Synergism as a phenomenon in solvent extraction of 4f-elements with calixarenes

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The main objective of the present review is to provide an overview on the synergistic solvent extraction of lanthanoids, in particularly on the use of β-diketone/calixarene *i.e.* acidic/neutral mixture, as well as the analysis of data hitherto reported in this scientific topic. Based on the previously presented results, the extraction efficiency has been careful examined and discussed mainly in terms of the corresponding equilibrium constants among other outlined extraction parameters. Furthermore, the evaluation of the chelating ligand structures and pK_a values are emphasized. Major conclusions on the role of calixarene's ligating groups towards the mechanism, the improved extraction enhancement and selectivity are additionally provided. Consequently, it is very important that the obtained remarkable architecture of the formed complexes with very high coordination numbers (10/12) including a few cyclic molecules is in accordance with the well-established principles of coordination 4f-ion chemistry. Finally, a critical analysis of the lanthanoid intra-group selectivity (light/middle, heavy/middle and light/heavy 4f-ion pairs) *versus* the extraction performance of the acidic/neutral combinations and, on the other hand, the nature of the water-immiscible molecular or ionic diluent used have also been carried out and are here presented and critically addressed.

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1. Introduction

1.1 Synergistic effect in solvent extraction

Solvent extraction has a long tradition ever since the 15th century when the alchemical manuscripts of Raymundus Lullus appeared. The first discovery of extraction method dates back to 1842 (ref. 1) when the French chemist Péligot discovered a novel

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method for U(VI) extraction with ethylacetate and diethyl ether. This was followed by intensive study and serious attempts were made to replace explosive diethyl ether with an equivalent diluent but without much success.[2] In the period from Bucholz's first publication[3] to the beginning of the 21st century, very important investigations were undertaken (Jungfleisch, Berthelot, Nernst, Morse) and a number of studies have been published dealing with various aspects of solvent extraction.[2] The need of molecules, which were able to increase extraction and separation of specific metallic ions made liquid extraction an expanding research field in the 20th century. One important milestone in the understanding of the extraction process undoubtedly was the discovery of the synergistic effect.[4] The term synergism is used to describe cases where the extractive capability of a mixture of extractants is greater than the sum of their individual extractive capabilities. The corresponding adjective is synergic and the term synergistic should not be used according to IUPAC Golden Book, but almost all scientists preferred the suffix "-istic". The first careful study of this phenomenon in 1958 was carried out by Blake *et al.*[5] from Oak Ridge National Laboratory (USA), who found that U(VI) is extracted synergistically by a mixture of dialkylphosphoric acid, $(RO)_2PO(OH)$ and a neutral organophosphorus reagent of the type $(RO)_3PO$. But the authors thought that this enhancement seems limited to this specific combination used. In an early publication Irving and Edgington[6] pointed out that this statement is too sweeping concerning the analysis of the problem realized of a number of analogous systems for U(VI) extraction including thenoyltrifluoroacetone (HTTA) instead of dialkylphosphoric acid, and as consequence indicated the following conditions for synergistic extraction of a metal:

- One of the extractants is capable of neutralizing the charge of the metal ion, preferably by forming a chelate complex.

- The second molecule (synergist) is capable of displacing any residual coordinated water from this formally neutral complex and rendering it less hydrophilic.

- The second agent is not hydrophilic and is coordinated less strongly than the first (chelating) extractant.

- The maximum coordination number of the metal and the geometry of the ligands are favourable.

