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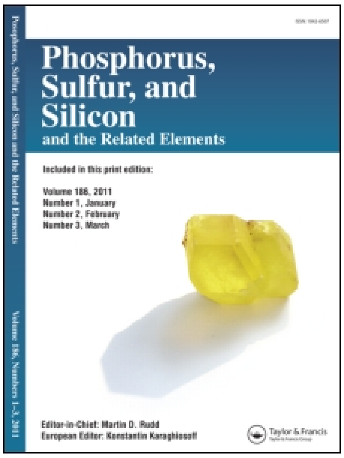

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SYNTHESIS OF DIPHOSPHINE DIOXIDES FOR EXTRACTION OF ACTINIDES USING SUPPORTED LIQUID MEMBRANES TECHNOLOGY

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Abstract A recurrent method for synthesis of linear and macrocyclic diphosphine dioxides has been applied to synthesize new phosphoryl ligands with P-C bonds, stable in strongly acidic aqueous solution and therefore useful for extraction and recovering of actinides from nuclear wastes. The influence of the structural parameters on their liquid-liquid extraction properties of plutonium and neptunium is studied. Plutonium and Neptunium can be removed from radioactive contaminated liquid wastes, using the supported liquid membrane technology with the more lipophilic organophosphorus extractants, which are a promising alternative to the CMPO (a carbamoylmethylphosphine), currently used for such extractions.

Key Words : diphosphine dioxide, actinide, extraction, supported liquid membrane, nuclear wastes.

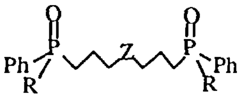
INTRODUCTION

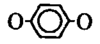
Nuclear fuel reprocessing operations produce medium level activity liquid wastes which are concentrated and disposed of in geological formations after embedding with regard to their activity associated with long-life radionuclides (actinides, strontium, ...).[1] Therefore it would be desirable to remove these very long-life radionuclides from the contaminated liquid wastes before embedding. This would allow these decontaminated wastes to be directed to surface repositories. One chemical separation process could be coupled transport through supported liquid membranes (SLM) using specific carriers.[2,3] Organophosphorus compounds have an exceptional ability for the extraction of hard cations, particularly actinides but monodentate organophosphorus compounds, even the most powerful ones, such as alkyl phosphine oxides only extract actinides (IV), (VI) and to a less extent (V), from low acidity media. Our strategy to improve actinide extracting power, consists in synthesizing cyclic diphosphine dioxides. Macrocycles of this types have been described but specific ways of synthesis are used.[4] It is interesting to dispose of a versatile synthetic method in order to design tailor-made ligands well-fitted to specific metallic cations extraction.

RESULTS AND DISCUSSION

Application Of The Recurrent Synthetic Method

The use of the recurrent method earlier reported [5] allows us a stepwise approach to linear or cyclic organophosphorus extractants more and more efficient, controlling the size, type of bridges between the phosphorus atoms, number, type and position of heteroatoms, number and type of side chains (Figure 1).



Z \ R	Ph	$n\,C_{12}H_{25}$	$(CH_2)_nOR'$
CH_2CH_2	1a	1a1	—
O	1b	1b1	1b2 *
	1c	1c1	1c2 **

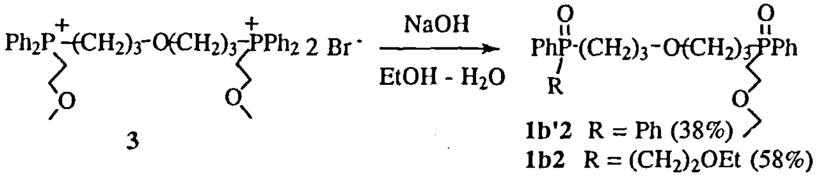
* n = 2, R' = Et ** n = 3, R' = Me

Z \ R		Ph	$n\,C_{12}H_{25}$
O	cis	2ac	2cc
	trans	2at	2ct
		2b***	—

*** mixture of diastereoisomers

Figure 1 Diphosphine dioxides obtained with the recurrent synthetic method.

The recurrent method affords us the possibility to synthesize homologs of Lariat crown-ethers affording additional coordination sites in the side chains which can participate to the complexation of cations.[6] One (**1b'2**) or two (**1b2**) phenyl groups can be substituted by $-(CH_2)_2-OEt$ thanks to the non specificity of clivage of the P-C bond in bis(β-functional)phosphonium salt **3** (Figure 2).[7]



$$Ph_2\overset{+}{P}-(CH_2)_3-O(CH_2)_3-\overset{+}{P}Ph_2\ 2\,Br^- \xrightarrow[EtOH\,-\,H_2O]{NaOH} PhP(O)(R)-(CH_2)_3-O(CH_2)_3-P(O)Ph$$

1b'2 R = Ph (38%)
1b2 R = $(CH_2)_2OEt$ (58%)

FIGURE 2 Alkaline hydrolysis of bis (β–functional)phosphonium salt.

