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The separation of trivalent actinides from lanthanides by dithiophosphinic acids from HNO_3 acid medium

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Abstract

The extraction of Am(III) and Eu(III) has been investigated using mixtures of synthesized aromatic dithiophosphinic acids (R_2PSSH) and tributylphosphate (TBP), trioctylphosphine oxide (TOPO) or tributylphosphine oxide (TBPO) in toluene from nitric acid (0.01–1.5 mol l^{-1}). There was no detectable extraction when R_2PSSHs were used alone as extractants for either Am(III) or Eu(III) ($D_{Am,Eu}<10^{-4}$) under the experimental conditions used in this study. High separation factors ($D_{Am}/D_{Eu}>20$) with $D_{Am}>1$ were achieved in the nitric acid range 0.1–1 mol l^{-1} by means of a synergistic mixture of bischlorodithiophosphinic acid with TBP, TOPO or TBPO. © 1998 Elsevier Science S.A.

Keywords: Solvent extraction; Actinides lanthanides separation; Dithiophosphinic acids

1. Introduction

The hazard potential of radioactive waste could be drastically reduced by separating the long-lived transuranic elements and their subsequent transmutation into short-lived or even stable nuclides [1]. Since the high-level liquid waste (HLLW) contains considerable amounts of lanthanides, which affect the efficiency of transmutation due to their high neutron absorption cross-sections, it is advisible to previously separate these lanthanides. The chemical separation of trivalent actinides (An) from lanthanides (Ln) is still one of the most difficult separation processes due to the great chemical and physical similarity of the two element groups. Problems are particularly posed by the identical oxidation states and the approximately equal ionic radii of the metals [2].

It is well known that extractants containing so-called soft donor atoms (N or S) have a certain selectivity for transplutonides(III). It is assumed that this effect can be explained by a greater complex stability (metal–ligand covalent bonding or steric effects) between the transplutonides and the soft donor ligands [3,4]. Recently, Zhu et al. [5,6] reported that they had obtained very high Am(III)/Eu(III) separation factors using purified Cyanex 301, whose main constituent is bis(2,2,4-trimethylpentyl)dithiophosphinic acid. On the other hand, Jarvinen et al. [7] showed that a separation with purified Cyanex 301 is only possible using tributylphosphate as the synergist.

In view of these contradictory results, we performed a study in which the results obtained by Zhu et al. [5] were confirmed for the first time. Purified Cyanex 301 shows a very high selectivity for Am(III) and Cm(III) over lanthanides(III). However, we have also been able to demonstrate that the purity level of Cyanex 301 has a considerable influence on actinide(III)/lanthanide separation, especially if tracer amounts ($<10^{-5}$ mol l^{-1}) of An(III) and Ln(III) are used [8,9]. It has also been shown in this study that irradiated Cyanex 301 only changes its extraction behavior insignificantly up to gamma doses of 10^5 Gy.

Of disadvantage, however, is the relatively high pH range of 3–4 in which this process works. Consequently, the pH value must be controlled or stabilized by a buffer during separation, especially if real waste solutions and Am(III) concentrations $>10^{-3}$ mol l^{-1} are involved. On the basis of the positive results on the separation of An(III) and Ln(III) with the aid of Cyanex 301, we investigated this substance class in more detail and synthesized significantly more acidic diorganyldithiophosphinic acids with the intention of achieving an An(III)/Ln(III) separation at pH values below 2.

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2. Experimental

2.1. Synthesis of aromatic dithiophosphinic acids

The bisphenyldithiophosphinic acid, $(C_6H_5)_2PS(SH)$, was prepared according to the procedure reported by Higgins et al. [10]. We also produced in a similar procedure bis(chlorophenyl)- and bis(fluorophenyl)dithiophosphinic acid [11]. The yields were between 50 and 70%. The three compounds were solids and could be recrystallized from isopropanol (purity >99.5% according to ^{31}P-NMR).

2.2. Radiation stability

The radiolytic stability of bis(chlorophenyl)- and bisphenyldithiophosphinic acid was tested by gamma irradiation in the cooling pond of the DIDO research reactor at the Research Centre Jülich. The gamma dose rate was approx. 4000 Gy h^{-1}. For the ^{31}P-NMR investigations approx. 100 mg of solid dithiophosphinic acid was irradiated with a total dose of 4×10^4, 1×10^5, 5×10^5 and 1×10^6 Gy.

