Extraction of Tb(III) with *N,N,N',N'*-tetrabutylmalonamide

SUN GUOXIN[1*], CUI YU[2], JIANG RUNTIAN[1], XU RONGQI[1] and SUN SIXIU[3]

[1]*Institute of Chemistry and Environmental Engineering, Jinan University, Jinan, 250022, P. R. China,*
[2]*Institute of Chemical Engineering, Jinan University, Jinan, 250022, P. R. China, and*
[3]*Institute of Chemistry, Shandong University, Jinan, 250100, P. R. China*

Abstract: The study on the extraction and separation of rare earths with new extractants is important in rare earth hydrometallurgy and nuclear fuel reprocessing. In this work, a new synthesis method of *N,N,N',N'*-tetrabutylmalonamide (TBMA) is described with a yield higher than 80 %. The extraction behavior of TBMA employing *n*-hexane-20 % *n*-octanol, benzene and toluene as diluents toward Tb(III) was investigated. The effect of the concentrations of nitric acid, lithium nitrate and extractant as well as the temperature on the extraction distribution ratio was studied in different diluents. The stoichiometry of the extracted species of Tb(III) conforms to $Tb(NO_3)_3 \cdot 3TBMA$. An attempt was made to determine the structure of the extracted species from IR and mol conductance data.

Keywords: synthesis, *N,N,N',N'*-tetrabutylmalonamide, extraction, Tb(III), diluent, structure.

INTRODUCTION

Amides have been proposed as promising alternate extractants to TBP in nuclear fuel reprocessing.[1,2] In addition to their improved extraction behavior toward actinides and fission products, these extractants offer distinct advantages over TBP, especially with respect to their complete incinerability (which helps in reducing the bulk of secondary nuclear waste), and the innocuous nature of their radiolytic degradation products (mainly carboxylic acids and amines) that can easily be washed out.
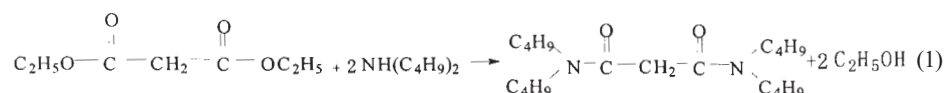
To partition the minor actinides (Np, Am, Cm) from the high level waste (HLW), a diamide process has been developed in France. However, the separation of Am (III) from Ln (III) is essential in this separation process.[3] Then it is worthy to study the extraction behavior or Ln(III) with amidic extractants from nitrate media.

The present paper reports a new one-step method to prepare *N,N,N',N'*-tetrabutylmalonamide (TBMA). Studies were carried out to investigate its extraction behavior toward Tb(III) under varying conditions. The stoichiometry of the extracted species of Tb(III) was evaluated. The effect of the diluent on the extraction behavior was also investigated.

EXPERIMENTAL

Synthesis and characterization of TBMA

TBMA was synthesized by reacting di-*n*-butylamine with malonic ester, according to the reaction:

$$C_2H_5O-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-OC_2H_5 + 2\,NH(C_4H_9)_2 \longrightarrow \underset{C_4H_9}{\overset{C_4H_9}{N}}-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-N\underset{C_4H_9}{\overset{C_4H_9}{}}+2\,C_2H_5OH \quad (1)$$

In a 500 ml reaction vessel flushed with nitrogen gas 80 ml malonic ester (0.53 mol) and 220 ml of di-*n*-butylamine (1.29 mol). The temperature was raised slowly to the boiling point and maintained at reflux for about eleven hours. After cooling to room temperature, 500 ml toluene was added and the solution was first washed with alkali (10 % by weight Na_2CO_3) and then hydrochloric acid (1.2 mol/L). The obtained crude reaction mixture was dried over anhydrous sodium sulfate and then vacuum distilled, the product boiling at 158–160 ºC at 10 mm Hg. The yield was around 80 %, which is much higher than the two-step method involving the reaction of the acyl chloride obtained from malonic acid with a secondary amine.[4] The product is 98 % pure as shown by ^{1}H-NMR spectroscopy element analysis and non-aqueous potentiometric titration.

