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Journal of Alloys and Compounds 271–273 (1998) 159–162

Journal of ALLOYS AND COMPOUNDS

Trivalent minor actinides/lanthanides separation, using organophosphinic acids

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Abstract

The present paper compares the abilities of purified Cyanex 301, Cyanex 302 and Cyanex 272 acids to extract and separate ^{241}Am from ^{152}Eu. Very high separation factors were observed when using Cyanex 301 acid after its purification through the precipitation of its ammonium salt in benzene. Some studies on synergistic mixtures, containing both purified Cyanex 301 acid and tri-*n*-butylphosphate (TBP), are also described. The stoichiometry of the adducts extracted in the organic phase was estimated through slopes analyses: unexpectedly, different results were observed for ^{241}Am(III) and for ^{152}Eu(III). © 1998 Elsevier Science S.A.

Keywords: Actinides; Lanthanides; Separation; Cyanex 301

1. Introduction

Concerning the reprocessing of nuclear spent fuel, the separation of trivalent minor actinides (americium and curium) from lanthanides is a key step in the 'Partitioning and Transmutation' strategy. Zhu et al. [1] have demonstrated that purified Cyanex 301 acid was able to separate ^{241}Am from ^{152}Eu with a tremendously high selectivity (S.F.$_{\mathrm{Am/Eu}}$~5900). Besides, Jarvinen et al. [2] have studied Cyanex 301 acid and other dialkyldithiophosphinic acids in synergistic mixtures with neutral solvating compounds (e.g.: TBP) and have shown the existence of mixed adducts.

2. Experimental

Commercial batches of Cyanex 272, 301 and 302 acids (see Fig. 1) usually contain some inorganic and organic impurities (ranging from 12% to 23% molar) which lower their selectivity. That is why Cyanex 272 and 302 acids were purified following the procedure described by Jarvinen et al. [2], based on the extraction of zinc from diluted sulphuric acid, leading to a final purity exceeding 95%. Cyanex 301 acid, on the other hand, was purified by several crystallisations of its ammonium complex in benzene (procedure proposed by Zhu et al. [1]). ^{31}P NMR analyses revealed that its final purity exceeded 99.8%.

Liquid–liquid extraction experiments were carried out using purified Cyanex acids (alone or with neutral extracting agents) dissolved in dodecane as the organic phases and sodium nitrate solutions, spiked with ^{241}Am and ^{152}Eu, as the aqueous phases ($V_{\mathrm{org}}=V_{\mathrm{aq}}=900$ μl). The distribution coefficients of the radionuclides were determined by counting 750 μl samples, withdrawn from both phases at equilibrium: $D_{\mathrm{M}}=\overline{A}_{\mathrm{M}}^{\mathrm{eq}}/A_{\mathrm{M}}^{\mathrm{eq}}$ ($\overline{A}_{\mathrm{M}}^{\mathrm{eq}}$ being the gamma activity of the radionuclide M in the organic phase and $A_{\mathrm{M}}^{\mathrm{eq}}$ in the aqueous phase, at equilibrium).

3. Results and discussion

3.1. ^{241}Am and ^{152}Eu extraction by purified cyanex acids

The extracting properties of the three purified bis(2,4,4-trimethylpentyl)phosphinic acids were compared (Fig. 2). Whereas Cyanex 272 acid (containing two oxygen atoms) always favoured the extraction of europium over that of ^{241}Am, even at trace level, Cyanex 302 acid (containing one oxygen and one sulphur atom) favoured the extraction of europium only when the latter was in macro concentrations in the aqueous solutions. In the case of tracer tests, the distribution coefficients of americium and europium were very high, and thus, the observed selectivi-