2.3. Extraction experiments

The synergist ligands tributylphosphate (Aldrich, p.a. quality), TOPO (Merck, p.a. quality) and TBPO (Aldrich, p.a. quality) were used as received without further purification. Variable concentrations of aromatic dithiophosphinic acids and synergist were dissolved in toluene (Burdick & Jackson, distilled in glass) as the diluent. The radiotracers ($<10^{-7}$ mol l^{-1}) ^{152}Eu(III) and ^{241}Am(III) (Blaseg Isotopendienst) were added from a stock solution simultaneously to the aqueous phase, which consists only of HNO_3 (0.01–1.5 mol l^{-1}). Equal volumes (2 ml) of phases were contacted for 10 min at room temperature (21°C). After centrifuging, an aliquot of 1 ml was sampled from both phases for analyses using a high-purity germanium spectrometer system (EG and G Ortec). The distribution ratio *D* was obtained as a ratio of the count rates in the organic phase to that in the aqueous phase.

3. Results and discussion

According to Zhu et al. [6] the following extraction mechanism is proposed for the extraction of Am(III) and Eu(III) with Cyanex 301, bis(2,4,4-trimethylpentyl)dithiophosphinic acid (HA).

$$M^{3+} + 2(HA)_{2org} \leftrightarrow MA_3(HA)_{org} + 3H^+ \quad M = Am, Eu. \tag{1}$$

It can be seen from Eq. (1) that the extraction equilibrium also depends on acid strength. It should therefore be possible to carry out an An(III)/Ln(III) separation at pH values below 3 with the more acidic aromatic dithiophosphinic acids. The pK_a values of bisphenyldithiophosphinic acid (pK_a = 2.70±0.2), bis(chlorophenyl)- (pK_a = 2.70±0.2) and bis(fluorophenyl)dithiophosphinic acid (pK_a = 2.62±0.4) determined by potentiometric titration are lower than that of Cyanex 301 (pK_a = 2.87±0.3). This can be explained by the −M effect of the benzene ring.

In contrast to Cyanex 301, the aromatic extractants did not dissolve well in nonpolar solvents such as *n*-dodecane. For this reason, all extraction experiments were carried out with toluene. The first investigations were carried out with $(C_6H_5)_2PS(SH)$ and, surprisingly, no extraction of Am(III) and Eu(III) ($D_{Am,Eu} < 10^{-4}$) from 1 M $NaNO_3$ took place at an equilibrium pH of 1.6. After adding TBP, on the other hand, a selective extraction of Am(III) from HNO_3 acid solutions took place. This is in contrast to Cyanex 301, which extracts Am(III) selectively over Eu(III). The extraction results with bisphenyl-, bis(chlorophenyl)- and bis(fluorophenyl)dithiophosphinic acid using TBP as the synergist from 0.01 to 0.4 mol l^{-1} nitric acid are shown in Fig. 1.

It can be seen that the extraction ratios of Am(III) and also Eu(III) strongly increase in the order $(C_6H_5)_2PS(SH) < (F - C_6H_4)_2PS(SH) < (Cl - C_6H_4)_2$-PS(SH). However, the selectivity in the investigated acidity range decreases in the same order with Am/Eu separation factors of 230–280, 41–57 and 28–31. This suggests that the extraction can be improved by incorporating even stronger electron-attracting groups (such as NO_2 or two Cl groups), whereas selectivity inversely decreases.

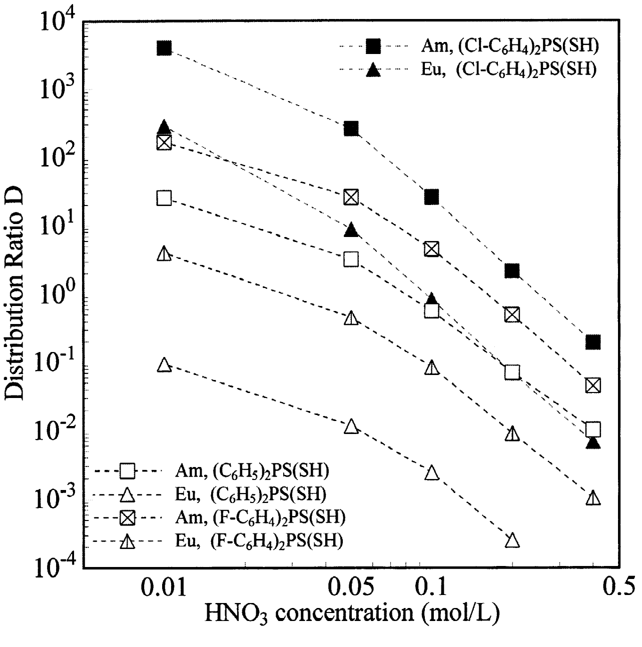

Fig. 1. Extraction of trace amounts of Am(III) and Eu(III) with 0.5 M dithiophosphinic acid and 0.25 M TBP in toluene from HNO_3.

