

A kinetic study on the extraction of americium (III) into CyMe₄-BTBP

Andreas Geist¹, Daniel Magnusson¹, Udo Müllich¹, Giuseppe Modolo²

¹Karlsruhe Institute of Technology, Karlsruhe, Germany,

²Forschungszentrum Jülich GmbH, Institut für Energie und Klimaforschung, Germany

Abstract

Extraction and stripping rates for the system Am (III) – NO₃⁻/CyMe₄-BTBP – TODGA – diluent were studied in a stirred cell. The very low extraction and stripping rates could be accelerated by adding TODGA or by replacing the 1-octanol diluent with cyclohexanone. Furthermore, extraction rate seems to correlate with the concentration of nitric phase in the organic phase. The use of a glycolate solution as stripping phase yields very high back extraction rates.

Introduction

CyMe₄-BTBP, 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-1,2,4-triazin-3-yl)2,2'-bipyridine [1][2] is the current European reference molecule for the separation of trivalent actinides from lanthanides. It is used in SANEX [3] and CHALMEX [4] processes developed in the framework of EUROPART [5] and ACSEPT [6]. Unfortunately, the extraction of Am (III) into CyMe₄-BTBP has slow kinetics which can be improved by adding a second extracting agent, presumably acting as a phase catalyst.

We studied extraction and stripping kinetics using the INE stirred cell [7] for the system Am (III) – NO₃⁻/CyMe₄-BTBP – TODGA – diluent. Rates for the extraction of Am (III) from 1 mol/L HNO₃ were measured as a function of concentrations (CyMe₄-BTBP, TODGA, nitric acid, and nitrate) and interfacial area. Also, cyclohexanone was used as diluent and compared with 1-octanol, the standard diluent. Am (III) stripping rates into dilute HNO₃ or into a glycolate solution were also measured.

Experimental

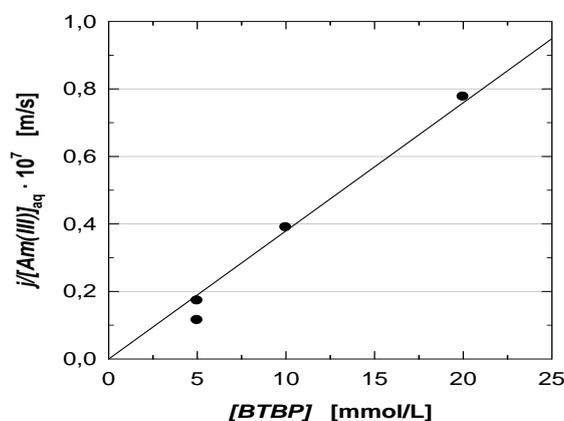
CyMe₄-BTBP was synthesised according to [2]. TODGA was synthesised according to [8]. Stirred cell experiments were performed as described in [7], however, samples were drawn and analysed for ²⁴¹Am (III) activity. Furthermore, phases were pre-equilibrated before being used in the stirred cell. All experiments were performed with aqueous and organic phase stirring speeds of $n = 300/\text{min}$ and at a temperature of $T = 20\text{ C}$.

Results and discussion

Extraction

The low extraction rates reported below imply that mass transfer is controlled by the rate of the chemical reaction while diffusion does not contribute to the overall mass transfer resistance (in a system with diffusive control, extraction rates would be in the range of $3 \cdot 10^{-5}\text{ m/s}$ for $n = 300/\text{min}$ [9]). This allows for studying the kinetics of the chemical reaction. With an organic phase consisting of CyMe₄-BTBP in 1-octanol, Am (III) extraction rate increases first order with [CyMe₄-BTBP], (see Figure 1).

Figure 1: Influence of BTBP concentration on Am(III) extraction rate organic phase, CyMe₄-BTBP in 1-octanol, aqueous phase, Am(III) in 1 mol/L HNO₃



Varying the nitrate concentration (1–3 mol/L) at a constant HNO₃ concentration of 1 mol/L has a small effect on Am (III) extraction rate, see Figure 2 (circles). This agrees with similar findings for *n*-Pr-BTP [7]. In contrast, Am (III) extraction rate increases approximately first order with HNO₃ concentration (triangles), which is quite different from results regarding *n*-Pr-BTP [7]. No quantitative conclusions can be drawn from these results but it seems that the HNO₃ concentration in the organic phase plays a significant role. This is in agreement with results from molecular dynamics calculations [10], showing that protonated BTBP is more surface active than unprotonated BTBP. In this way protonation would increase the BTBP concentration at the interface, which is the site of the chemical reaction (see below); extraction rate would increase accordingly, see Figure 1.

When TODGA is added to the solvent, Am (III) extraction rate increases and becomes practically independent of [CyMe₄-BTBP]. Adding 5 mmol/L TODGA [11] [12] increases Am (III) extraction rate by almost one order of magnitude. Extraction rate increases first order with TODGA concentration, as demonstrated by the open symbols and dashed regression line in Figure 3 which are corrected for the extraction rate for [TODGA] = 0.

