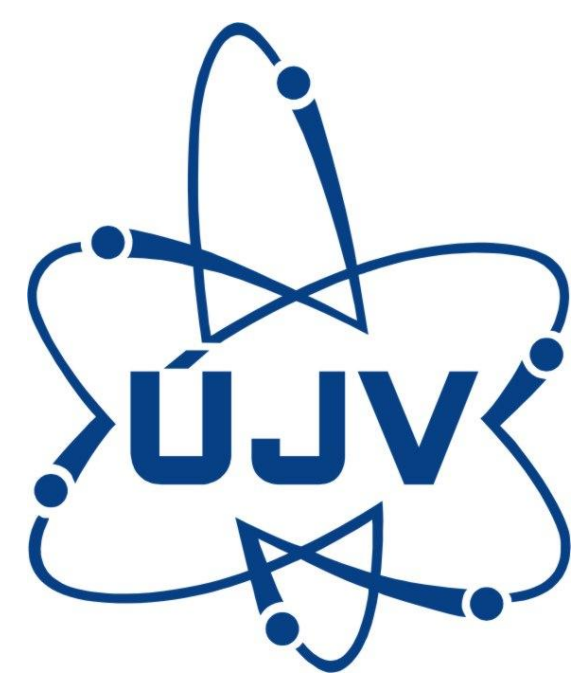


EVALUATION OF COBALT BIS(DICARBOLLIDE) ION DERIVATIVES WITH ATTACHED METAL CHELATING GROUPS FOR THEIR USE IN NUCLEAR WASTE TREATMENT



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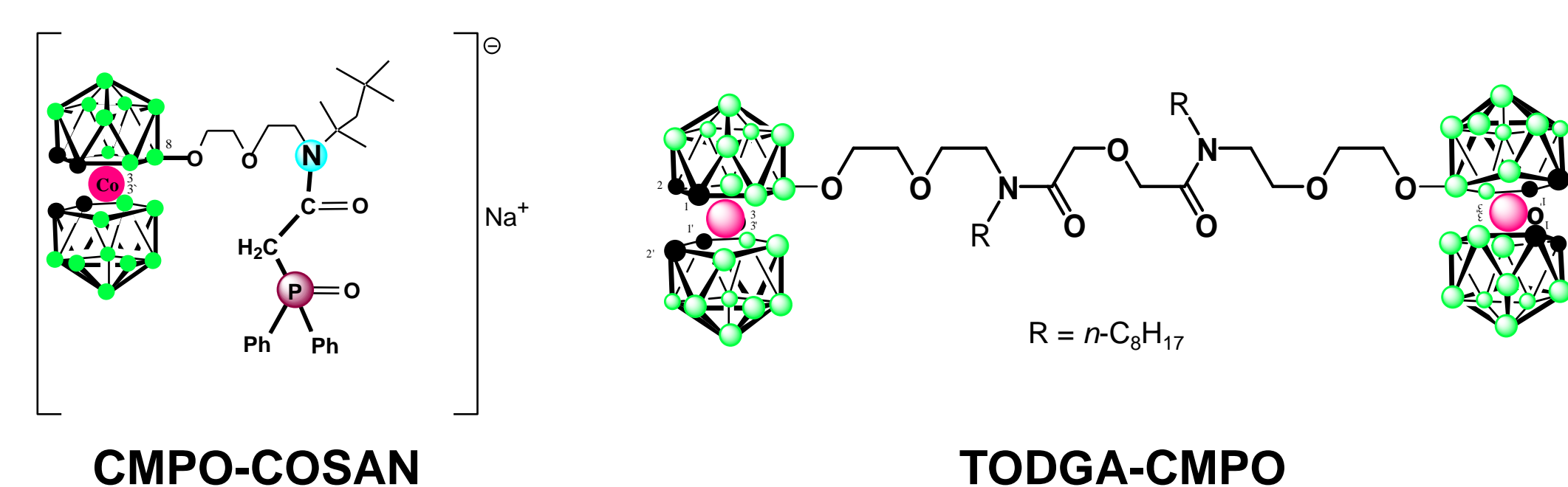
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INTRODUCTION

The nuclear power plants have provided affordable electric energy since 1955. However, they produce spent nuclear fuels, which can be i) stored in deep geological repositories under strict conditions or ii) reprocessed aiming to recover mainly uranium and plutonium (PUREX process) and other dangerous radionuclides, particularly minor actinides (^{241,243}Am, ²⁴⁵Cm, ²³⁷Np), which are responsible for the long-term radiotoxicity of the waste. Several processes have been proposed for separation of minor actinides, e.g. TRUEX, TRPO, DIDPA, TODGA, DIAMEX, SANEX. Recently, we developed alternative separation procedure with usage of cobalt bis(dicarbollide)(1-) [(1,2-C₂B₉H₁₁)₂-3-Co]⁻ (COSAN) covalently bounded with diphenyl-*N*-*tert*-octyl-carbamoyl-methyl-phosphine oxide via diethyleneglycol connector (CMPO-COSAN) or with two COSANs covalently bound to *N,N*-di-*n*-octyl-diglycolic acid diamide platform via diethyleneglycol connectors (TODGA-COSAN) for separations of actinides(III)/lanthanides(III) group from acidic waste solutions. However, the extractants did not provide any selective separation of An(III) from Ln(III) in extraction or in back-extraction step by using complexants. [1, 2]

Therefore the aim of this study was to develop new selective actinides(III) stripping procedure by using different DTPA-sodium nitrate solutions with or without buffers.