Preparation of the Tb(III) solution

1.6492 g Tb_2O_3 was dissolved in HNO_3 solution, and the solution was then evaporated to dryness. The residue was dissolved in 7.57 mol dm^{-3} nitric acid solution (26.41 ml) and diluted to 200 ml. The obtained solution contains 5.00×10^{-2} mol dm^{-3} Tb^{3+} and 1.00 mol dm^{-3} HNO_3. The series of 5.00×10^{-3} mol dm^{-3} Tb^{3+} solutions were then prepared by quantitative dilution.

Extraction of Tb(III) with TBMA

In Tb(III) distribution studies, solutions of desired concentrations of TBMA prepared in various diluents, such as 80 % *n*-hexane-20 % *n*-octanol, toluene and benzene, were employed after pre-equilibration at the respective acidities. Equal volumes of the organic and aqueous phases were agitated for 40 min (enough for equilibrium) at 25 ºC 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 concentration of the sample was determined using the Arsenazo-III spectrophotometric method and that in organic phase was obtained by subtracting the aqueous concentration from the total aqueous concentration of Tb(III). The distribution ratio (*D*) was calculated as the ratio of the concentration of the organic phase to that of the aqueous phase.

Characterization of the extracted species

The extracted species was prepared. The TBMA solution was shaken with a saturated solution of $Tb(NO_3)_3$, centrifuged and the organic phase separated. The organic solvent was removed and the residual was recrystallized from xylene.

FTIR spectra were recorded on an FTS-165 Spectrometer in the range 400–4000 cm^{-1}. KBr window cells were used. The scan times were 50 and the resolution was 2 cm^{-1}.

The conductance ratio was obtained with a DDS-11A conductometer employing DMSO as the diluent.

RESULTS AND DISCUSSION

Effect of nitric acid concentration on the extraction distribution ratio of Tb(III)

The extraction of Tb(III) from nitric acid solution in the range of 1.0–8.0 mol dm^{-3} was investigated. The results show that the extractability of TBMA for Tb(III) at higher HNO_3 concentration is very poor which may be due to the extraction of HNO_3.[5] Subsequently, the aqueous HNO_3 concentration was controlled at 0.10 mol dm^{-3} to avoid hydrolysis of the metal ions in the following experiments.

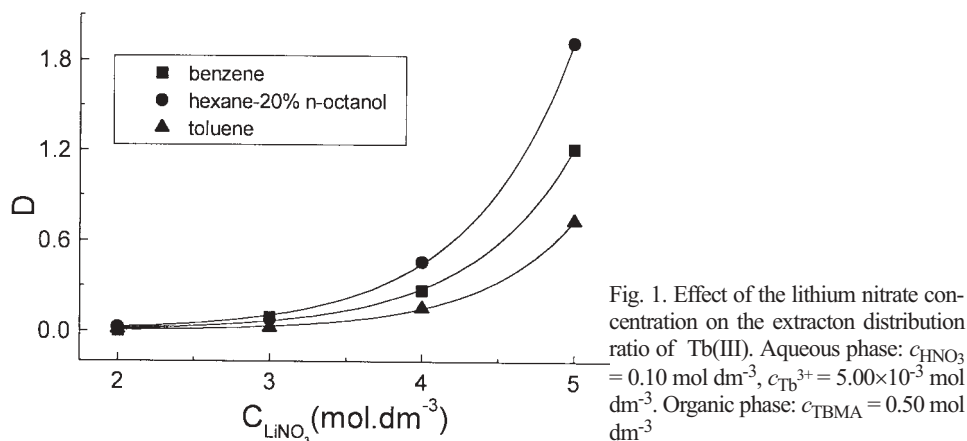*Effect of lithium nitrate concentration on the extraction distribution ratio of Tb(III)*

Fig. 1. Effect of the lithium nitrate concentration on the extracton distribution ratio of Tb(III). Aqueous phase: c_{HNO_3} = 0.10 mol dm^{-3}, $c_{Tb^{3+}}$ = 5.00×10^{-3} mol dm^{-3}. Organic phase: c_{TBMA} = 0.50 mol dm^{-3}

The effect of the lithium nitrate concentration on the extraction distribution ratio of Tb(III) is shown in Fig. 1. The distribution ratio of Tb(III) increased significantly with increasing LiNO$_3$ concentration in which the co-ion effect plays a crucial role. The extractability of TBMA for Tb(III) is in the order: *n*-hexane–20 % *n*-octanol > benzene > toluene. This behavior shows that the molecules of the extracted species have a higher polarity or ion nature than the unextracted species and are more stable in polar solvents.

