Mechanism of trivalent actinide/lanthanide separation using synergistic mixtures of di(chlorophenyl)dithiophosphinic acid and neutral O-bearing co-extractants

Galina Ionova,[a] Sergei Ionov,[b] Catherine Rabbe,*[c] Clément Hill,[c] Charles Madic,[c] Robert Guillaumont,[d] Giuseppe Modolo[e] and Jean Claude Krupa[d]

[a] *Institute of Physical Chemistry, Russian Academy of Sciences, Lenin prospect 31, 1107907 GSP-1, Moscow B-71, Russia*
[b] *Kurnakov Institute of General and Inorganic Chemistry, Lenin prospect 31, 1107907 GSP-1, Moscow B-71, Russia*
[c] *CEA Valrhô-Marcoule, DEN/VRH/SCPS, B.P. 17171, 30207 Bagnols/Cèze, France. E-mail: catherine.rabbe@cea.fr*
[d] *Institute de Physique Nucléaire Orsay, Bât. 100, 91406 Orsay cedex, France*
[e] *Institut fur Sichereitsforschung und Reaktortechnik, Forschungszentrum Jülich, Germany*

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The mechanism of synergistic selective extraction of Am(III) over Eu(III) from aqueous nitric acid solutions using di(chlorophenyl)dithiophosphinic acid [$(\mathrm{Cl}\Phi)_2$PSSH] and neutral O-bearing organophosphorus co-extractants (B) has been investigated. $(\mathrm{Cl}\Phi)_2$PSSH forms weaker complexes with Am(III) than R_2PSSH (where R = alkyl group). However, the Am(III)/$(\mathrm{Cl}\Phi)_2$PSSH complexes are stronger than the corresponding Eu(III)/$(\mathrm{Cl}\Phi)_2$PSSH complexes, although the difference is not as large as in the case of the corresponding complexes formed with R_2PSSH. The donor properties of co-extractants are also discussed. Chemical shifts in the ^{31}P NMR spectra of the organophosphorus co-extractants correlate qualitatively with the extractability of Am(III) and Eu(III) in $(\mathrm{Cl}\Phi)_2$PSSH + B synergistic mixtures. The synergistic effect determines the selectivity not only qualitatively but also quantitatively. The high selectivity observed using tri-2-ethylhexyl phosphate (T2EHP) is caused by a synergistic bonding effect for the Am(III) complex and an antagonistic effect for Eu(III).

A donor–acceptor mechanism is shown to promote Am(III) extraction for almost all B co-extractants. A contribution of entropy terms for extracted Eu(III) extraction is assumed to be significant. Interatomic distances $R_{\mathrm{Eu-S}}$ in the Eu(III) complexes are calculated.

The softness of S-bearing extractants XYPSSH (with X and Y = R, RO or $\mathrm{ClC_6H_4}$) is discussed from the point of view of the effective charge carried by the S atoms. The hardness of Eu(III) and Am(III) is evaluated.

Separation of the trivalent actinides/lanthanides [An(III)/Ln(III)] groups is one of the key problems facing any new partitioning and transmutation nuclear waste management strategy being studied worldwide.[1,2] In 1996, Zhu *et al.*[3] demonstrated that sulfur-bearing acidic extractants, R_2PSSH (where R = alkyl group), like Cyanex 301, exhibit extremely high efficiency for such a separation. Am/Eu separation factors ($\mathrm{SF_{Am/Eu}}$) as high as 5900 were obtained. Unfortunately, reasonably high Am(III) distribution ratios (D_{Am}) were only observed for a pH range of 3 to 5, which is not suitable for industrial process development. Attempts to shift the high Am(III) affinity to a practical low aqueous pH range, while maintaining high $\mathrm{SF_{Am/Eu}}$, were then carried out by using Cyanex 301 and O-bearing neutral co-extractants.[4–6] Finally, Modolo *et al.*[7a] were successful in modifying the nature of the substituents on dithiophosphinic acid. When replacing the alkyl groups R in R_2PSSH with electron-withdrawing groups, like phenyl, tolyl or halogen-substituted phenyl groups, synergistic mixtures involving these new dithiophosphinic acids and O-bearing neutral organophosphorus co-extractants were found to be able to extract selectively An(III) over Ln(III) from acidic aqueous feeds ($C_{\mathrm{HNO_3}}$ as high as 1.5 M can be used for the best case). Among the synergistic mixtures studied by Modolo *et al.*,[7a] the best for process development appears to be di(chlorophenyl)dithiophosphinic acid [$(\mathrm{Cl}\Phi)_2$PSSH] and tri-*n*-octylphosphine oxide (TOPO).

In a first paper,[8] we attempted to interpret the mechanism of the An(III)/Ln(III) group separation observed with the synergistic mixture of Cyanex 301 (R_2PSSH) and O-bearing neutral co-extractants. Numerous theoretical chemistry methods were used to interpret the observed An(III)/Ln(III) selectivity. It was demonstrated that high $\mathrm{SF_{Am/Eu}}$ values were due to a covalent effect in the M(III)–S bonds, which was greater for Am(III) than for Eu(III). This covalent effect could be controlled by the donor ability of the O atom of the neutral co-extractant.

The present article pursues the analysis using the data obtained by Modolo *et al.*,[7a] on Am(III)/Eu(III) separation obtained with synergistic mixtures comprising $(\mathrm{Cl}\Phi)_2$PSSH and neutral organophosphorus co-extractants. Table 1 shows the names, acronyms and semi-developed formulae of the acidic S-bearing extractants and the neutral co-extractants (B), while Table 2 gives some of the experimental results obtained by Modolo *et al.*[7a] used as a database for this work. Table 3 presents the experimental data[7a] related to the influence of the nature of the diluent on Am/Eu extraction and separation properties, also used as a database in this study.

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Table 1 Names, acronyms and semi-developed formulae of acidic S-bearing and neutral O-bearing extractants considered in this article

Name	Acronym	Semi-developed formula
Di(chlorophenyl)dithiophosphinic acid	$(Cl\Phi)_2PSSH$	$(ClC_6H_4)_2PSSH$
Bis(2,4,4-trimethylpentyl)dithiophosphinic acid	Cyanex 301 or HA or R_2PSSH	$[(H_3C)_3CCH_2CH(CH_3)CH_2]_2PSSH$
Di(2-ethylhexyl)dithiophosphoric acid	$D_2EHDTPA$	$[H_3C(CH_2)_3CH(C_2H_5)CH_2O]_2PSSH$
Trimethyl phosphate	TMP	$(H_3CO)_3P{=}O$
Tri-*n*-butyl phosphate	TBP	$(H_9C_4O)_3P{=}O$
Tri-*n*-hexyl phosphate	THP	$(H_{13}C_6O)_3P{=}O$
Tri-*n*-octyl phosphate	TOP	$(H_{17}C_8O)_3P{=}O$
Tri-*tert*-butyl phosphate	T*t*BP	$[(H_3C)_3CO]_3P{=}O$
Tri-2-ethylhexyl phosphate	T2EHP	$[H_3C(CH_2)_3CH(C_2H_5)CH_2O]_3P{=}O$
Triphenyl phosphate	TPP	$(C_6H_5O)_3P{=}O$
Triallyl phosphate	TAP	$(CH_2{=}CHCH_2O)_3P{=}O$
Dibutyl butylphosphonate	DB[BP]	$(H_9C_4O)_2(H_9C_4)P{=}O$
Di(2-ethylbutyl) 2-ethylbutylphosphonate	D(EB)[(EB)P]	$[(H_3C)_2CHCH_2CH(CH_3)O]_2(H_9C_4)P{=}O$
Di(4-methylpentyl-2) butylphosphonate	D(4-Mpe-2)[BP]	$[(H_5C_2)_2CHCH_2O]_2[(H_5C_2)_2CHCH_2]P{=}O$
Butyl dibutylphosphinate	B[DBP]	$(H_9C_4O)(H_9C_4)_2P{=}O$
Tri-*n*-butylphosphine oxide	TBPO	$(H_9C_4)_3P{=}O$
Tri-*n*-octylphosphine oxide	TOPO	$(H_{17}C_8)_3P{=}O$
Triphenylphosphine oxide	TPPO	$(H_5C_6)_3P{=}O$
Bis(2,4,4-trimethylpentyl)octylphosphine oxide	BPOPO	$[(H_3C)_3CCH_2CH(CH_3)CH_2]_2(H_{17}C_8)P{=}O$
Tri-isobutylphosphine sulfide	T*i*BPS	$[(H_3C)_2CHCH_2]_3P{=}S$
n-Octyl(phenyl)-*N*,*N*-di-isobutylcarbamoylmethylphosphine oxide	CMPO	$(H_{17}C_8)(C_6H_5)P(O)CH_2C(O)N[CH_2CH(CH_3)_2]_2$
N,*N*′-Di(ethyl-2-hexyl)dimethyl-2,2-butanamide	D2EHDMBA	$(H_3C)_3CCH_2C(O)N[CH_2CH(C_2H_5)C_4H_9]_2$
N,*N*′-Dimethyl-*N*,*N*′-dibutyltetradecylmalonamide	C14	$[(CH_3)(C_4H_9)NC(O)]_2CHC_{14}H_{29}$

Methods

Quantum chemistry calculations were performed with the GAUSSIAN 98 code[9] on a Silicon Graphics bi-processor workstation at CEA/Marcoule. The *ab initio* calculations used a 6-31G* basis set. The molecular geometry of all co-extractants and S-bearing extractants was fully optimized and the Mulliken net atomic charges were computed.

Table 2 Extraction of Am(III) and Eu(III) from aqueous nitric acid (0.2 M) by synergistic mixtures of $(Cl\Phi)_2PSSH$ (0.5 M) and B (0.25 M) in toluene (room temperature) and energy of the visible charge transfer band [$E(S \rightarrow Eu)$] observed for some extracted Eu(III) organic phases[7]

B	$D_{Am(III)}$ [a]	$D_{Eu(III)}$ [a]	$SF_{Am/Eu}$ [b]	$E(S \rightarrow Eu)$/eV
TMP	0.0046	0.000 37	12.3	
TBP	2.13	0.068	31.2	3.08
THP	1.59	0.033	48.3	
TOP	1.06	0.002	687.0	
T2EHP	1.28	0.001	1056.7	
TPP	0.0017	0.000 22	8.1	3.05
TAP	0.477	0.015	32.1	
TBPO	76.52	4.130	18.5	
TOPO	152.25	5.46	27.9	3.12
TPPO	69.5	1.800	38.5	
BPOPO	1.73	0.069	24.7	
T*i*BPS	0.02	0.002	10.2	

[a] $D_M = C_M^{org}/C_M^{aq}$ where C_M^{org} and C_M^{aq} are the M(III) organic and aqueous equilibrium concentrations, respectively. [b] $SF_{Am/Eu} = D_{Am(III)}/D_{Eu(III)}$.