Of course, this also has an adverse effect on reextraction (stripping), which is then only possible with strongly acid HNO_3 (>1 M).

The influence of the TBP concentration and of the extractant concentration during the extraction of Am(III) and Eu(III) with bis(chlorophenyl)dithiophosphinic acid from 0.2 M HNO_3 is shown in Fig. 2. It can be seen that the Am(III) distribution ratio only continues to increase slightly at extractant concentrations >0.5 M. The optimum TBP concentration ranges between 0.1 and 0.25 M, where Am/Eu separation factors between 90 and 31 are achieved. No extraction is observed without TBP.

We furthermore investigated the synergistic effect with various neutral triorganylphosphates and phospine oxides. Using mixtures of 0.25 M trimethyl or triphenylphosphate and 0.5 M bis(chlorophenyl)dithiophosphinic acid as the extractant, for example, no extraction of Am(III) and Eu(III) ($D_{Am,Eu} < 10^{-3}$) from 0.2 M HNO_3 was observed. On the other hand, we observed a selective extraction of Am(III) with a distribution ratio D_{Am} of 2 and a high Am/Eu separation factor of >1000 under the same conditions using tris(2-ethylhexyl)phosphate as the synergist. Obviously, the selectivity is caused by steric hindrance. At the phase boundary, however, a white voluminous precipitate was observed, which made phase separation difficult and was presumably caused by coextracted HNO_3 or H_2O. Therefore, no further investigations were carried out.

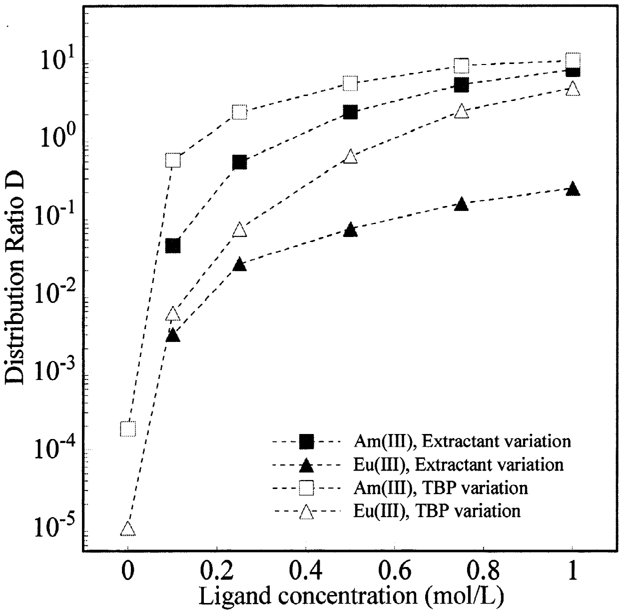

Fig. 2. Extraction of trace amounts of Am(III) and Eu(III) with bis(chlorophenyl)dithiophosphinic acid from 0.2 M HNO_3. For $(Cl–C_6H_4)_2PS(SH)$ variation the TBP concentration was 0.25 M. For TBP variation the $(Cl–C_6H_4)_2PS(SH)$ concentration was 0.5 M.

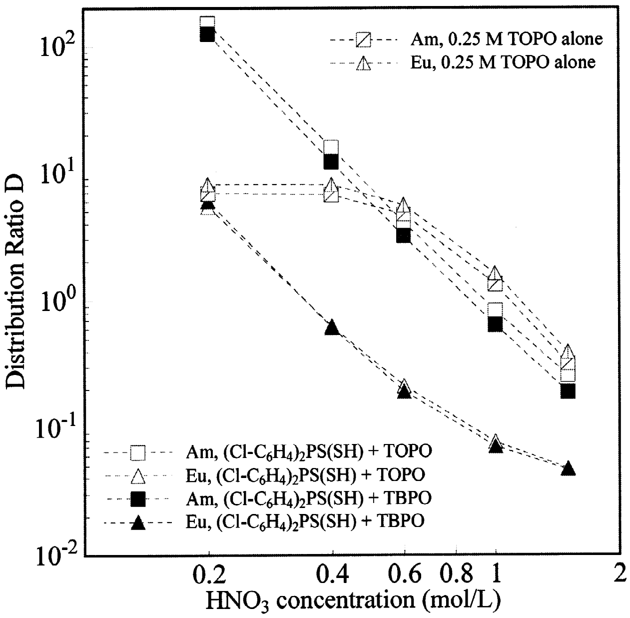

Fig. 3. Extraction of trace amounts of Am(III) and Eu(III) with 0.5 M bis(chlorophenyl)dithiophosphinic acid and 0.25 M tri-*n*-octyl- (TOPO) or tri-*n*-butylphosphine oxide (TBPO) in toluene from HNO_3. The comparison with 0.25 M TOPO in toluene.