Healy further showed that synergism is a general effect, occurring in the extraction of alkaline earth, lanthanoids and actinoids, Th(IV) and uranyl ions[7] and could be explained by the formation of a mixed complex involving the two reagents, which is more hydrophobic than the complexes involving one of the ligands. The synergistic effect can be expressed by the synergistic coefficient (SC) defined by Taube and Siekierski[8] as $SC = \log(D_{1,2}/D_1 + D_2)$, where: D_1, D_2 and $D_{1,2}$ denote the distribution ratios of a metal ion between organic and aqueous phase, containing one of the extractants and their mixture. It has been observed in many systems that by increasing the concentration of one of the extractants (and keeping the other one constant) the extraction first increases (known as the synergistic region) and then it starts decreasing (destruction of synergism or negative synergism). An assumption was made by Healy[7] that the presence of water in the organic phase appears to destroy the enol bond in the β-diketone compound completely forming the ketohydrate by direct reaction and have an appreciable effect on the breakdown of the synergism. The degree of anti-synergism depends on the quantity and nature of the second extractant. The term antisynergism has been used for a destruction of synergism, but some authors have objected to it as a contradiction in terms and have suggested that antagonism be used instead. The extraction is synergistic when SC > 0, and antagonistic when SC < 0. It has been observed in the extraction of trivalent actinoids and lanthanoids that the synergistic enhancement is sometimes very high (of the orders) up to 10^8 using HTTA instead of dialkylphosphoric acid (10^2).[7] This is one of the reasons for the great interest shown in the synergistic research studies of this class of metals *i.e.* f-elements.[9] In the pioneer work, Healy[7] suggested that when quoting stability constants produced by synergistic mixtures it is essential to refer to the diluent used because so-called "inert" diluents caused an extremely large variation in extraction system Am/HTTA/TBP(tri-*n*-butylphosphate)/HCl/(CHCl$_3$ < C$_6$H$_6$ < CCl$_4$ < hexane < cyclohexane). Numerous scientists demonstrated that the synergistic effect depends strongly on the choice of the diluent and is higher the lower its polarity.[10]
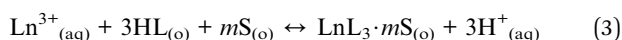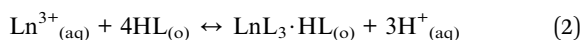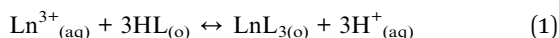
Over the years, thorough investigation of this phenomenon has appeared, the synergism has been found to be most effective when an acidic (HL) and a neutral (S) ligand are used together,[2,4–10] although other combinations between two acidic or two neutral extractants, anionic/neutral or even two anion exchangers compounds as well as cationic/anionic mixture are also possible.[11]

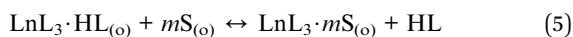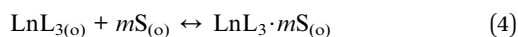## 1.2 Why lanthanoids are classified as strategic elements?

According to the Nomenclature of Inorganic Chemistry, The Red Book of IUPAC series, the 15 elements from La(57) to Lu(71) should be named 4f-elements or lanthanoids (Lns) but this term is not so adopted by the scientific community preferring still lanthanides. Coordination chemistry of 4f-ions has been attracted significant attention owing to their outstanding properties[12,13] and considering the growing levels of Lns present in the technosphere.[14,15] Rare earth elements (REs), the lifeblood of today's high-tech industry, are employed in a broad scale of environmental technologies, military industries, energy security and even in medical diagnostic. REs find application in many advanced materials including low energy light bulbs, fluorescent materials, high temperature superconductors, catalytic converters, high performance magnets ($Nd_2Fe_{14}B$, $SmCo_5$, Sm_2Co_{17}) and new wind turbines that are 70% more efficient than the standard ones. The 4f-elements turn up inside every computer, cell phones, DVD players, cameras, TVs, plasma and LCD screens, electric motors and generators of hybrid cars. These applications rely on distinct properties that result from their complex electronic structures and so substitution and recycling are low, difficult or not yet feasible. No viable substitutes demonstrating identical performances have been found over 50 years for europium inducing the red color in TV screens as well as over 30 years for samarium or neodymium in the powerful magnets.