Table 3 Effect of the type of diluent on the extraction and separation of Am(III) and Eu(III) by a synergistic mixture of $(Cl\Phi)_2PSSH$ (0.5 M) and TOPO (0.25 M) (in 0.5 M aqueous nitric acid at room temperature)[7]

Diluent	$D_{Am(III)}$	$D_{Eu(III)}$	$SF_{Am/Eu}$
Toluene	7.19	0.306	23.5
Xylene	8.83	0.385	22.9
tert-Butylbenzene	19.8	0.615	31.2
Tri-*iso*propylbenzene	55.8	1.23	45.6

Results and discussion

Hardness and softness in the separation of Am(III) and Eu(III) with acidic S-bearing extractants

During the last decade, acidic S-bearing extractants, di(2-ethylhexyl)dithiophosphoric acid acid (D2EHDTPA),[10] bis-(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301),[3–5] di(chlorophenyl)dithiophosphinic acid,[7] in synergistic mixtures with various neutral molecules involving a hard oxygen atom, were widely used in liquid–liquid extraction to separate An(III) from Ln(III) and, particularly, Am(III) from Eu(III). Numerous experimental data as well as a theoretical basis (as developed in the first paper of this series[8]) are used in order to briefly review and compare these extractants from the standpoint of their softness, and with respect to the hardness of Am(III) *vs.* Eu(III).

When used alone, the various acidic S-bearing extractants considered here exhibit different Am(III) and Eu(III) extraction abilities, expressed in terms of extraction equilibrium constants, K_{ex}. With $(RO)_2PSSH$ (D2EHDTPA)[10] for MA_3 extracted complexes ($A^- =$ D2EHDTP$^-$) log $K_{ex/Am} = -8.1$ and log $K_{ex/Eu} = -8.3$ where $K_{ex} = K_{ex} = [\overline{MA_3}][H^+]^3[M^{3+}]^{-1}[\overline{HA}]^{-3}$ (organic species are highlighted with an overbar). Using R_2PSSH (Cyanex 301)[5] for $MA_3 \cdot HA$ extracted complexes ($A^- =$ Cyanex 301 anion) log $K_{ex/Am} = -7.72 \pm 0.07$ and log $K_{ex/Eu} = -11.42 \pm 0.08$ where $K_{ex} = [\overline{MA_3 \cdot HA}][H^+]^3[M^{3+}]^{-1}[\overline{(HA)_2}]^{-3}$ with $(Cl\Phi)_2PSSH$[7] no extraction of Am(III) and Eu(III) for aqueous 0.2 M HNO_3 was found. From these results, both Am(III) and Eu(III) can be considered as hard Lewis acids in the complexes with D2EHDTPA, although Am(III) seems to be a significantly softer Lewis acid than Eu(III) in the extracted complexes with Cyanex 301.

The softness character of bases, s_b, corresponding to their ability to donate bonding electrons, is given in the literature.[11] The softness character of acidic S-bearing extractants can also be considered. Their s_b should vary[3–7,10] according to the series: $(RO)_2PSS^- < R(RO)PSS^- < (Cl\Phi)_2PSS^- < R_2PSS^-$. The softness of the PSS^- groups depends significantly on the substituents of the P atoms of these molecules. The oxygen atoms in the RO substituents attract electron density from the S atoms, resulting in decreasing basicity (softness) of the S atoms.

Table 4 Atomic and group charges calculated by *ab initio* quantum chemical methods in $XYPSS^-$ bases (X and Y = alkyl, aryl or alkoxy groups)

	Q(P)	$Q(S)_1$[a]	$Q(S)_2$[a]	Q(PSS)
X = Y = R	+0.743	−0.667	−0.668	−0.592
$X = Y = ClC_6H_4$	+0.730	−0.619	−0.619	−0.508
X = R; Y = OR	+0.943	−0.679	−0.686	−0.422
X = Y = OR	+1.095	−0.683	−0.683	−0.271

[a] The two S atoms of the ligands are almost equivalent, except in the case where X ≠ Y.

Quantum chemical calculations using the 6-31G* basis set are fully consistent with these extraction results for R_2PSSH and $(Cl\Phi)_2PSSH$ extractants: the sulfur atoms in R_2PSS^- have more negative charge than those in $(Cl\Phi)_2PSS^-$, as shown in Table 4. Moreover, the substituents R, RO and ClC_6H_4 significantly change the effective charge on the functional group PSS^-. The softness of the dithiophosphinic acids depends on the effective charge on the PSS^- moiety rather than only on the effective charges on the S atoms. This suggests that the extraction ability of dithiophosphinic acids is not only determined by the M–S bonds but also by the M–P repulsion.

According to a rough conventional view,[12–14] hard cations (acceptors or Lewis acids) coordinate to various hard ligands (donors or Lewis bases) mainly by electrostatic interactions. Conversely, soft cations form covalent bonds with soft ligands. However, the literature demonstrates that hard Ln(III) Lewis acids can be coordinated simultaneously with hard (O) and soft (S) donor atoms[15] in ion-pair complexes such as $\{Ln[(H_5C_2O)_2PSS]_2[TPPO]_2\}^+\{(H_5C_2O)_2PSS\}^-$, where Ln = Nd–Lu, or in neutral complexes of the type $Ln[(H_5C_2O)_2PSS]_3[TPPO]_2$, where Ln = La–Pr.

The coexistence of soft and hard donor atoms in complexes with hard Ln(III) or An(III) Lewis acids is also known in the case of the extraction of Am(III) and Eu(III) by: (i) D2EHDTPA with TBP,[10] (ii) purified Cyanex 301 in synergistic mixtures with TBP, T*t*BP, TPP, TOPO, CMPO, D2EHDMBA and C14[5] and by (iii) $(Cl\Phi)_2PSSH$ with B (Table 2). In ref. 8, it was shown that the mechanism of Am(III) and Eu(III) extraction by R_2PSSH with a hard (O) atom co-extractant B is mainly governed by the change in the nature of the M–S bond owing to the transfer of electron density in the system $O \leftrightarrow M \leftrightarrow S$: *the hard O atom controls the donor properties of the S atoms in the acidic S-bearing extractant.*

The combination of ligands with hard and soft donor atoms thus opens a wide range of possibilities for extraction in two-phase systems. The interpretation of the formation of these mixed complexes within Pearson's theory is a new task for solvent extraction chemistry. A key question in this field is the relative position of Am(III) and Eu(III) [and, more generally, of the two series of trivalent ions An(III) and Ln(III)] in Pearson's useful cation hardness/softness classification,[12,13] which is still used today.[14,16] The high selectivity for Am(III) *vs.* Eu(III) in solvent extraction using extractants with soft S donor atoms significantly modifies the conventional presentation.[11–14,16–18]

According to Pearson,[12,13] independently of their oxidation states, lanthanide and actinide ions as a group are classified as hard acids, but the position of the individual An(III) or Ln(III) ions on this hardness/softness scale is not known. This raises the following questions. (i) Does the hardness character (h_a) of An(III) and Ln(III) change along the f-block families? (ii) What is the difference in h_a between corresponding Ln(III) and An(III) ions along both series of elements?

Pearson's qualitative concepts were treated quantitatively by several groups.[11,16–18] The theory of hardness/softness based on quantum chemical perturbation theory was developed by Klopman[11] and a quantitative scale of hardness (h_a) was established for many cations, including a single f element, La(III). In this section, these calculations are extended to all trivalent f-block ions. The frontier orbitals, that is the highest occupied molecular orbital of a donor atom (or base) and the lowest empty orbital of the acceptor atom (or acid) were considered.[11] If the difference between these orbitals is large, very little electron transfer occurs from the donor to the acceptor atom, and the chemical bond is ionic. Conversely, partial charge transfer from the donor molecular orbital to the acceptor orbital results in covalent bonding. In this model, the electron transfer effect from the ligand L to the metal M (M ← L) leads to covalent bonding and decreasing ionicity of the M–L bond. Decreasing ionicity is more often responsible for a desolvation effect.

The hardness character h_a, measured in energy units, is defined as:

$$h_a = -E_{orb} + E_{des} \qquad (1)$$

where E_{orb} and E_{des} are the atomic orbital energy of the free ion M(III) and its desolvation energy, respectively, E_{orb} is given by:

$$E_{orb} = I^{3+} - b^2(I^{3+} - I^{2+}) \qquad (2)$$

where I^{3+} and I^{2+} are the third and the second ionization potentials of M, and b^2 is a variation parameter corresponding to the transferred electronic density. Klopman[11] proposed a constant value for the b^2 parameter equal to 0.25 for all cations, independent of their charge (z = 1 to 4). E_{des} is given by:

$$E_{des} = C \times 1.268 \times R_s^{-1}(1 - \varepsilon^{-1}) \times (3 - 2 \times 1.268 \times b^2) \qquad (3)$$

where C is a constant arising from unit conversions and is equal to 14.39 eV, R_s is the effective solvation radius of M and ε is the dielectric constant of the medium.

