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SOLVENT EXTRACTION OF THORIUM(IV) ION WITH N,N,N,N-TETRABUTYLSUCCINYLAMIDE FROM NITRIC ACID SOLUTIONS

You-Shao Wang, Chao-Hong Shen, Yong-hui Yang,
Jian-Kang Zhu, Bo-Rong Bao

Institute of Nuclear Research, Chinese Academy of Sciences
P.O. Box 800-204 Shanghai, China

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It was found that N,N,N,N-tetrabutylsuccinylamide (TBSA) in a diluent composed of 50% 1,2,3-trimethylbenzene (TMB) and 50% kerosene (OK) can extract thorium(IV) ion from a nitric acid solution. The results of the extraction study suggested the formation of a 1:4:1 thorium(IV) ion, nitrate ion and N,N,N,N-tetrabutylsuccinylamide complex as extracted species. The related thermodynamic functions were also calculated.

INTRODUCTION

Substituted alkylamides as extractants for actinides have been reported in many papers[1-3]. This kind of compound contains strongly polar C=O groups. Their chelating ability for metal cations is similar to those of

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extractants containing phosphorus. The compounds which contain no phosphorus atoms are important; they do not produce new solid waste because they are completely incinerable. The radiolytic and hydrolytic degradation products (carboxylic acids and amines) are not harmful to the process. They are considered as potential extractants for the reprocessing of nuclear fuel.

This paper discusses systematically the effects of $[HNO_3]$, $[Th^{4+}]$, [TBSA] and temperature on the extracting ability of TBSA for thorium(IV). The extraction reaction mechanism of thorium(IV) from nitric acid medium by TBSA and the related thermodynamic parameters are presented.

EXPERIMENTAL

TBSA was synthesized according to Stanley et al.[4]. The purity of the distilled product was checked by elemental analysis, IR and NMR spectroscopy. The purity of the product was higher than 98%. A typical extraction procedure was as follows: 0.5 ml of the aqueous phase which contained a certain amount of thorium(IV) ion and HNO_3 was shaken with 1 ml of the organic phase containing a given concentration of TBSA for 10 min, which was preequilibrated with a suitable nitric acid solution. The diluent was composed by of 50% 1,2,3-trimethylbenzene and 50% kerosene. Samples of both phases were analyzed immediately after phase separation. The concentration of thorium(IV) ion was determined by the chlorphosphonazo-mA spectrophotometric method[5], and then the distribution coefficient of thorium(IV) ion was calculated.

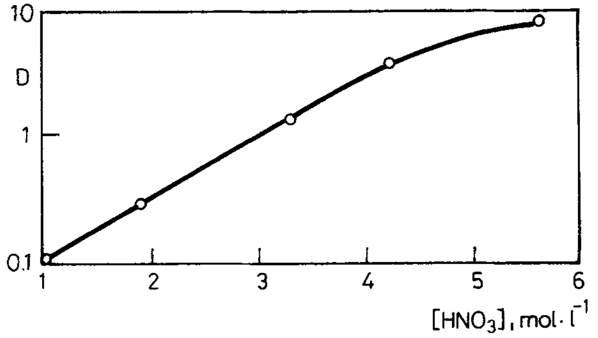


Fig. 1. Correlation between $lgD_{Th^{4+}}$ and $[HNO_3]$ at 25 °C. $[Th^{4+}] = 5.29 \times 10^{-3}$ mol/l, [TBSA] = 0.05 mol/l

RESULTS AND DISCUSSION

Figure 1 shows the effect of the concentration of HNO_3 on the distribution coefficient of thorium(IV) ion in the two phases. Accompanied with an increase in the concentration of HNO_3, the distribution coefficient of thorium(IV) increases in the region of our study. When the concentration of HNO_3 surpasses 4 mol/l, the curve shows that there is a maximum, which is due to the competition of thorium(IV) ions and HNO_3 for the coordination sites of TBSA.

Figure 2 illustrates the effect of thorium(IV) ion concentration on the distribution coefficient of thorium(IV) ion between the two phases. The distribution coefficient of Th^{4+} is an almost horizontal straight line with an increase in the concentration of thorium(IV) ion until a concentration of 8×10^{-3} mol/l.

Figure 3 indicates the effect of TBSA concentration on the extraction of thorium(IV) ion. The $lgD_{Th^{4+}}$ values increase linearly with the increasing concentra-

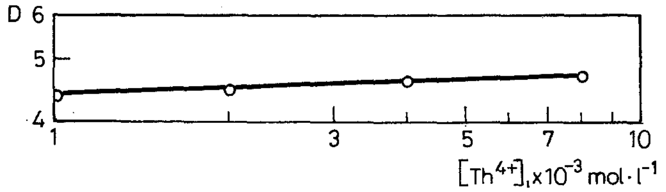


Fig. 2. Correlation between lgD$_{Th}$4+ and lg [Th^{4+}] at 25 °C. [TBSA] = 0.5 mol/l;[HNO$_3$] = 3.5 mol/l