1.3 Methods used for the investigation of the synergistic solvent extraction

Several methods (slope analysis, continuous variation, curve fitting, spectrophotometry and nuclear magnetic resonance)[4–10] have been proposed for the determination of the stoichiometry of the extracted species and the corresponding equilibrium constants. The slope analysis is the most widely used method because of its simplicity and effectiveness. The method is based on an examination of the variation of the distribution ratio (D) with the relevant experimental variables. A plot of the logarithm of the D vs. the logarithm of one of the variables (the concentration of the two extractants and of H^+), keeping the other two constant, indicates the stoichiometry of the extractable complex, a suitable equilibrium expression can be obtained, and consequently, the equilibrium constant can be computed. The application of the slope analysis method can be illustrated by the extraction of the trivalent 4f-ion Ln^{3+} with a chelating compound and with a mixture of HL and a neutral agent, S. The extraction of Ln^{3+} can be represented by the following equilibria:

$$Ln^{3+}_{(aq)} + 3HL_{(o)} \leftrightarrow LnL_{3(o)} + 3H^+_{(aq)} \tag{1}$$

$$Ln^{3+}_{(aq)} + 4HL_{(o)} \leftrightarrow LnL_3 \cdot HL_{(o)} + 3H^+_{(aq)} \tag{2}$$

$$Ln^{3+}_{(aq)} + 3HL_{(o)} + mS_{(o)} \leftrightarrow LnL_3 \cdot mS_{(o)} + 3H^+_{(aq)} \tag{3}$$

The formation of mixed complexes in the organic phase can be described by the following equation:

$$LnL_{3(o)} + mS_{(o)} \leftrightarrow LnL_3 \cdot mS_{(o)} \tag{4}$$

$$LnL_3 \cdot HL_{(o)} + mS_{(o)} \leftrightarrow LnL_3 \cdot mS_{(o)} + HL \tag{5}$$

The equilibrium constants K_L, $K_{L,S}$ and $\beta_{L,S}$ are given by the expressions:

$$K_{L(1)} = \frac{[LnL_3]_{(o)}[H^+]_{(aq)}^3}{[Ln^{3+}]_{(aq)}[HL]_{(o)}^3} = D_{L(1)}\frac{[H^+]_{(aq)}^{3+}}{[HL]_{(o)}^3} \tag{6}$$

$$K_{L(2)} = \frac{[LnL_3 \cdot HL]_{(o)}[H^+]_{(aq)}^3}{[Ln^{3+}]_{(aq)}[HL]_{(o)}^4} = D_{L(2)}\frac{[H^+]_{(aq)}^{3+}}{[HL]_{(o)}^4} \tag{7}$$

$$K_{L,S} = \frac{[LnL_3 \cdot mS]_{(o)}[H^+]_{(aq)}^3}{[Ln^{3+}]_{(aq)}[HL]_{(aq)}^3[S]^m} = D_{L,S}\frac{[H^+]_{(aq)}^{3+}}{[HL]_{(o)}^3 S_{(o)}^m} \tag{8}$$

$$\beta_{L,S(1)} = \frac{[LnL_3 \cdot mS]_{(o)}}{[LnL_3]_{(o)}[S]_{(o)}^m} = \frac{K_{L,S}}{K_{L(1)}} \tag{9}$$

$$\beta_{L,S(2)} = \frac{[LnL_3 \cdot mS]_{(o)}[HL]_{(o)}}{[LnL_3 \cdot HL]_{(o)}[S]_{(o)}^m} = \frac{K_{L,S}}{K_{L(2)}} \tag{10}$$

The equilibrium constants K_L, $K_{L,S}$ and $\beta_{L,S}$ are concentration constants and they are based on the assumption that the activity coefficients of the species do not change significantly under the experimental conditions employed.[16] If it is assumed that

$LnL_3 \cdot mS$ is the only synergistic species present in the organic phase, the values of $D_{L,S}$ can be calculated from the equation: $D_{L,S} = D - D_L$, where D is the overall distribution ratio. Taking logarithms on both sides of eqn (6)–(10), the following is obtained:

$$\log K_L = \log D_L + n\log[H^+] - n\log[HL] \tag{11}$$

$$\log K_{L,S} = \log D_{L,S} + n\log[H^+] - n\log[HL] - m\log[S] \tag{12}$$

$$\log \beta_{L,S} = \log K_{L,S} - \log K_L \tag{13}$$

The stoichiometry numbers n and m can be obtained from the slope of the plots of $\log D_{L,S}$ vs. pH, $\log[HL]$, or $\log[S]$ while keeping constant all others and the equilibrium constants can be computed from the eqn (11) and (12) using the experimental data.