The calculated hardness character h_a of Ln(III) and An(III) with the values of the different parameters used in the calcu-

Table 5 Calculated hardness character of Ln(III), Am(III) and Cm(III) and parameters used in eqn. (4)–(6). R_S is the effective solvation radius, E_{orb} and E_{des} are the orbital and desolvation energies respectively, and ΔH_h is the hydration enthalpy

	I^{2+}/eV	I^{3+}/eV	E_{orb}/eV	ΔH_h/eV	R_s/Å	E_{des}/eV	h_a/eV
La	11.06	19.18	17.15	34.32	1.960	21.75	4.60
Ce	10.85	20.2	17.86	34.82	1.932	22.07	4.20
Pr	10.55	21.62	18.85	35.30	1.906	22.37	3.52
Nd	10.73	22.1	19.26	35.62	1.888	22.57	3.32
Pm	10.9	22.3	19.45	35.87	1.875	22.73	3.28
Sm	11.07	23.4	20.32	36.10	1.863	22.88	2.56
Eu	11.24	24.92	21.50	36.64	1.836	23.22	1.72
Gd	12.09	20.63	18.50	36.80	1.828	23.32	4.83
Tb	11.52	21.91	19.31	37.24	1.806	23.60	4.29
Dy	11.67	22.8	20.02	37.31	1.803	23.65	3.63
Ho	11.8	22.84	20.08	37.80	1.780	23.96	3.88
Er	11.93	22.74	20.04	38.04	1.768	24.11	4.07
Tm	12.05	23.68	20.77	38.32	1.755	24.29	3.51
Yb	12.18	25.05	21.83	38.72	1.737	24.54	2.71
Lu	13.9	20.96	19.19	38.93	1.728	24.67	5.48
Ac	11.87	18.9	17.14	33.01	2.038	20.92	3.78
Th	11.83	20	17.96	33.81	1.990	21.43	3.47
Pa	11.7	20	17.93	34.19	1.967	21.67	3.74
U	11.9	20	17.98	34.99	1.922	22.17	4.20
Np	11.7	20.7	18.45	35.38	1.901	22.42	3.97
Pu	11.7	21.8	19.28	35.77	1.881	22.67	3.39
Am	12	22.4	19.80	36.13	1.862	22.90	3.10
Cm	12.41	21.2	19.00	36.40	1.848	23.07	4.07
Bk	12.3	22.3	19.80	36.77	1.829	23.30	3.50
Cf	12.5	23.6	20.83	37.03	1.817	23.47	2.64
Es	12.6	24.1	21.23	37.33	1.802	23.66	2.43
Fm	12.7	24.4	21.48	37.63	1.788	23.85	2.37
Md	12.8	25.4	22.25	37.92	1.774	24.03	1.78
No	13	27	23.50	38.29	1.757	24.27	0.77
Lr	14.8	23	20.95	38.36	1.754	24.31	3.36

Table 6 Scale of softness/hardness character for several bases and metal ions $M_{aq}{}^{n+}(n = 1–3)$

s_b/eV		h_a/eV			
Bases		Hard cations		Soft cations	
F^-	−12.18	Ga(III)	1.45	Hg(II)	−4.64
H_2O	−10.73	Eu(III)	1.72	Au(I)	−4.35
OH^-	−10.45	Ba(II)	1.89	Tl(III)	−3.37
Cl^-	−9.94	Cr(III)	2.06	Ag(I)	−2.82
Br^-	−9.23	Sr(II)	2.21	Cu(I)	−2.30
CN^-	−8.78	Fe(III)	2.23	Cd(II)	−2.04
SH^-	−8.59	Ca(II)	2.33	Tl(I)	−1.88
I^-	−8.31	Mg(II)	2.42	Cu(II)	−0.55
		Sm(III)	2.56	Na(I)	0.00
		Yb(III)	2.71	Ni(II)	0.29
		Am(III)	3.10	Li(I)	0.49
		Pm(III)	3.28	Fe(II)	0.69
		Nd(III)	3.32	Cr(II)	0.91
		Tm(III)	3.51		
		Pr(III)	3.52		
		Dy(III)	3.63		
		Be(II)	3.75		
		Ho(III)	3.88		
		Cm(III)	4.07		
		Er(III)	4.07		
		Ce(III)	4.20		
		Tb(III)	4.29		
		Ti(IV)	4.35		
		La(III)	4.60		
		Gd(III)	4.83		
		Lu(III)	5.48		
		Al(III)	6.01		

lations are given in Table 5. The values of R_s are derived from experimental values of hydration enthalpies using the Born–Haber equation. The ionization potentials of M(III) are taken from ref. 19–21. A classification of bases (in order of increasing softness) and metal ions in order of increasing hardness is shown in Table 6, where the h_a (calculated as described above) of Ln(III) (in italics), Am(III) and Cm(III) are included in the series of hard cations.

All trivalent lanthanides appear to be hard acids. However, the values of the lanthanide hardness character range over a rather wide (3.8 eV) interval, from 5.48 eV for Lu(III) to 1.72 eV for Eu(III). This range for the lanthanide hardness character is comparable to that for hard cations [4.6 eV from Al(III) to Ga(III)] and soft cations [5.6 eV from Cr(II) to Hg(II)].

The hardness character of Am(III), at 3.10 eV, is comparable to that of Nd(III) and is significantly higher than that of Eu(III) (1.72 eV). This result appears to disagree completely with extraction results, which show better extraction of Am(III) than Eu(III) by purified Cyanex 301, which was previously considered as evidence of the softer character of Am(III) compared with Eu(III).[5,22] This contradiction is discussed in the next section. Here, based on the extraction results, it can be concluded that the nature of the bonds in the $Am(R_2PSS)_3$ complexes approaches those in similar complexes with d-block transition elements. Although the Ln–S bond is weaker than the M–S bond (M being a d-block transition element), the difference is not very significant[15] for the complexes $Ln(R_2PSS)_3$ (where $R = C_6H_{11}$) and $Ln(R_2PSS)_4{}^-$ (where $R = CH_3, OC_2H_5$ and C_6H_{11}).

Fig. 1 shows the hardness trend across the f-block series. Plotted for comparison are the charge transfer energies of: (i) Cl → 4f and Cl → 5f in the $[LnCl_6]^{3-}$ and $[AnCl_6]^{3-}$ compounds,[23] (ii) Br → 4f and Br → 5f in the $[LnBr_6]^{3-}$ and $[AnBr_6]^{3-}$ compounds[23] and (iii) S → 4f and S → 5f in $Ln(R_2PSS)_3$ and $An(R_2PSS)_3$ (organic phase).[8]

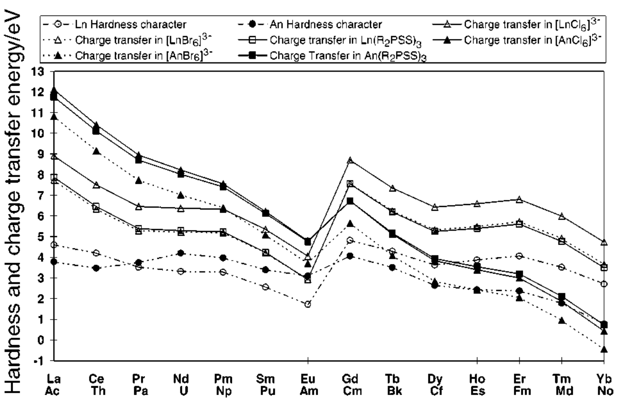

Fig. 1 Comparison of the variation in hardness character h_a of M(III) ions (M = Ln or An) across the 4f and 5f series and charge transfer energies in $[MX_6]^{3-}$ and $M(R_2PSS)_3$ complexes.

Fig. 1 shows that the trend in Ln(III) hardness character is similar to the trend in charge transfer energy. Although less obvious, a similar conclusion applies to An(III): the trend of $(h_a)_{An(III)}$ with Z is close to those observed for the charge transfer energies S → 5f, Cl → 5f and Br → 5f. Moreover, since the charge transfer energies in Ln(III) and An(III) complexes correlate with the corresponding $E^0_{3/2}$ redox potentials,[24] the Ln(III) and An(III) hardness character also correlates with $E^0_{3/2}$ (Fig. 2). Nevertheless, there are no physical reasons or explanations to accept the value of the charge transfer energy or the redox potential $E^0_{3/2}$ as a quantitative criterion for covalence in M(III)–L bonds (contrary to Klopman's statements[11]). The charge transfer energy L → 4f or 5f, and the redox potential $E^0_{3/2}$, are significant chemical parameters governing the ability of cations to accept electron density $[M^{3+}(L_3)^{-3} \rightarrow M^{(3-q)+}(L_3)^{-3+q}]$, but do not fully characterize the hardness of Ln(III) and An(III). In principle, a covalent effect can change the hardness character of a cation, such as Am(III), resulting in $(h_a)_{Am(III)} \ll (h_a)_{Eu(III)}$ in complexes with the soft base R_2PSS^- in the organic phase, as extraction results[5] have demonstrated.

The main aim of the present paper is to compare the An(III) and Ln(III) coordination extraction mechanisms by investigating the extraction of Am(III) and Eu(III) using a synergistic mixture of $(Cl\Phi)_2PSSH$ with a neutral organophosphorus compound bearing hard oxygen donor atoms.[7] In this regard, from the standpoint of base softness, $(Cl\Phi)_2PSSH$ appears to be a weaker extractant than R_2PSSH and the two mechanisms of extraction may be: (i) completely different, (ii) significantly modified or even (iii) similar. To the best of our knowledge, the first complexes of diphenyldithiophosphinic acid [an extractant with similar chemical properties to $(Cl\Phi)_2PSSH$] were prepared with the d transition elements Cr(III) (hard cation with $h_a = 2.06$ eV) and Ni(II) (soft cation with $h_a = 0.29$ eV).[25] We can therefore expect Eu(III) and Am(III), having different hardness character, to form complexes with $(Cl\Phi)_2PSSH$, which may be strengthened by donor–acceptor interactions with the hard O donor atom through electron density redistribution in the system: O → M(III) → S.

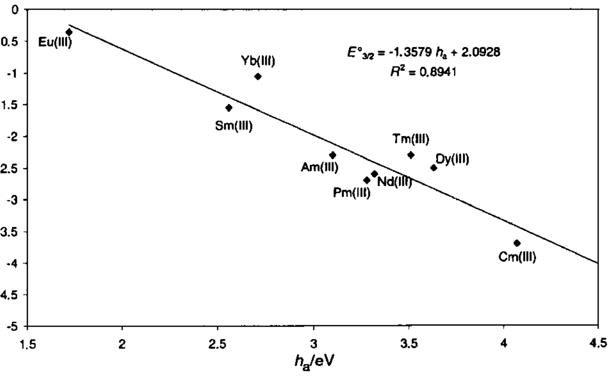

Fig. 2 Correlation between redox potentials $E^0_{3/2}$ and the corresponding hardness character h_a of M(III) (M = Ln and An) cations.