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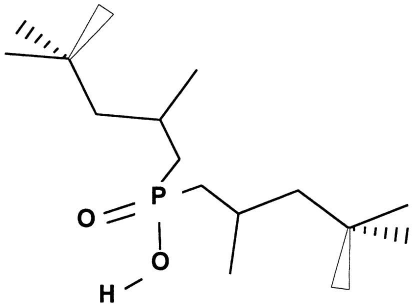
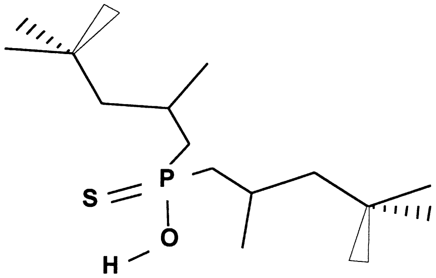
0925-8388/98/$19.00
PII: S0925-8388(98)00045-0



Cyanex 272



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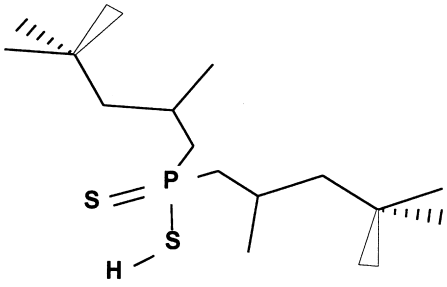


Cyanex 301

Fig. 1. Bis(2,4,4-trimethylpentyl)phosphinic acids.

ty was poor. On the contrary, in the case of purified Cyanex 301 acid, the observed separation factors were the highest ever reported in literature: S.F.$_{\text{Am/Eu}}$~6000 for trace level at pH_{eq}~3.4 and S.F.$_{\text{Am/Eu}}$>30000, when $[\text{Eu(NO}_3)_3]^\circ = 0.1\ \text{mol l}^{-1}$ at pH_{eq}~3.7. The stoichiometry of the complexes, formed in the organic phase with both americium and europium, were determined through slopes analyses.

$$\overline{2(\text{HCyanex})}_2 + \text{M}^{3+} \overset{K_{\text{ex}}}{\leftrightarrows} \overline{\text{M}^{3+}(\text{Cyanex})_3\text{HCyanex}} + 3\text{H}^+$$

where: M = Am or Eu, assuming Cyanex 301 acid to be dimerised in dodecane.

The extraction constants were determined through linear regression of the experimental values (plots of log D_{M} versus pH_{eq} and versus the initial concentration of Cyanex 301 acid), taking into account the possible complexation by nitrate anions in the aqueous phase: $\log K_{\text{ex}}(\text{Am}) = -7.72 \pm 0.07$ and $\log K_{\text{ex}}(\text{Eu}) = -11.42 \pm 0.08$ at 25°C. These values were in good agreement with those published by Zhu et al. [1].

3.2. '^{241}Am/^{152}Eu' separation by synergistic mixtures

As compared to the poor results obtained by Jarvinen et al. [2], a real synergistic effect was observed, both for the extraction of ^{241}Am and ^{152}Eu and for their separation, when purified Cyanex 301 was combined with TBP (Fig. 3). S.F.$_{\text{Am/Eu}}$ was maximum for a molar ratio of 10% TBP in the mixture. Unexpectedly, the stoichiometry of the extracted adducts (estimated through slope analysis), appeared to be different for americium and europium (Table 1). The following extraction equilibria were assumed:

$$\text{Am}^{3+} + 2(\overline{\text{HCyanex}}\ 301)_2 + \overline{\text{TBP}} \leftrightarrows \overline{\text{Am(Cyanex 301)}_3\ \text{HCyanex 301, TBP}} + 3\text{H}^+$$

$$\text{Eu}^{3+} + \text{NO}_3^- + (\overline{\text{HCyanex 301}})_2 + \overline{2\text{TBP}} \leftrightarrows \overline{\text{Eu NO}_3(\text{Cyanex 301})_2\ \text{TBP, TBP}} + 2\text{H}^+$$