Some limitations of the slope analysis method application is due to side reactions in the aqueous or organic phases as well as to the interaction between extractants.[4] Almost always the aqueous phase contains anion (ClO_4^-, Cl^-, NO_3^-, SO_4^{2-}) or other ions and to a certain degree they could form complexes with metal ions.[16,17] The kind of the extracted species depends on the nature of the aqueous-phase acid and its concentration. The method will also not give good results if some impurities are presented in the organic phase that are likely to form addition compounds with extractants. As it is well-known that the chelating agents are weak acids and neutral donors are bases, there is a possibility for interaction between them, which will reduce the concentrations of free ligands. Another limitation is the lack of knowledge of the activity coefficients. In all experiments, assumption is made that activities may be replaced by concentrations at constant ionic strength.[18]

The chemistry of synergistic systems is much more diverse seeing the variety of molecules and the possibility of so numerous combinations. The present review is restricted to the examination of systems in which one of the extractants is β-diketone and the role of the synergistic agent is played by calixarene. This review covers the literature until the end of September 2015, and to the best of our knowledge no reviewers high-lighting this specific synergistic concept caused by calixarene molecules in solvent extraction have been previously published. Increasing number of new exotic or simple reagents and accumulating knowledge of novel extraction systems have been elaborated during the years. Although, they are not treated comprehensively in this survey, their contribution to the progress of separation science and technology is significant.

The following discussion is divided into different sections regarding (i) the nature and the extractant behaviour of β-diketones and calixarenes; (ii) the extraction mechanism and the corresponding equilibrium constants; (iii) the synthesis of solid complexes is also considered in a more simplistic view; (iv) particularly relevant are the investigations focused on the possible interaction between extractants in the organic medium; (v) synergistic enhancement and metal selectivity in 4f-series are also discussed. Finally, the obtained results, in what concerns the extraction efficiency and selectivity of the

systems chelating ligand/calixarene are further critically outlined and addressed in comparison with similar literature data available.

2.   Solvent extraction of 4f–elements using acidic chelating/neutral couple of extractant molecules

2.1   β-Diketones as chelating agents for lanthanoids: characteristic and efficacy

Organic extractants facilitate the transfer of the metal ions from the aqueous to organic phase in solvent extraction. Since its discovery, a great deal of interest has been focused on the synergism in the extraction of metal ions by β-diketones.[7] Usually, they dissociate at low pH to form anionic ligands that form strong metallic complexes. Consequently, it is essential that an extractant and its metal complex have a very low solubility in water and a high solubility in the water-immiscible phase. Thenoyltrifluoroacetone (HTTA) was introduced as an analytical reagent by Calvin and Reid in 1947 and has been extensively used as an extractant for Lns, Fig. 1. Owing the presence of trifluoromethyl group, it has high acidity in the enol form ($pK_a = 6.23$), which in turn is useful in the extraction of many metals at low pH.[19]

The next category is 4-acyl-1-phenyl-3-methyl-5-pyrazolones, α-substituted β-diketones with pK_a: 2.5–4.[20,21] Since, the first advantageous synthesis proposed by Jensen in 1959, acylpyrazolones are one of the most widely used O-donors in coordination chemistry. The method is based on direct acylation of pyrazolones with acyl chlorides or anhydrides in the presence of calcium hydroxide, Scheme 1.[22] The various synthetic modifications on the basic structure were applied by chemists in order to increase their ability to complex formation with metals and to ameliorate the extraction strength and the separation of elements with similar chemical properties like 4f and 5f-ions, coinage elements or early transition metals.[23] The influence of various *para*-substituted 4-aroyl-3-methyl-1-phenyl-pyrazol-5-ones on the extraction process of lanthanoids has been also investigated,[24] Table 1. It is interesting to note that the compound 3-methyl-4-(4-methylbenzoyl)-1-phenyl-pyrazol-5-one can adopt four different tautomers, determined by the combination of the keto–enol tautomerism of pyrazolone and the attached 4-acyl carbonyl group. The single crystal XRD and solid NMR structural analyses revealed that three desmotropes are obtained, two of them as two different conformational polymorphs, and probably this is the first record in the literature, when more than two desmotropes of a given molecule has been reported.[25]