Experimental data base and scope of anticipated problems

An analysis of the experimental data presented in Table 2 raises problems that must be solved to interpret the synergistic effect on the extractability of Am(III) and Eu(III). Accordingly, some co-extractants B were classified into two groups.

Group 1: TBP and TBPO; TOP and TOPO; T2EHP and BPOPO. The first class of co-extractants B shows a simple and clear regularity for the extractability of Am(III) and Eu(III). Extractability with TBP is less than with TBPO, since the O atom is a weaker donor in the former co-extractant than in the latter. In fact, the low electron affinity of the butyl group in TBPO induces a high basicity in the O atom and thus a strong synergistic effect. Conversely, the high electron affinity of the butyl-O group in TBP induces a low basicity in the O atom, and hence a weak synergistic effect.

In the extraction of Am(III) and Eu(III) from 2.0 M $LiNO_3$–0.01 M HNO_3 by 0.25 M TBP or TBPO,[26] $SF_{Am/Eu}$ was found to be <1, whereas extraction with $(Cl\Phi)_2PSSH$ + TBP or TBPO gave greater selectivity ($SF_{Am/Eu} \gg 1$). Hence, the questions arising for this first class of co-extractants are: does Am(III) form stronger complexes with $(Cl\Phi)_2PSSH$ than Eu(III), and is the selectivity due to the effect of stronger Am–S bonds in comparison with Eu–S bonds or to the net synergistic effect, or both?

In the case of Am(III) and Eu(III) extraction with the synergistic mixture Cyanex 301 + TOPO,[5] the $SF_{Am/Eu}$ is again <1, similar to what is observed for the complexes $M(NO_3)_3 \cdot n$TOPO, where no M–S bond is formed. The main difference between the two extractants, Cyanex 301 (R_2PSSH) and $(Cl\Phi)_2PSSH$, thus concerns their different Am/Eu selectivity, when employed in synergistic combinations with the same co-extractants B, TBP and TOPO. For the two branched phosphate and phosphine oxide co-extractants, T2EHP and BPOPO respectively, the extractability of Am(III) is greater than that of Eu(III), but the selectivity is greater for T2EHP.

Group 2: TOP, T2EHP and TOPO. The higher selectivity observed with T2EHP demands a theoretical explanation.

Synergistic effect in the systems M(III)/$(Cl\Phi)_2$PSSH/B

The synergistic effect can be evaluated by considering the ratio of the distribution ratios for the extraction of M(III) by synergistic mixtures and by $(Cl\Phi)_2PSSH$ alone. Thus:

$$\Delta^{\mathrm{syn}}_{\mathrm{M}}(\mathrm{B}) = \log D_{\mathrm{M}/(\mathrm{Cl}\Phi)_2\mathrm{PSSH/B}} - \log D_{\mathrm{M}/(\mathrm{Cl}\Phi)_2\mathrm{PSSH}} \quad (4)$$

To be able to calculate $\Delta^{syn}_{M}(B)$, $D_{M/(Cl\Phi)_2PSSH}$ must be evaluated for the extraction with $(Cl\Phi)_2PSSH$ alone, because these data were not determined experimentally at similar pH values. This will be done in the following.

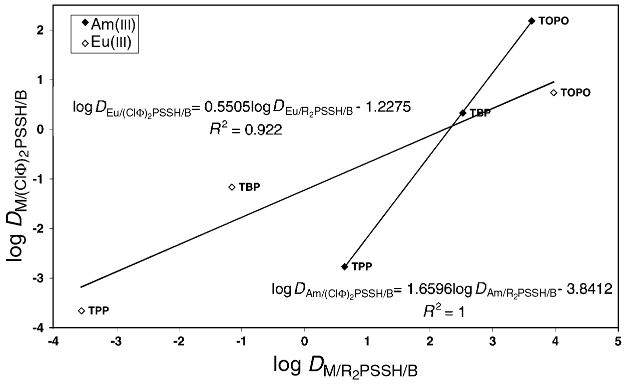

Fig. 3 Correlation between log $D_{M/R_2PSSH/B}$ corresponding to the extraction of Am(III) and Eu(III) by Cyanex 301 + B systems[5] and log $D_{M/(Cl\Phi)_2PSSH/B}$ with three common co-extractants: TPP, TBP and TOPO.

The data on the extraction of Am(III) and Eu(III) by the two sets of synergistic systems Cyanex 301 (R_2PSSH) + B[5] and $(Cl\Phi)_2PSSH$ + B (Table 2) refer to three common co-extractants (TBP, TOPO and TPP). Fig. 3 shows that the extractability of Am(III) and Eu(III) are linearly related in log–log plots of the two systems using these co-extractants. On the other hand, the extractability of Am(III) and Eu(III) in the absence of B is known for R_2PSSH.[5] With these two series of data, and from the linear relationships of Fig. 3, the distribution ratios can thus be calculated for the extraction of Am(III) and Eu(III) by $(Cl\Phi)_2PSSH$. The following results were obtained for the experimental conditions given in Table 2: log $D_{Am/(Cl\Phi)_2PSSH} = -2.31$ (*i.e.* $D_{Am/(Cl\Phi)_2PSSH} = 0.0049$) and log $D_{Eu/(Cl\Phi)_2PSSH} = -2.65$ (*i.e.* $D_{Eu/(Cl\Phi)_2PSSH} = 0.0023$). These data show that, in these experimental conditions, the affinity of $(Cl\Phi)_2PSSH$ for Am(III) and Eu(III) is rather weak.

In the case of the extracted complexes $M(NO_3)_3B_3$,[26] an excellent linear correlation is observed between log $D_{Am(III)}$ and log $D_{Eu(III)}$, but there is almost no selectivity in the extraction [Fig. 4(a)]. In the extraction of Am(III) and Eu(III) by Cyanex 301 + B synergistic mixtures, a poor correlation is observed between the extractabilities of the two metal ions [Fig. 4(b)], although good selectivity ($SF_{Am/Eu}$) is observed for B = TPP, T*t*BP and D2EHDMBA, for which the extractability of Am(III) seems frozen while that of Eu(III) varies sharply. In the extraction of Am(III) and Eu(III) by $(Cl\Phi)_2PSSH$ + B synergistic mixtures, two co-extractants (TOP and T2EHP) do not enter in the correlation between the extractabilities of the two M(III) ions [Fig. 4(c)]. Without these co-extractants, the correlation coefficient would be very good ($R^2 = 0.99$). From these facts, it follows that a high selectivity between Am(III) and Eu(III) means a strong synergistic effect for Am(III) complexes and/or a strong antagonistic effect for Eu(III) complexes.

Table 7 shows the values of the synergistic effects $\Delta^{syn}_{M}(B)$ for the extraction of Am(III) and Eu(III) by $(Cl\Phi)_2PSSH$ + B mixtures, calculated according to eqn. (4). The data in Table 7 support the following qualitative considerations: the synergistic effect depends on the cation complexation with extractants and on the compatibility of the donor atoms in B and the S-bearing extractants.

Fig. 5 shows the difference in the synergistic effects for Am(III) and Eu(III) [$\Delta^{syn}_{Am/Eu}(B) = \Delta^{syn}_{Am}(B) - \Delta^{syn}_{Eu}(B)$] for various B, along with the observed experimental selectivity $SF_{Am/Eu}$.[8] The following conclusions can be drawn from Table 7 and Fig. 5. (i) Although the synergistic effects for Am(III) and Eu(III) change irregularly on the scale of increasing selectivity (*i.e.* from TPP to T2EHP), the difference in synergistic effects for the two metals [$\Delta^{syn}_{Am/Eu}(B)$] appears to be a monotonic function of the selectivity (these values only differ by the constant value log $D_{Am/(Cl\Phi)_2PSSH}$ − log $D_{Eu/(Cl\Phi)_2PSSH}$). (ii) When

Table 7 Synergistic effect $\Delta^{syn}_{M}(B)$ in the reaction M/$(Cl\Phi)_2$PSSH + B ↔ M/$(Cl\Phi)_2$PSSH/B

B	$\Delta^{syn}_{Am}(B)$	$\Delta^{syn}_{Eu}(B)$	Comments
TMP	−0.03	−0.78	Decrease, Am < Eu
TBP	2.64	1.48	Increase, Am > Eu
THP	2.51	1.17	Increase, Am > Eu
TOP	2.34	−0.17	Increase, Am
T2EHP	2.42	−0.27	Increase, Am
TPP	−0.46	−1.01	Decrease, Am < Eu
TAP	1.99	0.82	Increase, Am > Eu
TBPO	4.19	3.27	Increase, Am > Eu
TOPO	4.49	3.39	Increase, Am > Eu
TPPO	4.15	2.91	Increase, Am > Eu
BPOPO	2.55	1.49	Increase, Am > Eu
T*i*BPS	0.61	−0.05	Increase Am

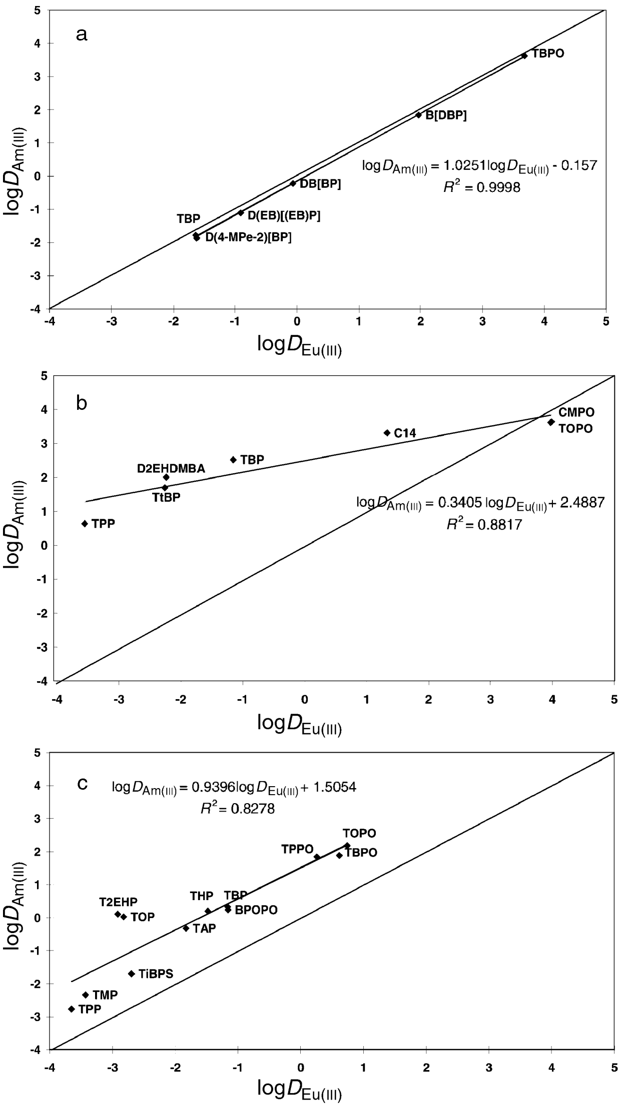

Fig. 4 Three correlations between the extractability of Am(III) and Eu(III): (a) M(III)/NO_3/B extracted complexes;[29] (b) M(III)/R_2PSSH/B extracted complexes;[5] (c) M(III)/(ClΦ)$_2$PSSH/B extracted complexes.[7] The lines between the data points correspond to the least squares adjustments of the data and the diagonal lines correspond to log $D_{\mathrm{Am(III)}}$ = log $D_{\mathrm{Eu(III)}}$, that is $\mathrm{SF}_{\mathrm{Am/Eu}} = 1$.