Effect of TBMA concentration on the extraction distribution ratio of Tb(III)

The effects of the extractant concentration in various diluents on the extraction distribution ratio of Tb(III) are compared in Fig. 2 which shows the dependence of the extraction distribution ratios of Tb(III) on the TBMA concentration in different diluents. The plots of log D *vs.* log c_{TBMA} gave slopes of about 3 in all the employed diluents, which indicates that the stoichiometry of extracted species in the different diluents is the same and is Tb(NO$_3$)$_3$·3TBMA. Thus, the extraction reaction can be represented by

$$Tb^{3+} + 3NO_3^- + 3TBMA_{(o)} = Tb(NO_3)_3 \cdot 3TBMA_{(o)} \qquad (2)$$

for which the equilibrium constant, K_{ex}, is

$$K_{ex} = \frac{[Tb(NO_3)_3 \cdot 3TBMA]_{(o)}}{[Tb^{3+}][NO_3^-]\ [TBMA]^3_{(o)} \gamma_{Tb^{3+}} \gamma^3_{NO_3^-}} = \qquad (3)$$

$$= \frac{D(1 + \beta_1[NO_3^-])}{[NO_3^-]^3 [TBMA]^3_{(o)} \gamma_{Tb^{3+}} \gamma^3_{NO_3^-}}$$

where the subscript (o) refers to the species present in the organic phase, β_1 is the coordination constant of Tb^{3+} and NO$_3^-$ and is equal to 1.3±0.05.[6] The NO$_3^-$ and Tb^{3+} ions activity
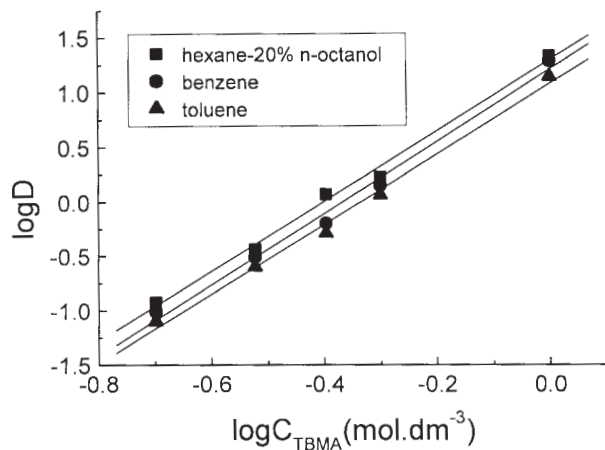
Fig. 2. Effect of the TBMA concentration in various diluents on the extraction of Tb(III) Aqueous phase: $c_{HNO_3} = 0.10$ mol dm^{-3}, $c_{Tb^{3+}} = 5.00\times10^{-3}$ mol dm^{-3}, $c_{LiNO_3} = 5.00$ mol dm^{-3}

coefficients are constant in the study of the effect of the TBMA concentration on the extraction distribution ratio of Tb(III). Then let

$$K'_{ex} = K_{ex} \cdot \gamma_{Tb^{3+}} \gamma^3_{NO_3^-} = \tag{4}$$

$$= \frac{D(1+\beta_1[NO_3^-])}{[NO_3^-]^3[TBMA]^3_{(o)}}$$

The values of K'_{ex}, calculated from Eq. (4), are 1.00 ± 0.05, 0.88 ± 0.04, 0.65 ± 0.04 mol^{-6} dm^6 for *n*-hexane– 20 % *n*-octanol, benzene and toluene, respectively.

Distribution studies as a function of temperature

The effect of temperature on the extraction equilibrium is shown in Fig. 3 which indicates that the distribution decreases with increasing temperature in all the diluent systems.