Another type of chelating compounds not so exploited, 3-methyl-4-acyl-5-isoxazolones, has more stronger acidities (lower pK_a values: 1.23) and very high enhancing extraction power, Fig. 1.[19,26] Low pK_a value of 4-benzoyl-3-phenyl-5-isoxazolone (HPBI) is due to the presence of heterocyclic isoxazolone group, which enhances the dissociation of the β-diketone anions. The presence of phenyl group with –I effect, on the other hand, imports the desired partitioning behavior of the ligand and makes β-H atom more acidic.

The lanthanoids exist almost exclusively in trivalent state in coordination complexes or supramolecular assemblies. Usually, tris-complexes LnL$_3$ containing three chelating ligands (HL) for an ion have been formed in solid state or as a result of the complexation in solution, Fig. 2. When dealing with HTTA,[27–29] HPBI[26] or HP[30–34] the extraction equilibria of lanthanoids can be described by the equation:

$$Ln^{3+}_{(aq)} + 3HL_{(o)} \rightleftharpoons [LnL_3]_{(o)} + 3H^+_{(aq)} \qquad (14)$$

The extraction species of various actinoid ions (Pu^{4+}, UO$_2$$^{2+}$, Th^{4+}, Np^{4+}) of the same type, chelates (1 : 4) were created in xylene operating with these organic compounds as well: for example Pu(PBI)$_4$, Th(PBI)$_4$ or Np(PBI)$_4$ incorporating four anions of HPBI.[35–38]

But the coordination sphere of the trivalent ion is unsaturated, so the lanthanoid can expanded it coordinating additionally water molecules for example LnL$_3$·(H$_2$O)$_x$, x = 2 or 3, Fig. 2.[39]

In some cases complexes with different chemical composition from that 1 : 3 (metal : ligand) ratio can be obtained. For example, eight coordinated Eu(III) complex was synthesized with the stoichiometry [Eu(TTA)$_2$(C$_2$H$_5$OH)$_4$]Cl possessing distorted square antiprism coordination polyhedron, Fig. 2.[27] The most common coordination number of lanthanoid complexes is eight or nine, which is close to the sum of 6s, 6p and 5d orbitals.

Albinsson has established that at least two complexes exist, LnAa$_3$ and the self-adduct LnAa$_3$·HAa in the organic phase (C$_6$H$_6$) and for the lower lanthanoids (especially La) a second self-adduct, LnAa$_3$(HAa)$_2$ was supposed to be extracted as well with acetylacetone (HAa).[40] The solvent extraction behavior of
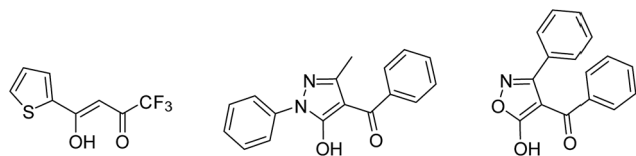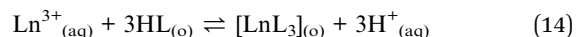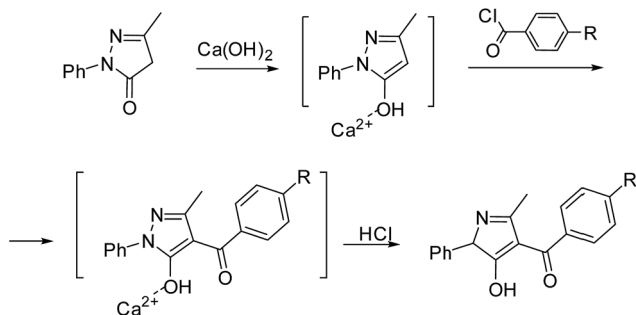

Fig. 1   Structural formulas of the chelating extractants (HTTA, HP and HPBI, respectively).