The best results so far have been achieved with the synergistic combination of bis(chlorophenyl)dithiophosphinic acid and trioctylphosphine oxide (TOPO). Similar results were obtained with tributylphosphine oxide (TBPO). As can be seen from Fig. 3, the Am(III) distribution ratios increase by approx. two orders of magnitude compared to TBP (e.g., $D_{Am,TOPO} = 152$ and $D_{Am,TBP} = 2$, respectively, for 0.2 M HNO_3) with comparable Am/Eu separation factors of approx. 30. The synergistic effect becomes even more apparent (Fig. 3) when comparing the extraction of Am(III) and Eu(III) using only TOPO, a typical hard donor extractant, which cannot discriminate between Am(III) and Eu(III). At acid concentrations <0.6 mol l^{-1} HNO_3, $D_{Am(mixture)}$ increases and $D_{Eu(mixture)}$ decreases in comparison to $D_{Am,Eu(TOPO\ alone)}$. On the other hand, it was observed for acid concentrations >0.6 mol l^{-1} that the Am(III) distribution ratio is comparable ($D_{Am(mixture)} = D_{Am(TOPO\ alone)}$) and that of Eu(III) ($D_{Eu(mixture)} < D_{Eu(TOPO\ alone)}$) clearly decreases so that a separation takes place.

As can be seen from Fig. 4, the Am/Eu separation factors increase with decreasing TOPO concentrations. However, as in the case of using tris(2-ethylhexyl)phosphate as the synergist, a precipitate was formed at TOPO concentrations <0.2 mol l^{-1}. This problem may perhaps be solved by using another solvent or adding a modifier, such as TBP.

An important aspect for partitioning is the irradiation behavior of the extractant. The extent of the radiolytic degradation of bisphenyl- and bis(chlorophenyl)dithiophosphinic acid was first determined by estimating the residual extractant content using quantitative ^{31}P-NMR. Only slight decomposition (<2%) was observed after a high gamma dose of 1×10^6 Gy. This shows that the aromatic

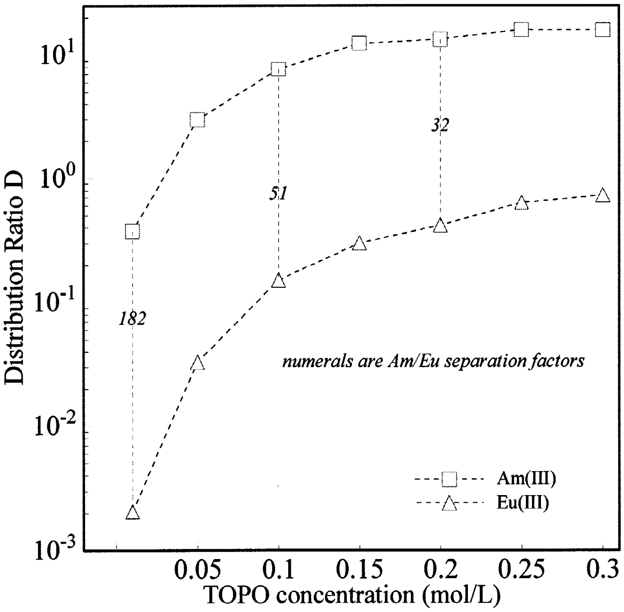

Fig. 4. TOPO dependency for Am(III) and Eu(III) extraction with 0.5 M bis(chlorophenyl)dithiophosphinic acid in toluene from 0.4 M HNO_3.

dithiophosphinic acids are clearly more stable than the dialkyl compound Cyanex 301. At the same dose of 1×10^6 Gy more than 80% of the Cyanex 301 had decomposed, forming approx. 6.3% Cyanex 302 (monothioderivate), 5% Cyanex 272 and a balance of undefinable compounds [8].

4. Conclusion

This study has shown that it is possible to carry out the difficult An(III)/Ln(III) separation with high selectivity even in strongly acid medium (up to 1 M HNO_3) using aromatic dithiophosphinic acids and TBP or TOPO as the synergist. The high radiation resistance of the extractant was also demonstrated. We therefore believe that it will be possible with this extraction system to process An(III)/Ln(III) fractions originating from process solutions of the partitioning of high-level liquid waste (e.g., from TRUEX, TRPO or the DIAMEX process).

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