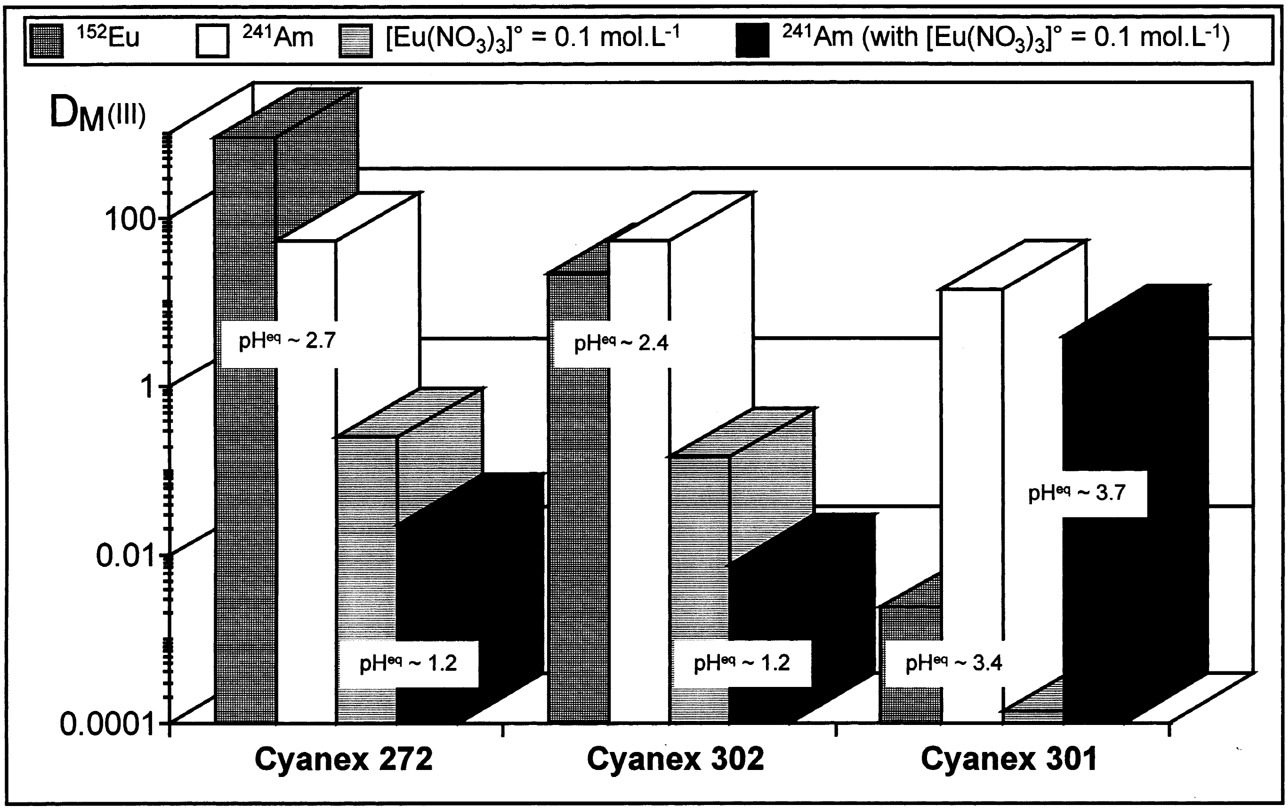
It was furthermore possible to 'modulate' the extraction efficiency and selectivity of purified Cyanex 301 by combining it with other synergists (i.e.: 'TPP', TriPhenylPhosphate, 'DPSO', DiPhenylSulphOxide). Depending on the characteristics of the synergist (charge density, steric hindrance,...), either the distribution coefficients or the S.F.$_{\text{Am/Eu}}$ were increased (Fig. 4).