Scheme 1   Synthesis of 4-aroyl-3-methyl-1-phenyl-pyrazol-5-ones (HL).[22]

Table 1 4-Aroyl-3-methyl-1-phenyl-pyrazol-5-ones

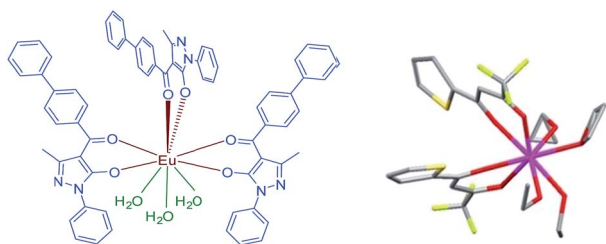| −R	Abbreviation	Chemical name
−H	HP	4-Benzoyl-3-methyl-1-phenyl-5-pyrazolone
−CH$_3$	HPMMBP	3-Methyl-4-(4-methylbenzoyl)-1-phenyl-pyrazol-5-one
−C$_6$H$_5$	HPPMBP	3-Methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one
−F	HPMFBP	4-(4-Fluorobenzoyl)-3-methyl-1-phenyl-pyrazol-5-one
−CF$_3$	HPMTFBP	3-Methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-one

Fig. 2 The suggested structures of Eu(PPMBP)$_3$·3H$_2$O[39] ©2015, The Japan Society for Analytical Chemistry and the structure of [Eu(TTA)$_2$(C$_2$H$_5$OH)$_4$]Cl from single crystal X-ray diffraction[27] ©2008, Elsevier.

all 4f-elements has been investigated using 3-methyl-1-phenyl-4-benzoyl-5-pyrazolone (HP) and the composition of the species has been determined as LnP$_3$·HP.[41,42] A wealth of previously published results using various solvents have shown that the extraction equilibria of lanthanoids with 4-acylpyrazolones can be described by the equation:[24,41–51]

$$Ln^{3+}_{(aq)} + 4HL_{(o)} \leftrightarrow LnL_3 \cdot HL_{(o)} + 3H^+_{(aq)} \quad (15)$$
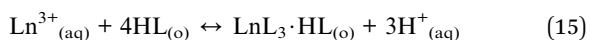
The species of the type Th(X)P$_3$·HP (where X = NO$_3^-$ or ClO$_4^-$) were also announced for 5f-ions by Mohapatra et al.[52]

The structure of these complexes could be compared with those of the mixed synergistic complexes. The three pyrazolone anions neutralize the lanthanoid cation charge and the four neutral HL molecule acts as a synergist displacing water molecules from the inner coordination sphere rendering the self-adducts less hydrophilic, so such an effect can be named self-synergism.

The corresponding equilibrium constants for the extraction of trivalent lanthanoids and actinoids with some chelating extractants calculated on the basis of eqn (1) and (2) are summarized in Table 2.

The data show that the values of log K of HPBI are higher (up to 8 times) than those obtained for the extraction of metals of the 4f-series with HTTA as well as approximately 4 times higher as compared with 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone (HP) as a chelating extractant. It can be concluded, from the collected data in Table 2, that the equilibrium constant values increase as the pK_a values decreases i.e. the inverse linear correlation of extraction constant with respect to the pK_a. The correlation of the equilibrium constants for La(III) extraction with pK_a of the used compounds was shown in Fig. 3.