Here, log *D* were plotted as a function of $1/T$ and these were found to be straight lines in the temperature range studied. The data were subjected to least-squares analysis using a
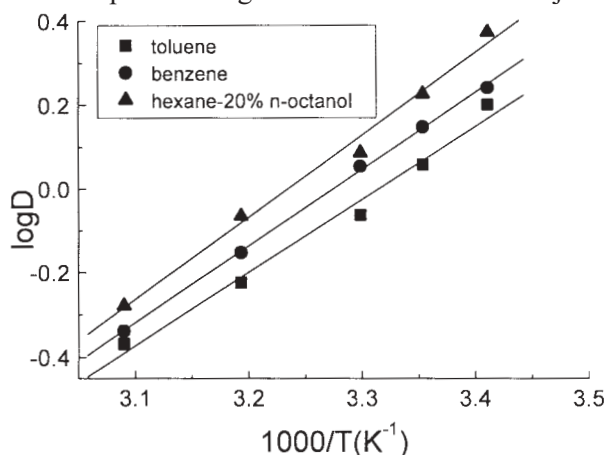

Fig. 3. Effect of temperature on the extraction equilibrium. Aqueous phase: $c_{HNO_3} = 0.10$ mol dm^{-3}, $c_{Tb^{3+}} = 5.00 \times 10^{-3}$ mol dm^{-3} Organic phase: $c_{TBMA} = 0.50$ mol dm^{-3}.

computer program and from the obtained values of the slopes, the change in enthalpy, ΔH, in each case was evaluated using the Van't Hoff's equation:

$$\Delta H = -2.303 \, R \frac{\partial \log D}{\partial (1/T)} \tag{5}$$

The values of ΔH for the extraction of Tb(III) with TBMA in different diluents, such as n-hexane –20 % n-octanol, benzene and toluene, were –37.49, –34.94, –33.26 kJ/mol, respectively.

Structure characterization of the extracted species

The IR spectrum of Tb(NO$_3$)$_3$·3TBMA is shown in Fig. 4.

Compared with the IR spectrum of the extractant, the free carbonyl absorption peak has disappeared and a new one at 1616.07 cm^{-1} has appeared in the IR spectrum of the extracted species. This band can be attributed to the interaction between the complexed amide in the inner sphere which established that TBMA is complexed with Tb(III) through its C=O. It is said that there are a couple of peaks at about 1300 cm^{-1} and 1500 cm^{-1} typical for a coordinated nitrate anion. However, they cannot be designated clearly in these spectra due to the stronger TBMA absorption. A peak corresponding to N–O stretching of a coordinated nitrate anion was observed at 1031.55 cm^{-1}, which indicates that coordinated nitrate anions exist in the extracted species molecules. The peak at 1377.8 cm^{-1} is the absorption peak of free nitrate anions, which shows that free nitrate anions exist in the extracted species molecules.[7]
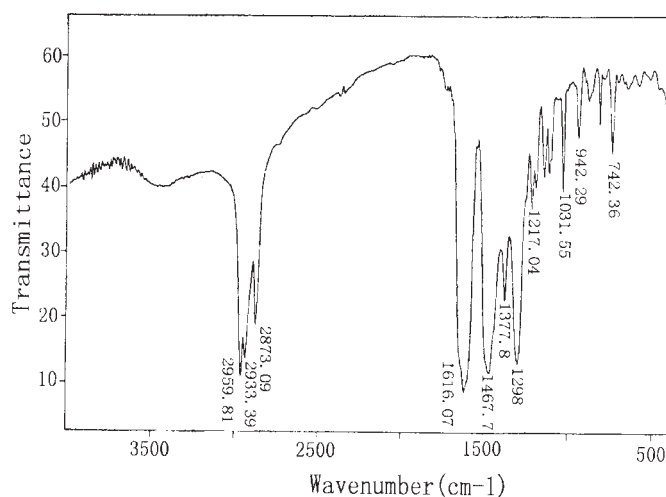

Fig. 4. IR spectrum of Tb(NO$_3$)$_3$·3TBMA.