4. Conclusions

The purification route of commercial Cyanex 301 acid was confirmed. The high S.F.$_{\text{Am/Eu}}$ reported by ZHU et al. [1] was also confirmed. A synergism of both extraction and 'Am/Eu' separation was revealed when using purified Cyanex 301 with neutral extracting agents. Different behaviours were pointed out for americium and europium when using TBP as the synergist. However, the limiting step when extracting trivalent metallic cations from acidic aqueous solutions still remained the dissociation of Cyanex 301 acid (pKa = 2.6). That is why stronger dialkyldithiophosphinic acids should be synthesised and tested in the future.

Acknowledgements

The author wishes to thank Power Reactor and Nuclear Fuel Development Corporation for practical support and Cogema for partly funding this research.



Aqueous phases : $[NaNO_3]° = 1$ mol.L^{-1}; $[Eu(NO_3)_3]° = 0$ or 0.1 mol.L^{-1}; ^{241}Am and ^{152}Eu (tracers)

Organic phases : Purified Cyanex 272 or 302 acid : 1 mol.L^{-1} in dodecane

Purified Cyanex 301 acid : 0.5 mol.L^{-1} in dodecane (temp. = 25 ± 1°C)

Fig. 2. Extraction of ^{241}Am and europium by purified Cyanex acids.

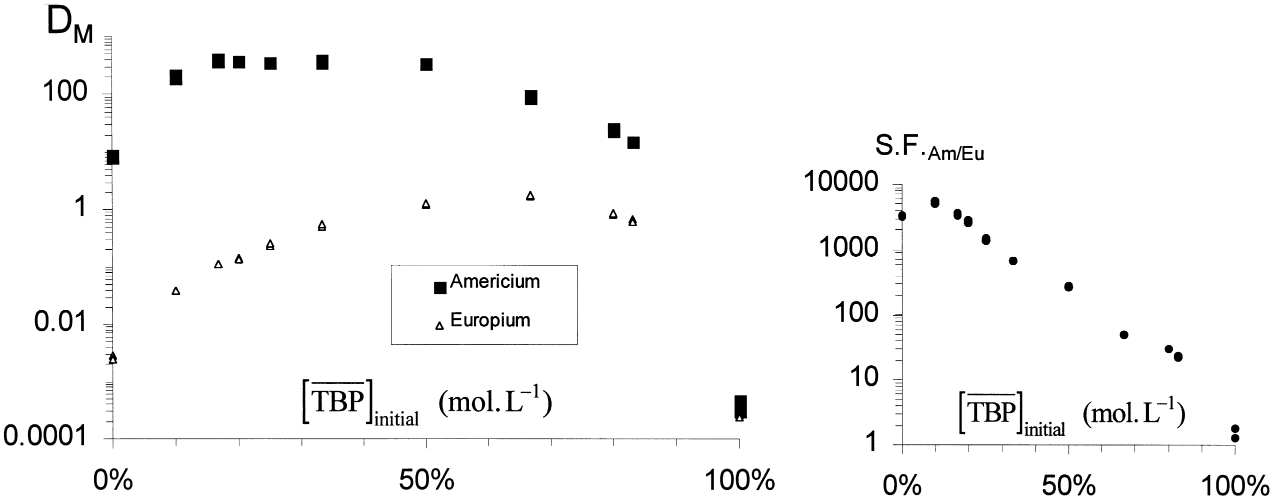
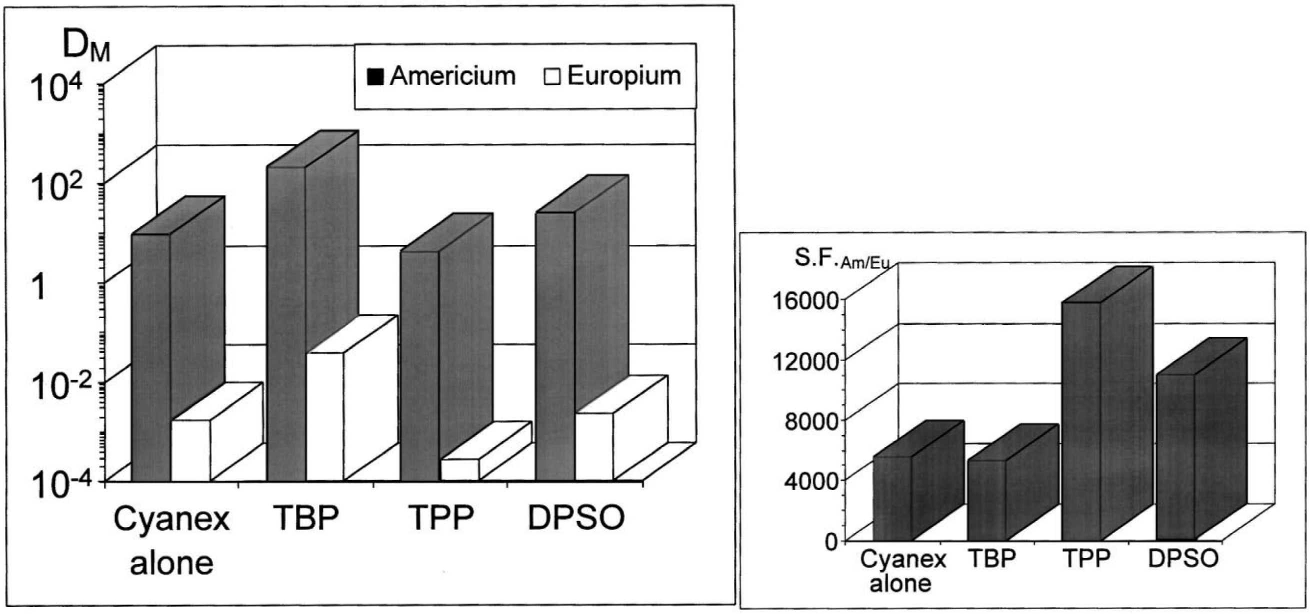