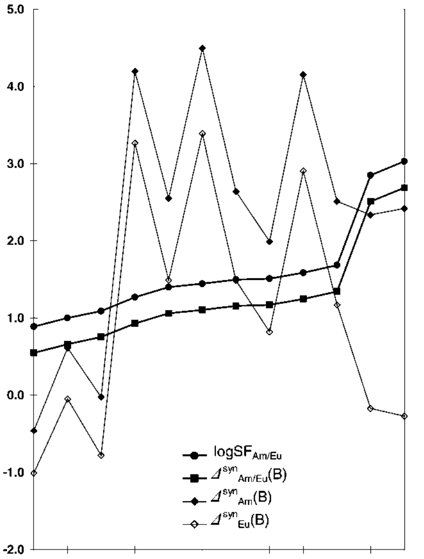

Fig. 5 Comparison of synergistic effect and selectivity in M/(ClΦ)$_2$PSSH/B systems for twelve co-extractants B.

$\Delta^{\mathrm{syn}}_{\mathrm{M}}(\mathrm{B}) \geq 0$, the synergistic effects are bonding, that is the co-extractants B promote the formation of M–S bonds. The synergistic bonding effect is stronger for complexes of Am(III) than for those of Eu(III). This effect, added to a slightly better extraction of Am(III) than Eu(III) by (ClΦ)$_2$PSSH, results in the good selectivity $\mathrm{SF}_{\mathrm{Am/Eu}}$. (iii) When $\Delta^{\mathrm{syn}}_{\mathrm{M}}(\mathrm{B}) < 0$, an antagonistic effect occurs. It is stronger for complexes of Eu(III) than for those of Am(III); as usual in the theory of the chemical bond, the bonding effect is more effective in promoting bonds than the antibonding effect is in preventing bond formation. (iv) The high selectivity observed using T2EHP and TOP is caused by a bonding effect for Am(III) and an antibonding effect for Eu(III). (v) In the case of phosphine oxides such as TBPO, TOPO and TPPO, strong synergistic effects are observed for both cations and $\Delta^{\mathrm{syn}}_{\mathrm{Am}}(\mathrm{B}) > \Delta^{\mathrm{syn}}_{\mathrm{Eu}}(\mathrm{B})$ by approximately one logarithmic unit. The branched phosphine oxide, BPOPO, has a lower synergistic effect, but exhibits almost the same selectivity as the others. (vi) Finally, the soft co-extractant, T*i*BPS, in combination with the soft (ClΦ)$_2$PSSH acid, shows almost no synergistic effect for the complexation of Eu(III) and a weak one for Am(III). The selectivity is accordingly low.

In the first paper of this series,[8] the interrelation between the interatomic distances $R_{\mathrm{Eu–S}}$ and $R_{\mathrm{Eu–O}}$ and the shifts in charge transfer energy S → Eu(III) in Eu/R_2PSSH/B complexes was shown to depend on the donor ability of the co-extractants: for strong donors, decreasing $R_{\mathrm{Eu–O}}$ corresponds to increasing $R_{\mathrm{Eu–S}}$ and charge transfer energy $E(\mathrm{S} \rightarrow \mathrm{Eu})$ while for weak donors, increasing $R_{\mathrm{Eu–O}}$ corresponds to decreasing $R_{\mathrm{Eu–S}}$ and $E(\mathrm{S} \rightarrow \mathrm{Eu})$.

In the case of Eu/(ClΦ)$_2$PSSH/B complexes, the interpretation of the absorption spectra presents difficulties: the bands are broad because of a strong coupling with phonons. Fortunately, however, the trend in $E(\mathrm{S} \rightarrow \mathrm{Eu})$ for Eu/(ClΦ)$_2$PSSH/B and Eu/R_2PSSH/B complexes with B = TPP, TBP and TOPO is the same, although the absolute values of $E(\mathrm{S} \rightarrow \mathrm{Eu})$ differ. This trend may be interpreted if we consider that a single co-extractant induces the same type of synergistic effect with both S-bearing extractants.

In ref. 8, the interatomic distances $R_{\mathrm{Eu–S}}$ in Eu/R_2PSSH/B complexes were calculated from the charge transfer energy $E(\mathrm{S} \rightarrow \mathrm{Eu})$ in these complexes and an equation was developed connecting $R_{\mathrm{Eu–S}}$ with $\Delta^{\mathrm{syn}}_{\mathrm{Eu}}(\mathrm{B})$:

$$\Delta^{\mathrm{syn}}_{\mathrm{Eu}}(\mathrm{B}) = a \times [R_{\mathrm{Eu–S}}]^2 + b \times R_{\mathrm{Eu–S}} + c \qquad (5)$$

where constants $a = -110.13$, $b = 710.43$ and $c = -1139.1$.

Keeping in mind the same trend in $E(\mathrm{S} \rightarrow \mathrm{Eu})$ in both Eu/(ClΦ)$_2$PSSH/B and Eu/R_2PSSH/B complexes, we can use

Table 8 $\Delta^{\mathrm{syn}}_{\mathrm{Eu}}(\mathrm{B})$ and interatomic $R_{\mathrm{Eu–S}}$ distances in Eu/(ClΦ)$_2$-PSSH/B and Eu/R_2PSSH/B complexes[8]

	(ClΦ)$_2$PSSH		R_2PSSH	
B	$\Delta^{\mathrm{syn}}_{\mathrm{Eu}}(\mathrm{B})$	$R_{\mathrm{Eu–S}}$/Å	$\Delta^{\mathrm{syn}}_{\mathrm{Eu}}(\mathrm{B})$	$R_{\mathrm{Eu–S}}$/Å
TBP	1.48	3.01	1.43	3.00
TPP	−1.01	2.96	−0.97	2.96
TOPO	3.39	3.05	6.55	3.25
TMP	−0.78	2.97		
THP	1.17	3.00		
TOP	−0.17	2.98		
T2EHP	−0.27	2.98		
TAP	0.82	3.00		
TBPO	3.27	3.05		
BPOPO	1.49	3.01		
TPPO	2.91	3.04		
T*i*BPS	−0.05	2.98		
T*t*BP			0.32	2.98
DOTA			0.35	2.98
C14			3.91	3.07
CMPO			6.57	3.25

eqn. (5) to evaluate the $R_{\mathrm{Eu-S}}$ distances with the $\Delta^{\mathrm{syn}}_{\mathrm{Eu}}$(B) given in Table 7 for Eu/(ClΦ)$_2$PSSH/B complexes. The calculated $R_{\mathrm{Eu-S}}$ values and those in Eu/R$_2$PSSH/B for comparison are given in Table 8, together with $\Delta^{\mathrm{syn}}_{\mathrm{Eu}}$(B). The following conclusions can be drawn. In Eu/(ClΦ)$_2$PSSH/TOPO complexes, the co-extractant TOPO does not possess as high a donor ability as in Eu/R$_2$PSSH/TOPO; the effect of TOPO on $R_{\mathrm{Eu-S}}$ is therefore less. In Eu/(ClΦ)$_2$PSSH/B complexes no co-extractant which is as strong a donor as CMPO was used in the extraction with Cyanex 301; as a result, no $R_{\mathrm{Eu-S}}$ as long as 3.25 Å was obtained. The range of $R_{\mathrm{Eu-S}}$ distances is determined by the synergistic effect: it is narrower for Eu/(ClΦ)$_2$PSSH/B complexes ($3.05 > R_{\mathrm{Eu-S}} > 2.96$ Å) than for Eu/R$_2$PSSH/B complexes ($3.25 > R_{\mathrm{Eu-S}} > 2.96$ Å).

Moreover, the Eu–S distance in the Eu(ClΦ)$_2$PSSH complex without a co-extractant was roughly evaluated from the correlation between $R_{\mathrm{Eu-S}}$ and $E(\mathrm{S} \rightarrow \mathrm{Eu})$ (Fig. 6), where B = TPP, TBP and TOPO. From the plot, we find that $R_{\mathrm{Eu-S}} = 2.97$ Å. If we compare this value with the $R_{\mathrm{Eu-S}}$ value of 3.03 Å obtained for Eu/R$_2$PSSH complexes,[8] and taking account of the estimated ± 0.05 Å uncertainty, we can conclude that these distances are the same.

In our previous paper, we studied the mechanism of the synergistic effect in the extraction of Am(III) and Eu(III) by R$_2$PSSH (Cyanex 301).[8] In this section, the synergistic effects of the two extractants (ClΦ)$_2$PSSH and R$_2$PSSH with the common co-extractants TBP, TPP and TOPO are compared in Fig. 7, which shows an antagonist effect with TPP ($\Delta^{\mathrm{syn}}_{\mathrm{M}} < 0$) and synergistic effects with TBP and TOPO ($\Delta^{\mathrm{syn}}_{\mathrm{M}} > 0$).