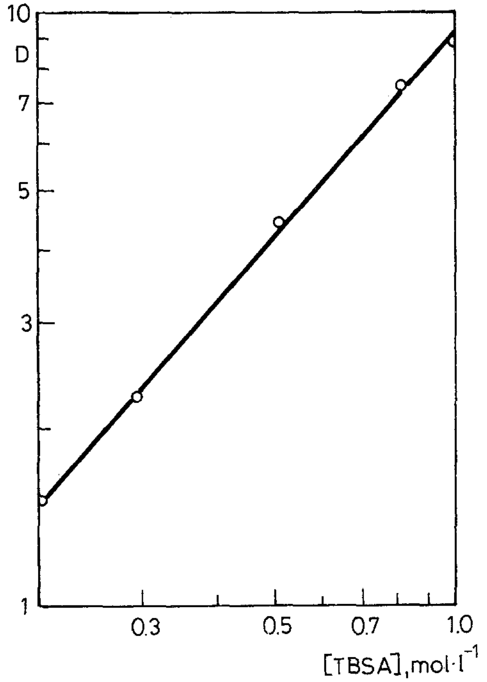


Fig. 3. Correlation between lgD$_{Th}$4+ and lg [TBSA] at 25 °C. [Th^{4+}] = 5.00x10^{-3} mol/l; [HNO$_3$] = 3.5 mol/l

tion of TBSA, and the slope is 1.1. This result shows that the binding ratio of TBSA with thorium(IV) ion is 1:1. The results illustrate that the concentrations of HNO$_3$ and TBSA are the main factors which can affect the

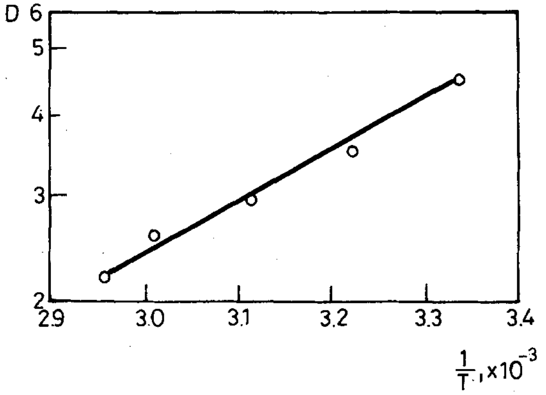


Fig. 4. Correlation between $\lg D_{Th^{4+}}$ and $\frac{1}{T}$. $[Th^{4+}]$ = 5.00×10^{-3} mol/l: [TBSA] = 0.5 mol/l; $[HNO_3]$ = 3.5 mol/l

distribution coefficient of thorium(IV) ion. The extraction data indicate that TBSA is equally good for the extraction thorium(IV) ion from nitric acid medium when compared with TBP and N,N-dialkylamide[6].

Figure 4 illustrates the effect of temperature on the distribution coefficient of thorium(IV) ion. The $\lg D_{Th^{4+}}$ values increase linearly with the increase of $\frac{1}{T}$. This result shows that the extraction of thorium(IV) ion from the aqueous phase to the organic phase is an exothermic process and the enthalpy of Th^{4+} extraction is -17.56 kJ/mol.

In these extraction studies, TBSA in the organic phase was in a large excess compared with thorium(IV) ion in the aqueous phase. The results suggest that a 1:4:1 complex of thorium(IV) ion, NO_3^- and TBSA was extracted into the organic phase. Thus, the extraction reaction of the present system can be expressed by Eq. (1)

$$Th^{4+}_{(aq)} + 4NO^-_{3(aq)} + TBSA_{(org)} = Th(NO_3)_4 \cdot TBSA_{(org)} \quad (1)$$

Then, the extraction constant (K_{ex}) can be defined as

$$K_{ex} = [Th(NO_3)_4 \cdot TBSA]_{org}[Th^{4+}]_{aq}^{-1}[NO_3^-]_{aq}^{-4}[TBSA]_{org}^{-1} \qquad (2)$$

and Eq. (2) can be rearranged as

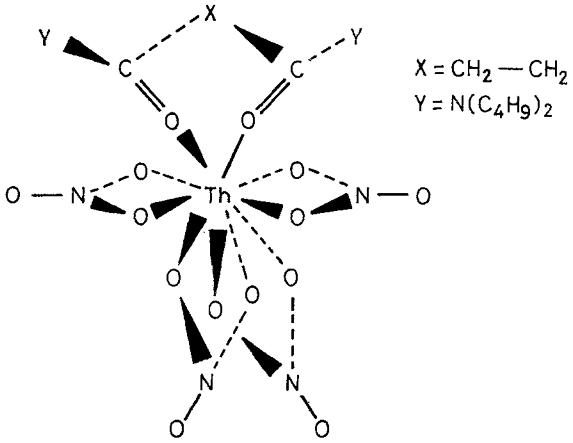
$$K_{ex} = D_{Th}[NO_3^-]_{aq}{}^{-4}[TBSA]_{org}^{-1} \qquad (3)$$

or

$$lgD_{Th} = lgK_{ex} * 4lg[NO_3^-]_{aq} + lg[TBSA]_{org} \qquad (4)$$

According to Eq. (4)([HNO_3] = 3.5 mol/l, [NO_3^-] = 3.26 mol/l[7]; the conditions of [TBSA] and [Th^{4+}] for calculating K_{ex} see Fig. 3), the value of K_{ex} (50% TMB + 50% OK) was evaluated to be 0.081 ± 0.006.

The suggested structure of the 1:4:1 complex which consisted of Th^{4+}, NO_3^- and TBSA can be expressed as follows:



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