions of octahedral complexes in which L is the extractant:

$$[M(H_2O)_6^+] + L^- \xrightarrow[\text{fast}]{} \underset{\substack{\text{outer sphere}\\ \text{associate}}}{[L^-,M(H_2O)_6^+]} \xrightarrow[\text{slow}]{K} [ML(H_2O)_5] + H_2O$$

This has been experimentally observed for aqueous-phase reactions.

Therefore, whenever the complex is not extracted into the organic phase, thermodynamically very stable complexes can be expected to react slowly with the extractant.

In the extraction of trivalent ions, for example, if the aqueous medium contains only weakly complexing ligands (Cl^- or NO_3^-), the extraction kinetics are very fast. On the other hand, in the presence of polyaminocarboxylic acids, such as EDTA, which are powerful complexing agents, the extraction reaction proceeds only slowly, and extraction and separation of rare earth pairs is improved by the addition of EDTA (15).

Effect of Thiocyanate Ion

Table 2 shows the variation of the extraction efficiency on addition of NH_4SCN solution to the aqueous phase during synergistic extraction by the (HTTA + TOA)/benzene system. Any observed decrease achieved becomes somewhat less with an increase of thiocyanate ion concentration. This may be attributed to the basicity of the thiocynate ion in comparison with nitrate that could replace it, not only in the aqueous phase working as a masking agent, but also in the adduct synergistic species in the organic phase, $M(TTA)_3 \cdot TOA \cdot HNO_3$, especially when the thiocyanate concentration is increased, and the substitution is somewhat limited because the organic phase was equilibrated with nitrate, not with thiocyanate, i.e., it depends on the stabilities of the complex formed and the adduct.

TABLE 2
Effect of Thiocyanate Addition on the Extraction Efficiency
at [0.01 M HTTA + 1% TOA] in Benzene

NH_4SCN	La (%)	Nd (%)	Y (%)	Tm (%)	Lu (%)
0.0005	2.6	4.9	27	32.4	45
0.001	2.2	8.6	30.1	43.3	48.9
0.005	1.4	10	35.4	42.1	57.1

Effect of EDTA

Table 3 shows the change of extraction efficiency on addition of EDTA solution to the aqueous phase during synergistic extraction by the (HTTA + TOA)/benzene system. On addition of a low concentration of EDTA, an aqueous substitution takes place for all ions on account of the M–TTA complex formation, so the extraction efficiency is decreased by a gradual increase in the concentration of EDTA, the calcium ion interacts with it to leave the HTTA molecules to form M(TTA) and the adduct species. An increase of the extraction percent could be explained on the basis of the rate of exchange between Ca-EDTA chelate and the trivalent ions. The rate constant of exchange is opposite the sequence of complex stability constants, and the rate constants exhibit a minimum at holmium, for example (17).

In order to emphasize the calcium ion role in our synergistic extractant system, a preequilibrated HTTA + TOA (0.1 M and 1%) mixture in benzene was employed to extract the mentioned REE in the absence of the calcium concentration used, without and with EDTA addition. Decreases of extraction percent and selection have been observed with nearly no effect on EDTA addition (Table 4).

TABLE 3
Effect of EDTA Addition on the Extraction Efficiency at [0.01 M HTTA + 1% TOA] in Benzene

EDTA [M]	La (%)	Nd (%)	Y (%)	Tm (%)	Lu (%)
0.0005	0	9	42.5	43.4	56.5
0.001	0	6.7	57.5	62.8	68.5
0.005	17.1	60.8	100	100	100

TABLE 4
Effect of EDTA Addition on the Extraction Efficiency at [0.01 M HTTA + 1% TOA] in Benzene from 0.01 M HNO_3 (in the absence of calcium ion)

	La (%)	Nd (%)	Y (%)	Tm (%)	Lu (%)
Without EDTA	5.9	7.1	15.5	14.1	22.7
0.001 M EDTA	4.7	11.6	36	32.3	34

CONCLUSION

Selective extraction of REE from calcium nitrate/nitric acid medium can be made by synergistic extraction of 0.01 M HTTA + 1% TOA in benzene.

The presence of calcium ion (8.3 g/L) enhances the extraction of heavy rare earths rather than light rare earths by this system.

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