Antagonistic effects of TPP. Two main mechanisms can be considered for the antagonist synergistic effects observed with TPP: steric incompatibility of the soft donor atoms S of acidic S-bearing extractants and the hard O atom of B in the M(III) coordination polyhedra, and coordination incompatibility of soft and hard donor atoms in the S-bearing extractant and co-extractant respectively, resulting in decreasing basicity of the soft donor atoms S caused by back electron transfer: soft donor → cation → hard donor.

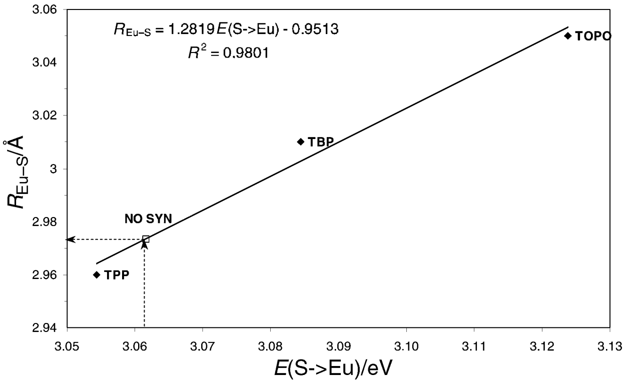

Fig. 6 Correlation between $E(\mathrm{S} \rightarrow \mathrm{Eu})$ charge transfer energy and Eu–S distances in Eu/(ClΦ)$_2$PSSH/B complexes. The $R_{\mathrm{Eu-S}}$ value in the complex without B is inferred from the correlation.

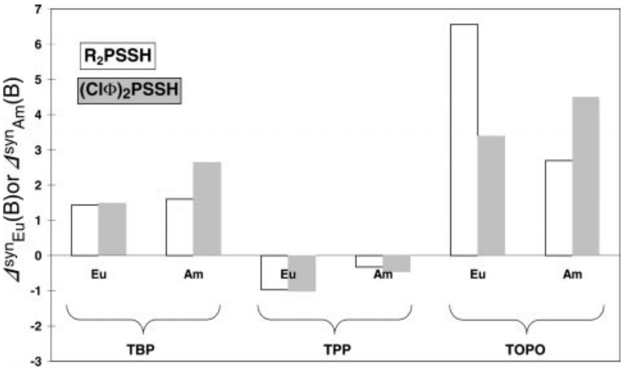

Fig. 7 Comparison of synergistic effects for R$_2$PSSH and (ClΦ)$_2$PSSH for three common co-extractants (TBP, TPP and TOPO).

In the case of TPP, with both (ClΦ)$_2$PSSH and R$_2$PSSH extractants, the antagonistic effect could stem from the steric effect arising from the relative arrangement of the phenyl groups of TPP. It is greater for complexes of Eu(III) than for those of Am(III), undoubtedly because Eu(III) has a smaller ionic radius than Am(III), but the synergistic effects are similar for both systems [$\Delta^{\mathrm{syn}}_{\mathrm{Am}}$(B) equal to -0.46 for (ClΦ)$_2$PSSH and -0.28 for R$_2$PSSH systems]. Moreover, the values of $\Delta^{\mathrm{syn}}_{\mathrm{Eu}}$(B) are roughly the same (≈ -1.0) for the Eu(III) complexes for both systems. It is thus clearly acceptable to find $R_{\mathrm{Eu-S}}$ 2.96 Å for both systems in Table 8. The high selectivity SF$_{\mathrm{Am/Eu}}$ observed for the R$_2$PSSH + TPP mixture[8] is obtained by good complexation of Am(III) with R$_2$PSSH and the antagonistic effect of TPP in Eu/R$_2$PSSH/TPP complexes. On the contrary, selectivity is low with the (ClΦ)$_2$PSSH + TPP mixture (see Table 2) because of the weak complexation of Am(III) with (ClΦ)$_2$PSSH.

Synergistic effects of TBP. The extractability of Eu(III) and synergistic effects $\Delta^{\mathrm{syn}}_{\mathrm{Eu}}$(TBP) with (ClΦ)$_2$PSSH and R$_2$PSSH are approximately the same. However, the synergistic effect for Am/(ClΦ)$_2$PSSH complex(es) is higher [$\Delta^{\mathrm{syn}}_{\mathrm{Am}}$(TBP) = 2.64] than for Am/R$_2$PSSH complex(es) [$\Delta^{\mathrm{syn}}_{\mathrm{Am}}$ (TBP) = 1.60]. The mechanism of the synergistic effect is thought to be the same for both extractant systems and once again, the difference in SF is mainly due to good complexation of Am(III) with R$_2$PSSH and to poor complexation with (ClΦ)$_2$PSSH. As far as Eu(III) is concerned, the distance $R_{\mathrm{Eu-S}} = 3.0$ Å is the same in both Eu/(ClΦ)$_2$PSSH/TBP and Eu/R$_2$PSSH/TBP complexes since the $\Delta^{\mathrm{syn}}_{\mathrm{Eu}}$(TBP) values are very close for both systems.

Synergistic effects of TOPO. The synergistic effect for both extractants and both M(III) cations are strong but $\Delta^{\mathrm{syn}}_{\mathrm{Eu}}(\mathrm{TOPO}) = 6.55 > \Delta^{\mathrm{syn}}_{\mathrm{Am}}(\mathrm{TOPO}) = 2.70$ with R$_2$PSSH, while $\Delta^{\mathrm{syn}}_{\mathrm{Eu}}(\mathrm{TOPO}) = 3.39 < \Delta^{\mathrm{syn}}_{\mathrm{Am}}(\mathrm{TOPO}) = 4.49$ for (ClΦ)$_2$PSSH. The synergistic effects thus differ sharply for the two extraction systems. From the calculations in Table 8, a distance $R_{\mathrm{Eu-S}} = 3.05$ Å was obtained in the Eu/(ClΦ)$_2$PSSH/TOPO complex showing that $R^{(\mathrm{Cl\Phi})_2\mathrm{PSSH}}_{\mathrm{Eu-S}} < R^{\mathrm{R_2PSSH}}_{\mathrm{Eu-S}}$. It thus appears that the Eu R$_2$PSSH TOPO complex is stable mainly owing to the existence of the strong Eu–O(TOPO) bond, whereas Eu/(ClΦ)$_2$PSSH/TOPO is stable mainly due to the presence of Eu–S bonds.

The selectivity SF$_{\mathrm{Am/Eu}} < 1$ of the extraction by R$_2$PSSH + TOPO also shows that the nitrate anion can participate in M(III) complex formation. The long Eu–S distance and weak complexation with R$_2$PSSH, but the strong complexation of M(III) with TOPO (and possibly with NO$_3^-$) are the main reasons why SF$_{\mathrm{Am/Eu}} < 1$ for two complexes as different as M(NO$_3$)$_3$(TOPO)$_3$ and M/R$_2$PSSH/TOPO. Conversely, the selectivity ratio SF$_{\mathrm{Am/Eu}}$ is $\gg 1$ for M/(ClΦ)$_2$PSSH)/TOPO complexes, no doubt due to the stronger M–S$_{(\mathrm{Cl\Phi})_2\mathrm{PSSH}}$ bonds formed. In conclusion, each co-extractant B has its specific influence.

Donor properties of co-extractants B

The different $R_{\mathrm{Eu-S}}$ distances in Eu/(ClΦ)$_2$PSSH/B complexes compared with Eu/(ClΦ)$_2$PSSH reflect the additional effects due to the change in basicity of the S atoms and the change of Eu–S/Eu–O bond energies caused by electron transfer within the O ⇔ M(III) ⇔ S system. This process is mainly thought to result in the enthalpy mechanism of M–S bond reconstruction in the complexes. Another aspect of the change in M–S distances is the steric effect, that is the arrangement of the soft S atoms around the cation. This process is mainly thought to result in the entropy mechanism of M–S bond reconstruction during the synergistic extraction of M(III). Caution is therefore necessary with regard to these qualitative proposals because both effects are usually superimposed in extraction data.

Keeping this in mind, these effects can be considered using quantum chemical calculations of the effective charges in the co-extractants. In fact, we proposed that the synergistic effect of the B molecules depends on the basicity of the hard oxygen atom in accordance with the statement: the more negative the charge on the oxygen atom in the co-extractant, the higher its donor ability, and the larger the distribution ratios $D_{\mathrm{Am(III)}}$ and $D_{\mathrm{Eu(III)}}$. The effective charges Q(O) were calculated for all phosphates and phosphine oxides B using an *ab initio* method with a 6-31G* basis set. The correlation ($R^2 = 0.79$) between the experimental values log D_{Am} and Q(O) is quantitatively in line with the above statement [Fig. 8(a)]. Note that the basicity of the hard oxygen atoms in phosphates (TBP, THP, TOP, T2EHP and TAP) is almost the same. According to the correlation, their Am(III) extractability should be similar. Consequently, the enthalpy role in the formation of Am/(ClΦ)$_2$PSSH/B complexes is thought to be significant for all co-extractants.

Fig. 8(b) shows the correlation between log $D_{\mathrm{Eu(III)}}$ and Q(O). This correlation is not as good as that with log $D_{\mathrm{Am(III)}}$. In the case of Eu(III), the synergistic effect sharply decreases from TBP to TOP and T2EHP [which have similar Q(O)], meaning that the extraction mechanism differs from that for Am(III). We can again conclude that, thermodynamically, the mechanism of Eu(III) extraction with TOP and T2EHP differs from that for Am(III). This is possibly due to different enthalpy/entropy contributions. The enthalpy extraction mechanism is certainly due to the greater covalency of Am–S bonds in comparison with Eu–S bonds.

Finally, the donor properties of B molecules with respect to the synergistic effect can be classed as strong (TOPO, TBPO, BPOPO and TPPO), intermediate (TBP, THP, TOP, T2EHP and TAP) and weak (TPP and TMP). The branched co-extractant BPOPO, which displays peculiar behavior, has a highly donating oxygen but gives low extractability in its complexes, and is thus excluded from the classification. For the strong and weak donor categories, $\Delta^{\mathrm{syn}}_{\mathrm{Am/Eu}}$(B) and SF$_{\mathrm{Am/Eu}}$ are not high. High SF$_{\mathrm{Am/Eu}}$ values are only obtained with the intermediate donors, since in this case, the synergistic effects differ for Am(III) and Eu(III).