Fig. 3. Extraction of ^{241}Am and ^{152}Eu by synergistic mixtures of Cyanex 301 and TBP.

Table 1
Experimental slopes of the linear variations of log D_{Am} and log D_{Eu} with pH_{eq} and with the initial concentrations of both TBP and dimerised Cyanex 301

Experimental slope	log D_M vs pH_{eq}	log D_M vs log$[(\text{Cyanex 301})_2]_{\text{initial}}$	log D_M vs log$[\text{TBP}]_{\text{initial}}$
^{241}Am	2.8 ($r^2=0.998$)	1.9 ($r^2=0.991$)	0.9 ($r^2=0.986$)
^{152}Eu	2.0 ($r^2=0.990$)	1.2 ($r^2=0.985$)	2.0 ($r^2=0.983$)



Aqueous phase : ^{241}Am & ^{152}Eu (tracers) in $[NaNO_3]° = 0.1$ mol.L^{-1} solutions, buffered with sulfanilic acid (0.02 mol.L^{-1}); $pH_{initial} = pKa = 3.2$

Organic phases : Purified Cyanex 301 (0.54 mol.L^{-1}) and solvating agent (0.06 mol.L^{-1}) in dodecane (temp. = 25 ± 1°C)

Fig. 4. Extraction of ^{241}Am and ^{152}Eu by synergistic mixtures of Cyanex 301 and TBP.

References

[1] Y. Zhu, J. Chen, R. Jiao, Solvent Extract. Ion-exchange 14(1) (1996) 61–68.

[2] G.D. Jarvinen, R.E. Barrans, N.C. Schroeder, K.L. Wade, M.M. Jones, B.F. Smith, J.L. Mills, G. Howard, H. Freiser, S. Muralidharan, in: K.L. Nash, G.R. Choppin (Eds.), Separations of f Elements, Plenum Press, New-York, 1995, pp. 43–62.