Extractants



Extraction tests

The extraction experiments were performed in closed test-tubes using aliquots of each phase (volume ratio 1:1) and shaking for 1 h on a horizontal shaker in a thermostated box at 25 ± 0.1°C. After shaking, the test-tubes were centrifuged and aliquots of each phase (commonly 0.5 mL) were taken for analysis using a single-channel γ analyzer with a NaI (TI) well detector or ICP-MS.

The distribution ratio of metal ion (D_{Me}) was determined as a ratio of the concentration of the metal ion in the organic and aqueous phases.

Separation of Am(III) and fission products from a model PUREX feed

Metal	[M]	Extractant	
		CMPO-COSAN	TODGA-COSAN
Cr	9.5·10 ⁻⁴	< 0.01	0.03
Fe	1.8·10 ⁻²	0.07	< 0.01
Ni	4.5·10 ⁻⁴	< 0.01	0.04
Cu	1.7·10 ⁻⁴	< 0.01	< 0.01
Rb	4.0·10 ⁻⁴	0.03	0.11
Sr	1.0·10 ⁻³	< 0.01	< 0.01
Y	5.6·10 ⁻⁴	0.68	1.01
Zr	5.0·10 ⁻³	< 0.01	< 0.01
Mo	3.6·10 ⁻⁴	0.10	0.08
Ru	2.0·10 ⁻³	0.04	< 0.01
Rh	4.1·10 ⁻⁴	0.08	< 0.01
Pd	1.5·10 ⁻³	> 100	0.16
Ag	7.4·10 ⁻⁵	2.13	2.33
Cd	9.0·10 ⁻⁵	< 0.01	0.07
Cs	2.3·10 ⁻³	< 0.01	0.02
Ba	1.0·10 ⁻³	0.02	< 0.01
La	9.3·10 ⁻⁴	1.16	1.61
Ce	2.2·10 ⁻³	1.50	2.06
Pr	8.6·10 ⁻⁴	1.67	2.03
Nd	2.7·10 ⁻³	1.54	8.78
Sm	5.5·10 ⁻⁴	2.18	1.81
Eu	1.2·10 ⁻⁴	2.00	3.77
Gd	1.4·10 ⁻⁴	1.67	2.20
Am	5.0·10 ⁻⁷	2.42	1.07

0.04M CMPO-COSAN in HMK/TPH (1:1); synthetic feed in 3M HNO₃ (1:1), 0.1 M H₂C₂O₄
0.05M TODGA-COSAN in HMK/D (1:1); synthetic feed in 3M HNO₃ (1:1), 0.1 M H₂C₂O₄, 0.05M HEDTA

Extractant properties

- CMPO-COSAN and TODGA-COSAN are soluble in less polar mixtures of HMK/TPH or HMK/D (1:1), which are ecological and technologically acceptable solvents
- both extractants are sufficiently stable against hydrolysis (in 3M HNO₃)

Separation systems developed previously

- good extraction yield of Am/Ln ($1 < D_{Me} < 9$)
- good separation of Am/Ln from majority of fission products presented in model PUREX feed ($DF_{Am,Ln/Me} > 5$)
- undesired co-extraction of some fission products was suppressed by addition of complexants to the feed
 - the oxalic acid for complexation mainly Zr and Mo
 - HEDTA for complexation mainly Pd
- nonetheless, undesired co-extraction of Ag has not been solved yet
- Am/Ln can be effectively stripped from loaded organic phase by using 0.25M (NH₄)₂H₃DTPA + 1M NH₄ citrate, pH ~ 7 ($D_{Am,Ln} < 0.01$) – no selective actinides separation possible