As a range of diphosphine dioxides were obtained, the influence of the structural parameters (bridges between the two phosphoryls, side chains and macrocyclic effect) on extractant properties could be studied.[8]

Extraction Results

The diphosphine dioxides obtained by the recurrent method have been first tested in liquid - liquid extraction of Pu (IV) and Np (V).[8b,c] The results obtained (Table 1) are to be compared with those of octyldiphenylphosphine oxide **4** (monodentate ligand) and to CarbamoylMethylPhosphine Oxide **5**, which is considered till now as the most powerfull extractant of actinides. [9]

	1a	**1b**	**1c**	**1a1**	**1b1**	**1c1**	**1b2**	**1b'2**	**1c2**	**2at**	**2ac**	**2ct**	**2cc**	**4**	**5**
D_{Pu}	0.06	0.11	17	12	20	35	35	14.2	30	0.1	0.5	28	41	0.16	22
D_{Np}	0.6	0.45	1	0.5	0.9	1.2	1.2	1	4.1	0.45	0.35	1.1	1.8	0.19	0.85

Table 1 Distribution coefficients D with extractants 10^{-2} M in NPHE.

The distribution coefficients D_{Pu} are increased by a factor of two when the extractant is cyclic. The replacement of the phenyl group by a less elecronegative alkyl group increased the D_{Pu} and leads to a better solubilization of the extractant in NitroPhenylHexylEther (NPHE). The replacement of a phenyl group by an ether substituent increased the extraction of plutonium, and compounds with two ether substituents are more effective than those with only one. The substitution of a methylene group by an oxygen atom or a hydroquinonic group in the bridge linking the two phosphoryl groups improved the extraction of plutonium; the hydroquinonic group leading to a more effective compound.

Compound **1c1** containing simultaneously alkyl groups linked to phosphoryl groups and the hydroquinonic groups in the bridge is a very effective plutonium extractant owing to the combination of the two effects. It must be noticed that only **2cc**, a macrocyclic compound, is more efficient.

Transport Experiments

The selective solvents used for extraction are often very expensive and thus limit the use of the techniques mentioned above; work was therefore carried out in this study on the use of selective solvents with liquid membranes technology. The use of neutral carriers E such as phosphine oxides leads to the coupled co-transport of cations and nitrate anions through the SLM.[2] When concentrates or fission product solutions are used as the feed solution [NaNO3 (4M), HNO3 (1M)] and demineralized water as the stripping solution, the concentration gradient of the nitrate anions will force the transport of actinide cations Ac^+ against their own concentration gradient, thus leading to increase their concentration in the stripping solution (Figure 3). The transport of ^{237}Np, ^{239}Pu from their synthetic aqueous solutions in $NaNO_3$ (4M) and HNO_3 (1M), was followed by regular measurement of the decrease of radioactivity in the feed solution by α spectrometry analysis. This allowed the determination for the constant permeabilities P

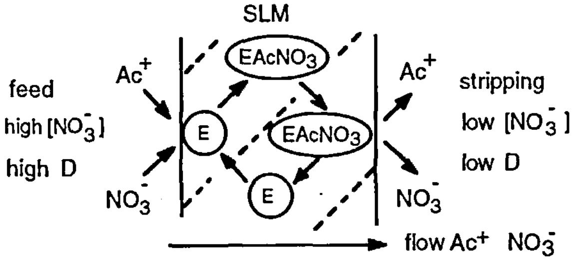


FIGURE 3 Transport Mechanism through SLM

(Table 2) for the actinide permeation through the SLM with the most promising compounds [8b,c] as described in the model of mass transfer proposed by P. Danesi.[3]

	1a1	**1b1**	**1c1**	**1b2**	**1c2**	**2ct**	**2cc**	**5**
P_{Pu}	2.37	2.47	1.95	0.37	0.94	2.17	3	3.44
P_{Np}	0.23	0.62	1.43	0.1	0.1	0.84	0.84	0.74

Table 2 Permeability P ($cm.h^{-1}$) with extractants 10^{-2} M in NPHE.

CMPO **5**, although exhibiting smaller distribution coefficients than **2cc**, is a slightly better carrier for plutonium (IV). In the case of neptunium (V), the hydroquinonic bridged compound **1c1** and to a less extent, macrocyclic compounds **2cc** and **2ct**, are better carrier than CMPO.

CONCLUSIONS

These transport experiments prove the interest of developing bidentate cyclic compounds such as **2cc** or bidentate linear compounds such as **1c1** to achieve the α decontamination on supported liquid membranes. Yet, as diphosphine dioxides are not efficient for the uptake of actininides (III) which are the more difficult to extract, we are developping further a new family of polyphosphine polyoxides whose first extraction results are particularly promising.

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