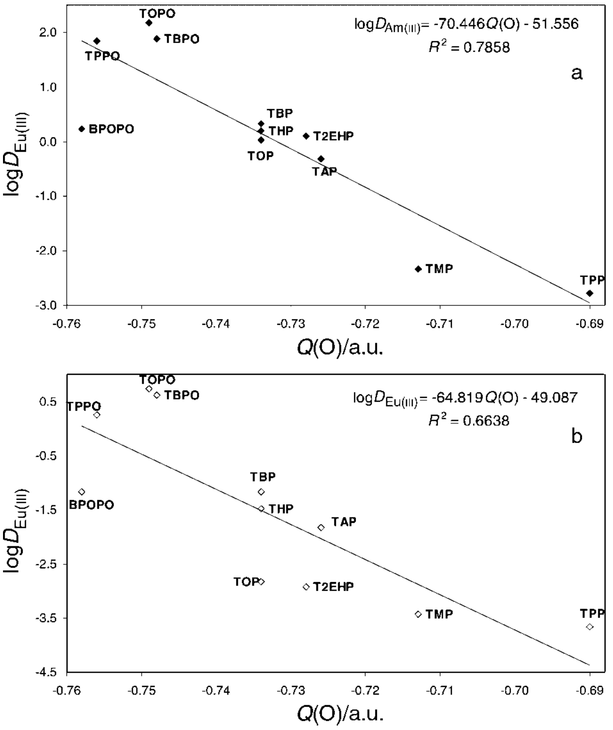

Fig. 8 Correlation between Q(O) of B and the extractability of (a) Am(III) and (b) Eu(III).

^{31}P NMR chemical shifts of the molecules B and their synergistic effects

A correlation was demonstated[8] between the chemical shifts $\delta(^{31}\mathrm{P})$ of the neutral organophosphorus co-extractants and the extractability of Eu(III) and Am(III) in the synergistic extraction with Cyanex 301. A similar correlation can be also expected for (ClΦ)$_2$PSSH + B synergistic systems.

The $\delta(^{31}\mathrm{P})$ values of all co-extractants used in ref. 7 are not known. The following approach is used to estimate unknown values. The values of $\delta(^{31}\mathrm{P})$ (relative to 85% H_3PO_4) for R(R′O)$_2$PO molecules, with different R and R′, were shown[27] to be identical within ±2 ppm uncertainty: $C_2H_5(C_4H_9O)_2PO$ (31 ± 2); $C_4H_9(C_4H_9O)_2PO$ (32 ± 1); $C_9H_{19}(C_4H_9O)_2PO$ (31 ± 1); $C_{10}H_{21}(C_4H_9O)_2PO$ (32 ± 1); $CH_3(C_2H_5O)_2PO$ (30 ± 1); $C_2H_5(C_2H_5O)_2PO$ (32.5 ± 1); $C_8H_{17}(C_8H_{17}O)_2PO$ (32 ± 1). According to these data, and since $\delta(^{31}\mathrm{P})$ is 1 ± 1 for TBP and TEP [$(C_2H_5)_3PO$], the same value is postulated for the neutral organophosphate molecules TMP, THP, TOP, T2EHP and TAP. The $\delta(^{31}\mathrm{P})$ value for TPP is assumed to be equal to −18,[27] and that for TPPO is 23–25.[27,28] In the case of strongly branched trialkylphosphine oxides, the $\delta(^{31}\mathrm{P})$ values are lower by 4–8 than those of *n*-alkylphosphine oxides.[27,28] A value of $\delta(^{31}\mathrm{P}) = 36$ is used for BPOPO, as a value $\delta(^{31}\mathrm{P}) = 40$ (identical to that of CMPO)[8] is assumed for TOPO and TBPO.

The effective charges on the P atoms in B molecules were also calculated (same method as previously). Fig. 9 shows that these Q(P) values are proportional to the estimated $\delta(^{31}\mathrm{P})$ values. Two conclusions can be drawn. First, the estimated $\delta(^{31}\mathrm{P})$ values seem reasonable. Second, Q(O) and Q(P), which are characteristics of the donor ability of the hard co-extractant, are both correlated with $\delta(^{31}\mathrm{P})$. In fact, the $\delta(^{31}\mathrm{P})$ values of B can be used to establish correlations with the extractability of Am(III) and Eu(III) by (ClΦ)$_2$PSSH + B synergistic mixtures.

Fig. 10 shows the correlation between $\delta(^{31}\mathrm{P})$ of B and log $D_{\mathrm{M(III)}}$ corresponding to (ClΦ)$_2$PSSH + B synergistic mixtures. The nearly equal values of log $D_{\mathrm{Am(III)}}$ with TBP, THP, TOP and T2EHP are in good agreement with the $\delta(^{31}\mathrm{P})$ shifts in these molecules. This is also in agreement with the Q(O) and Q(P) charges and with the same synergistic effect. These correlations can be interpreted as an enhanced enthalpy effect in the extraction of Am(III) with the co-extractants considered. Note that the TMP ligand is certainly partially present in the aqueous phase, owing to its lower lipophilicity in comparison with the other organophosphates studied. This precludes a simple interpretation of the TMP data.

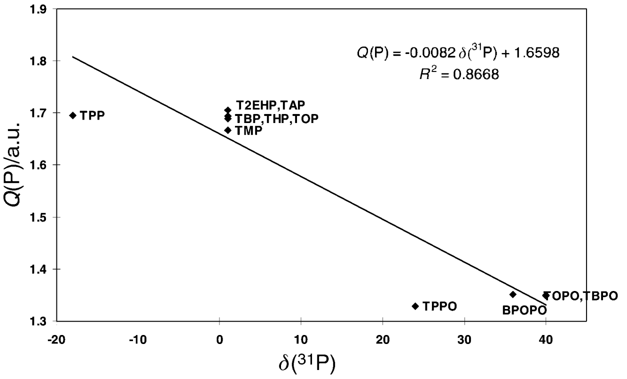

Fig. 9 Correlation between Q(P) of B and the corresponding $\delta(^{31}\mathrm{P})$ NMR chemical shift relative to 85% H_3PO_4.

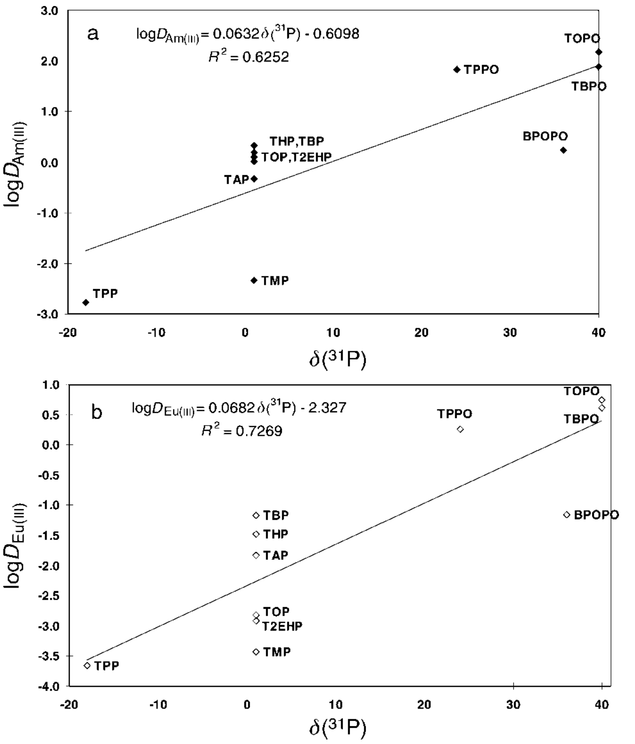

Fig. 10 Correlation between (*a*) log $D_{Am(III)}$ or (*b*) log $D_{Eu(III)}$ and the $\delta(^{31}P)$ NMR chemical shift of B relative to 85% H_3PO_4.

It follows from the correlations in Fig. 10 that a significant effect for Am/Eu selectivity arises from the crowding of the branched RO groups in the co-extractants, as in the case of T2EHP. For the extraction of Am(III), the effect of branched RO groups is weak but for Eu(III) it is strong: for phosphates having the same donor properties but different alkyl groups, there is a relatively small variation of $D_{Am(III)}$, whereas the variation of $D_{Eu(III)}$ is large. This different behavior determines the high selectivity observed.

Extraction mechanism with respect to the stability of the M(III)/B and M(III)/(ClΦ)$_2$PSSH complexes

Eqn. (4) describes the synergistic effect as the addition of a co-extractant to the complex M/(ClΦ)$_2$PSSH. We shall now consider another way to form the mixed complex M/(ClΦ)$_2$PSSH/B through the interaction of the two parent complexes, according to the schematic reaction (6) characterized by an equilibrium constant K_{stab}.

$$\mathrm{M/(Cl\Phi)_2PSSH + M/B \leftrightarrow M/(Cl\Phi)_2PSSH/B + M} \qquad (6)$$

The thermodynamics of mixed complex formation from parent complexes was previously described[29] using the stabilization constant, K_{stab}. Since the qualitative aspects of the extraction mechanism are mainly considered here, instead of K_{stab} the proportional term $\Delta_M^{stab}(B)$ is used:

$$\Delta_M^{stab}(B) = \log D_{M/(Cl\Phi)_2OSSH/B} - \log D_{M/B} - \log D_{M/(Cl\Phi)_2PSSH} \qquad (7)$$

Comparison of eqn. (4) and (7) leads to:

$$\Delta_M^{syn}(B) = \log D_{M/B} + \Delta_M^{stab}(B) \qquad (8)$$

meaning that the synergistic effect involves two parameters characterizing the stabilization of the mixed complex and the formation of the M/B complex. Considering only the difference in parameters between Am(III) and Eu(III), the following equation can be introduced:

$$\log SF_{Am/Eu} = \Delta_{Am/Eu}^{M/(Cl\Phi)_2PSSH} + \Delta_{Am/Eu}^{M/B} + \Delta_{Am/Eu}^{stab}(B) \qquad (9)$$

with:

$$\log SF_{Am/Eu} = \log D_{Am/(Cl\Phi)_2PSSH/B} - \log D_{Eu/(Cl\Phi)_2PSSH/B} \qquad (10)$$

$$\Delta_{Am/Eu}^{M/(Cl\Phi)_2PSSH} = \log D_{Am/(Cl\Phi)_2PSSH} - \log D_{Eu/(Cl\Phi)_2PSSH} \qquad (11)$$

$$\Delta_{Am/Eu}^{M/B} = \log D_{Am/B} - \log D_{Eu/B} \qquad (12)$$

$$\Delta_{Am/Eu}^{stab}(B) = \Delta_{Am}^{stab}(B) - \Delta_{Eu}^{stab}(B) \qquad (13)$$