Figure 2: Influence of HNO₃ or NO₃⁻ concentration on Am(III) extraction rate organic phase, 10 mmol/L (circles) or 20 mmol/L (triangles) CyMe₄-BTBP in 1-octanol, aqueous phase, Am(III) in (1 mol/L HNO₃+NH₄NO₃) (circles) or HNO₃ (triangles)

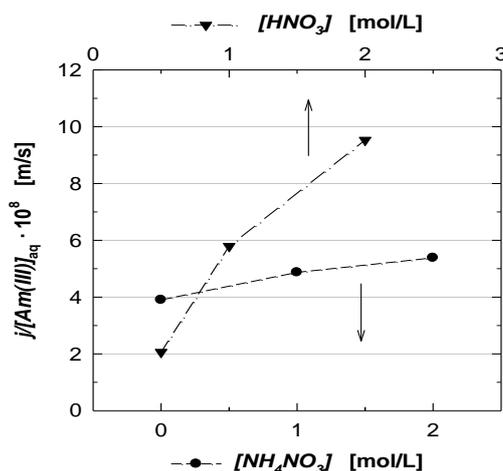
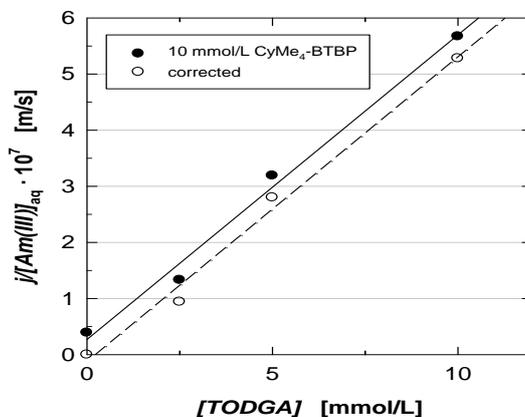
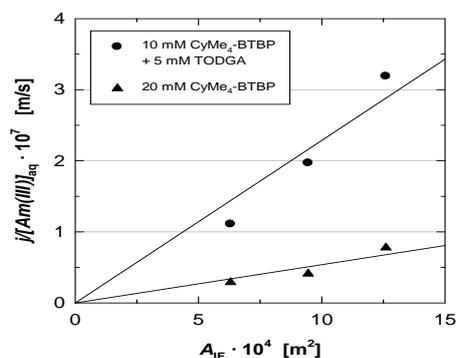


Figure 3: Influence of TODGA concentration on Am(III) extraction rate organic phase, 10 mmol/L CyMe₄-BTBP + TODGA in 1-octanol, aqueous phase, Am(III) in 1 mol/L HNO₃



Reducing the interfacial area with a baffle [7] to 75% and 50% Am (III) results in decreasing Am (III) extraction rates. Extraction rate increases first order with interfacial area (see Figure 4) both for CyMe₄-BTBP and for (CyMe₄-BTBP+TODGA) in 1-octanol, meaning that the rate determining chemical reaction is located at the interface.

Figure 4: Influence of interfacial area on Am(III) extraction rate organic phase, as indicated, aqueous phase, Am (III) in 1 mol/L HNO₃



Replacing 1-octanol with cyclohexanone has a positive kinetic effect, as already observed in shaking tube kinetic experiments [13]. For the extraction of Am (III) from 1 mol/L HNO₃ into different solvents, the following extraction rates were measured:

- $3.9 \cdot 10^{-8}$ m/s (10 mmol/L CyMe₄-BTBP in 1-octanol);
- $5.7 \cdot 10^{-7}$ m/s (10 mmol/L CyMe₄-BTBP + 10 mmol/L TODGA in 1-octanol);
- $7.4 \cdot 10^{-7}$ m/s (10 mmol/L CyMe₄-BTBP in cyclohexanone).

When using cyclohexanone (c) instead of 1-octanol (a) Am (III) extraction rate increases by a factor of approx. 20 and is even slightly higher than that for an organic phase containing 10 mmol/L TODGA in 1-octanol (b).

Stripping

Rates for stripping Am (III) from an organic phase [loaded with Am (III) by extracting from 0.01 mol/L HNO₃+2 mol/L NH₄NO₃] were measured (see Table 1). TODGA also accelerates stripping into dilute HNO₃ by approx. an order of magnitude. However, stripping into 0.5 mol/L glycolate solution (pH = 4) results in an even higher stripping rate, in agreement with batch kinetic tests [2]. The Am (III) stripping rates (except for stripping into glycolate solution) are below 10^{-6} m/s indicate chemical regime. However, the stripping rate into glycolate solution indicates a significant diffusive influence [7].

Table 1: Am (III) stripping rates

Organic phase	Aqueous phase	Stripping rate
10 mmol/L CyMe ₄ -BTBP in 1-octanol	0.05 mol/L HNO ₃	$2.7 \cdot 10^{-8}$ m/s
10 mmol/L CyMe ₄ -BTBP + 10 mmol/L TODGA in 1-octanol	0.05 mol/L HNO ₃	$4.6 \cdot 10^{-7}$ m/s
10 mmol/L CyMe ₄ -BTBP + 10 mmol/L TODGA in 1-octanol	0.5 mol/L ammonium glycolate pH = 4	$2.5 \cdot 10^{-6}$ m/s

Note: Organic phase loaded from phases as indicated.

Conclusions

CyMe₄-BTBP's slow Am (III) extraction and stripping kinetics were confirmed and quantified in stirred cell experiments. Both with and without TODGA, the rate limiting step for the extraction of Am (III) into CyMe₄-BTBP in 1-octanol is located at the interface. TODGA acts as a phase transfer catalyst, contributing to the extraction mechanism and increasing the rate of the rate determining step. Cyclohexanone seems to have a similar effect.

The trends for the extraction and stripping of Am (III) observed in this study are in good agreement with results for the extraction and stripping of Eu (III) from a kinetic study performed in a rotating membrane cell [14].

Acknowledgements

The financial support of the Commission of the European Community (project ACSEPT, FP7-CP-2007-211 267) is acknowledged.

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