Selective stripping of actinides

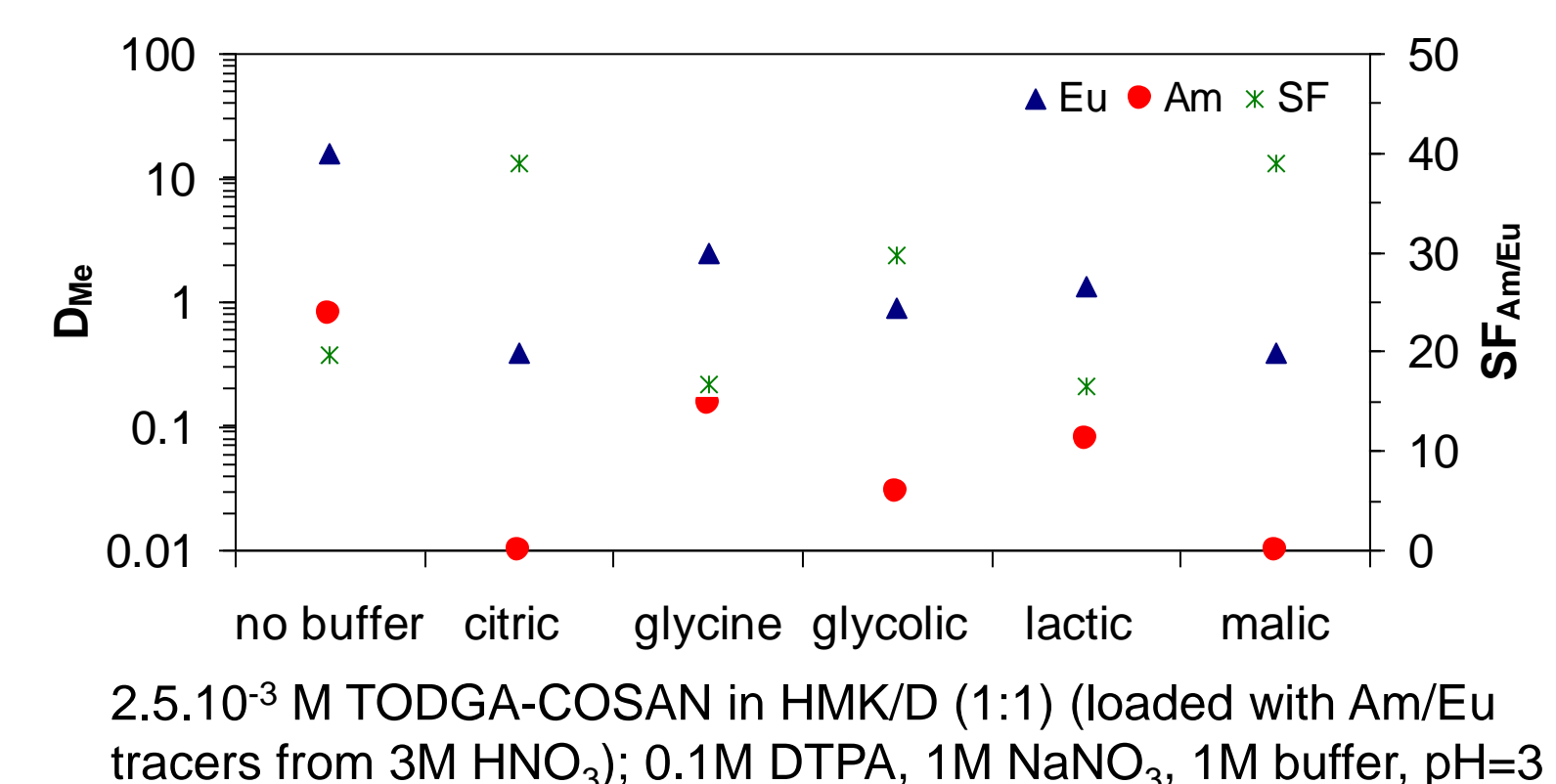
System with CMPO-COSAN

Stripping solution	pH	D _{Am}	D _{Eu}
0.05M DTPA + 1M NaNO ₃	2	> 100	> 100
0.05M DTPA + 1M NaNO ₃	3	> 100	> 100
0.05M DTPA + 1M NaNO ₃	4	> 100	> 100
0.1M DTPA + 1M NaNO ₃	3	> 100	> 100
0.1M DTPA + 1M NaNO ₃	4	3.47	3.96

5.10⁻³ M CMPO-COSAN in HMK/D (1:1) (loaded with Am/Eu tracers from 3M HNO₃); 0.05–0.1M DTPA, 1M NaNO₃, variable pH

- in case of system with CMPO-COSAN, no Am selective stripping was obtained ($SF_{Am/Eu} \sim 1$)
- in case of system with TODGA-COSAN, selective Am stripping was possible ($SF_{Am/Eu} \sim 17$, glycine or lactic acid), however, the stripping was sensitive to pH changes

System with TODGA-COSAN



CONCLUSION

Both extractants, CMPO-COSAN and TODGA-COSAN, enable efficient separation of An(III)/Ln(III) from bulk of fission products presented in simulated PUREX feed.

In case of system with CMPO-COSAN, no selective Am(III)/Eu(III) separation could be achieved. Therefore, the possible use of extractant would lie in envisaged joint extraction of An(III)/Ln(III) groups before the pertinent second step, i.e. the An(III)/Ln(III) separation by another process (e.g. SANEX).

In case of system with TODGA-COSAN, effective Am(III) stripping could be achieved by DTPA solution buffered by glycine or lactic acid. Drawback is the high sensitivity of stripping to pH changes.

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Acknowledgment

We thank for partial financial supports from the Grant Agency of the Czech Republic (Project No. 104/09/0668), from Project LC-523 of the Ministry of Education, and from Research Plan AVOZ40320502 of AS CR.