The determined molar conductance of the extracted species is 142.06 S cm^2 mol^{-1}, which is bigger than the value of 130 S cm^2 mol^{-1}. This indicates that one of the three nitrate anions in the extracted species molecules is coordinated and the other two are dissociated.[8]

Chelated coordination is the normal mode for coordination of nitrate anions with the rare earth ions.[9,10] So the structure of the extracted ionic species can be expressed as shown in Fig. 5:
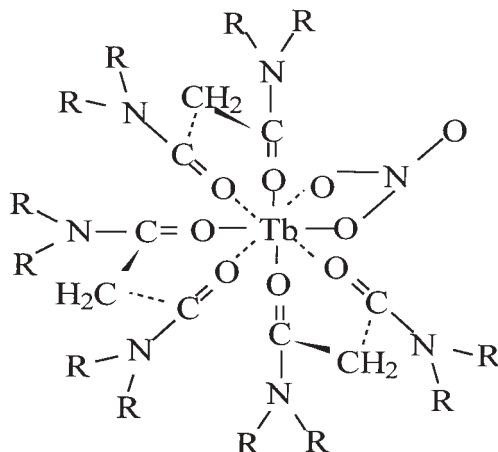

Fig. 5. The structure of the extracted ionic species.

where R = C_4H_9. This kind of extracted species structure make it more stable and more extractable in more polar diluents. This is consistent with the results of the diluent effect on the extraction.

CONCLUSION

TBMA may be prepared directly by the reaction of malonic ester with di-*n*-butylamine. The yield decreases if diluent exists in the system. This new method results in higher yields and lower pollution than the normal two-step preparation procedure.

Tb(III) may be extracted with TBMA from nitrate media, but not at higher nitric acid concentrations, to form ionic extracted species [Tb(NO$_3$)·3TBMA](NO$_3$)$_2$. This phenomenon makes possible the easy separation of U(VI)[11] from Tb(III) in nuclear fuel reprocessing.

ИЗВОД

ЕКСТРАКЦИЈА Tb(III) ПОМОЋУ *N,N,N',N'*-ТЕТРАБУТИЛМАЛОНАМИДА

SUN GUOXIN[1], CUI YU[2], JIANG RUNTIAN[1], XU RONGQI[1] и SUN SIXIU[3]

[1]*Institute of Chemistry and Environmental Engineering, Jinan University, Jinan, 250022, P. R. China,* [2]*Institute of Chemical Engineering, Jinan University, Jinan, 250022, P. R. China u* [3]*Institute of Chemistry, Shandong University, Jinan, 250100, P. R. China*

Проучавање екстракције и сепарације ретких земаља важно је са гледишта хидрометалургије ретких земаља и репроцесирања нуклеарног горива. У овом раду описана је нова метода синтезе *N,N,N',N'*-тетрабутилмалонамида (ТВМА) са приносом већим од 80 %. Такође, проучаване су екстракционе особине ТВМА према Tb(III) коришћењем смеше *n*-хексана и 20 % *n*-октанола, или бензена или толуена као дилуента. Проучаван је и утицај концентрације азотне киселине, литијум-нитрата и екстракционог средства, као и температуре, у разли-

читим дилуентима. Стехиометрија екстраховане врсте одговара формули $Tb(NO_3)_3 \cdot 3TBMA$. Покушано је да се структура екстраховане врсте одреди на основу IR спектроскопских података и података о моларној проводљивости.

REFERENCES

1. G. Sun, J. Han, B. Bao, S. Sun, *Radiochim. Acta* **83** (1998) 27
2. M. Weiql, A. Geist, K. Gompper, J. Kim, *Solv. Extr. Ion Exch.* **19** (2001) 215
3. G. Tian, Y. Zhu, J. Xu, *Solv. Extr. Ion Exch.* **19** (2001) 993
4. G. Thiollet, C. Musikas, *Solv. Extr. Ion Exch.* **7** (1989) 813
5. M. C. Charbonnel, C. Musikas, *Solv. Extr. Ion Exch.* **6** (1988) 461
6. C. Atlans, I. Donalde, *J. Inorg. Nucl. Chem.* **41** (1981) 1383
7. J. Wu, *Recent Technology and Application of FT-IR Spectra*, Science and Technoloy Publishing House, Beijing, 1994
8. W. J. Geary, *Coord. Chem. Rev.* **7** (1971) 81
9. Ch. Huang, *Rare Earth Coordination Chemistry*, Science Publishing House, Beijing, 1997
10. P. Byers, M. Drew, M. Hudson, N. Isaacs, C. Madic, *Polyhedron* **13** (1994) 349
11. Y. Sh. Wang, G. X. Sun, *J. Radioanal. Nucl. Chem.* (*Lett.*) **224** (1997) 151.