This model is only qualitative and has been proposed to analyze the trend in the change of contributions of different terms for the overall selectivity log $SF_{Am/Eu}$. The parameters in eqn. (10) and (11) are known. The values of and log $D_{M/B}$

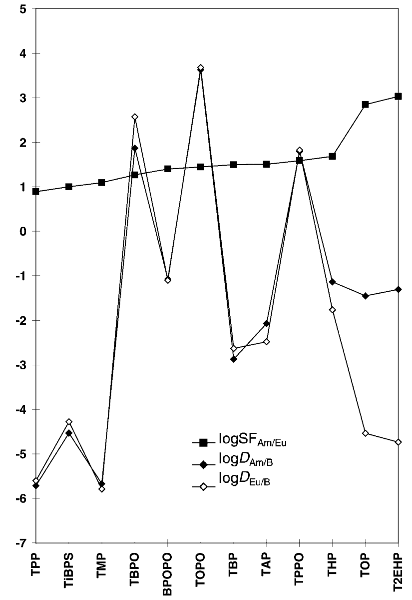

Fig. 11 Comparison between the Am/Eu selectivity and the stabilization of the M/B parent complexes for 12 co-extractants B.

Table 9 Different contributions to the formation of mixed complexes from eqn. (10) and (11)[a]

B	M(III)	log $D_{M/(Cl\Phi)_2PSSH/B}$	log $D_{M/B}$	$\Delta_M^{stab}(B)$
TMP	Eu(III)	−2.34	−5.67	5.64
	Am(III)	−3.43	−5.79	5.01
TBP	Eu(III)	0.33	−2.87	5.51
	Am(III)	−1.17	−2.63	4.11
THP	Eu(III)	0.20	−1.14	3.65
	Am(III)	−1.48	−1.76	2.93
TOP	Eu(III)	0.03	−1.45	3.79
	Am(III)	−2.82	−4.54	4.36
T2EHP	Eu(III)	0.11	−1.30	3.72
	Am(III)	−2.92	−4.74	4.46
TPP	Eu(III)	−2.77	−5.71	5.25
	Am(III)	−3.66	−5.60	4.59
TAP	Eu(III)	−0.32	−2.07	4.06
	Am(III)	−1.83	−2.48	3.30
TBPO	Eu(III)	1.88	1.87	2.32
	Am(III)	0.62	2.57	0.70
TOPO	Eu(III)	2.18	3.63	0.86
	Am(III)	0.74	3.68	−0.29
TPPO	Eu(III)	1.84	1.79	2.36
	Am(III)	0.26	1.83	1.08
BPOPO	Eu(III)	0.24	−1.07	3.62
	Am(III)	−1.16	−1.10	2.59
T*i*BPS	Eu(III)	−1.70	−4.53	5.14
	Am(III)	−2.70	−4.28	4.23

[a] log $D_{M/(Cl\Phi)_2PSSH}$ = −2.31 for Eu(III) and −2.65 for Am(III).

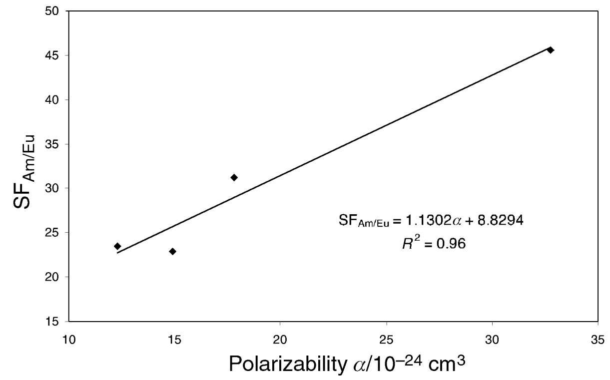

Fig. 12 Correlation between $SF_{Am/Eu}$ and the polarizability of diluent molecules for the synergistic mixture $(Cl\Phi)_2PSSH$ + TOPO.

and $\Delta_M^{stab}(B)$ are calculated as follows. Using the data from ref. 8, $\Delta_M^{stab}(B)$ were calculated for B = TBP, TPP and TOPO. All other $\Delta_M^{stab}(B)$ values can then be derived from the correlation $\Delta_M^{stab}(B)$ *vs.* log $SF_{Am/Eu}$. log $D_{M/B}$ values for Am(III) and Eu(III) were determined from eqn. (7) and (8).

All the results are summarized in Table 9 while Fig. 11 compares some of the terms calculated from eqn. (7) and (8) for different B. This suggests the following remarks. The extractability of M(III) by synergistic mixtures is the result of competition between the stabilization (or destabilization) of mixed complexes and the destabilization (or stabilization) of the parent complexes M/B. The effects are diametrically opposed according to the following: the weaker the M–O bond, the stronger the M–S bond. Three kinds of complexes can be observed. (i) Weak M/B complexes for both cations, with log $D_{Am/B}$ close to log $D_{Eu/B}$, for B = TPP, T*i*BPS and TMP. Low Am/Eu selectivities are observed in this case. (ii) Strong M/B complexes for both cations, with log $D_{Am/B}$ > log $D_{Eu/B}$, for B = TBP, TAP, THP, TOPO, TPPO, BPOPO and TBPO, which results in intermediate Am/Eu selectivities. (iii) Weak M/B complexes with log $D_{Am/B} \gg$ log $D_{Eu/B}$, for B = T2EHP and TOP. This corresponds to a strong reversible stabilization effect, especially for Am(III) and, as a result, high Am/Eu selectivity is observed.

Influence of the diluent

The influence of the type of diluent on the extraction of traces of Am(III) and Eu(III) by 0.5 M $(Cl\Phi)_2PSSH$ + 0.25 M TOPO from nitric acid was previously investigated.[7] To interpret the data, M(III) extraction properties are compared with the polarizability of the diluent molecules. It is well known that the polarizability of a molecule increases with molecular size, and it was observed[14,30] that polarizability runs parallel to covalency or softness. Linear relationships were observed between log $D_{M(III)}$ values and the polarizability of the diluent molecules: (i) for Am(III) log $D_{Am(III)} = 0.04\alpha + 0.38$ (with $R^2 = 0.93$) and (ii) for Eu(III) log $D_{Eu(III)} = 0.03\alpha + 0.81$ (with $R^2 = 0.94$). Fig. 12 shows that the selectivity, $SF_{Am/Eu}$, increases with increasing polarizability of the diluent molecules. Diluent molecules with large volumes and branched structures are expected to lead to increasing Am/Eu selectivity.

Conclusions

The present work demonstrates that Pearson's classification of acids and bases into hard, soft and intermediate appears to be incomplete for its application to the selective separation of trivalent lanthanides and actinides by liquid–liquid extraction. The insufficiencies concern (i) the change in the hardness of f-block elements across the series and (ii) the relative affinity of donor atoms (here O and S) for the complexation of Ln(III) and An(III).

Although trivalent lanthanides and actinides can be considered as hard acids, it is shown that the quantitative treatment of Pearson's ideas concerning the ability of an acid to accept electrons or of a base to give electrons,[11] results in a wide hardness variation across the lanthanide and actinide series. In the conventional classification,[12–14] the hard cations Am(III) and Eu(III) prefer to coordinate with hard bases, but the experimental results show that Am(III) and Eu(III) form complexes with the soft dithiophosphonate and dithiophosphonic acid ligands.

Moreover, under Klopman's classification,[11] Eu(III) appears to be a less hard acid than Am(III), but again experience reveals the opposite. It is proved that covalency effect(s) can change the respective parameters of hardness of Ln(III) and An(III) ions.

Finally, the key problem in the classic theory of hardness/softness concerning the combination of soft and hard donor atoms in the first coordination sphere of An(III) or Ln(III) may not be clearly understood. This problem concerns the theory of synergism and the formation of mixed complexes. It is unclear whether hard Am(III) or Eu(III) complexation with the soft R_2PSS^- ligands will be strengthened by the presence of groups bearing hard oxygen atoms in neutral co-extractants. It is shown that the M–S bonds may be strengthened or weakened depending on the donor ability of the hard oxygen atoms.

These fundamental problems in the application of hardness/softness theory to the chemistry of Am(III) and Eu(III) were solved through the study of their synergistic selective extraction from aqueous nitric acid solution using di(chlorophenyl)dithiophosphinic acid and neutral organophosphorus co-extractants. Several analyses are discussed in this paper: (i) quantum chemical calculations of the donor properties of co-extractants, (ii) analysis of $\delta(^{31}P)$ NMR chemical shifts of the co-extractants, (iii) analysis of the S → Eu(III) charge transfer energy in mixed $Eu/(Cl\Phi)_2PSSH/B$ complexes, (iv) qualitative thermodynamic calculations of the synergistic effect, and (v) evaluation of the Eu–S interatomic distances in mixed complexes with several co-extractants B. These analyses suggest a rule of design of hard co-extractants to strengthen (or weaken) the M–S bonds: the addition of neutral strong donor co-extractants bearing O atoms to an existing S-ligand weakens the M–S bonds and increases the M–S distance. The addition of neutral weak donor co-extractants results in the opposite effect.

From the data on the extractability of Eu(III) and Am(III) by $(Cl\Phi)_2PSSH$ + B mixtures, where B are phosphates, we can conclude that steric hindrance exerts a greater effect on the extraction of Eu(III) than Am(III). The importance of such steric effects was also pointed out recently by Baaden *et al.* in the complexation of Ln(III) ions by R_2PSSH acidic ligands with different R groups.[31] In the case of Eu(III), which has a smaller ionic radius than Am(III), we can conclude that the steric effect may be preponderant, whereas in the case of Am(III), which forms more covalent bonds than Eu(III), the donor–acceptor mechanism of extraction appears to predominate.

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