Almost linear correlation was observed for lanthanum extraction behavior changing β-diketone's acidity. The

difference in the extraction enhancement is seen changing the type of the compound i.e. typical β-diketone and β-diketones, in which the heterocyclic ring contained one of the ketonic groups (acylpyrazolone and isoxazolone). On other hand, in terms of chemical structure in a β-diketone family (benzoylacetone(HBA)/HTTA), the substituent effect of the CF$_3$ group, which is very well acknowledged in solvent extraction,[19,45] is clearly demonstrated, Table 2 and Fig. 4. It is established that the substituted pyrazolones in para-position cause quantitative changes in the synergistic extraction of lanthanoids with CHCl$_3$.[24] The obtained log K values with 4-fluorophenyl terminal group (an electron withdrawing substituent) are larger than the case when electron donating (−CH$_3$) groups are introduced in the benzoyl moieties. So, acid dissociation constants are important parameters for a quantitative understanding of complex equilibria and is of fundamental significance in order to predict the substance efficiency. In liquid–liquid extraction of Lns with molecular solvents, great attention has been paid to the exact pK_a value of the ligand and this parameter has been carefully adjusted by introduction of various substituents.[24,45,46]

It is seen from the data presented in Table 2 that the equilibrium constants increase with increasing atomic number of the metals as expected from their decreasing ionic radii form La to Lu due to the lanthanoid contraction, Fig. 4. With increasing atomic number, ionic radii decrease at constant charge, and consequently the charge densities increase and formation of extractable complex is favoured for heavier lanthanoids.

2.2 Calixarenes as ligands in coordination chemistry of 4f-elements

Molecular design has enjoyed a long history from the preliminary "trial and error" stage to the contemporary computer aided "molecular modeling". Higher extraction efficiency with macrocyclic ligand should be expected due to multicentered coordination with metallic species. Calixarenes, the third generation of supramolecules (after cyclodextrins and crown ethers), have first seen the light of day in the nineteenth century in the laboratory of Adolf von Baeyer, but their oligomeric nature was delineated in the 1970's by Gutshe[54] who gave the compounds their presently accepted name (Gr: calyx meaning vase or chalice and arene indicating the presence of aryl residues in the macrocyclic array), Fig. 5. The similarity with chalice pointing out the presence of a cup-like structure, when the macrocycles assume the conformation cone, in which all aryl groups are oriented in the same direction (because rotation around the methylene bridge is possible). In calix[4]arene (the internal volume being around 10 nm^3), four conformations,

Table 2 log K values of lanthanoids using different chelating agent, $\mu = 0.1/Cl^-$ medium/$CHCl_3{}^a$

Ln^{3+}	HBA	HTTA	HPPMBP	HPMMBP	HP	HPMFBP	HPMTFBP	HPBI
La	−21.81	−11.06	−6.21	−6.12	−5.84	−5.16	−3.24	−1.33
Nd		−10.12	−5.84	−4.17	−4.35	−3.91	−2.74	−0.54
Eu		−8.68	−5.57	−3.89	−3.42	−3.37	−2.47	0.06
Ho		−8.56	−4.97	−3.37	−3.24	−2.84	−1.88	0.36
Lu		−8.15	−4.58	−3.12	−2.83	−2.62	−1.62	0.70
U^{6+}		−2.44			0.63			1.40
Th^{4+}		2.25			6.96			8.26
Np^{4+}		5.68						10.11
Pu^{4+}		7.31			13.75			10.76
pK_a	8.96	6.23	4.23	4.02	3.92	3.52	4.40	1.23

^{a} Notes: HBA – benzoylacetone; HPBI – $ClO_4{}^-$ medium; actinoids[53] – xylene, $CHCl_3$, C_6H_6, toluene; $Ln(TTA)_3$, $Ln(PBI)_3$ and $LnL_3 \cdot HL$ (where HL is 4-acylpyrazolone).
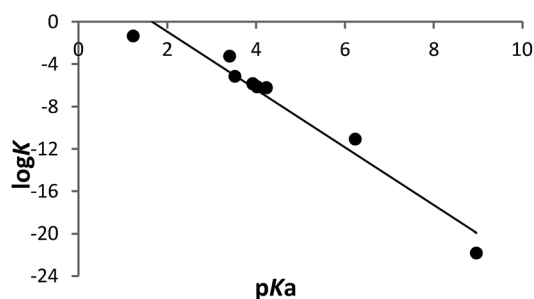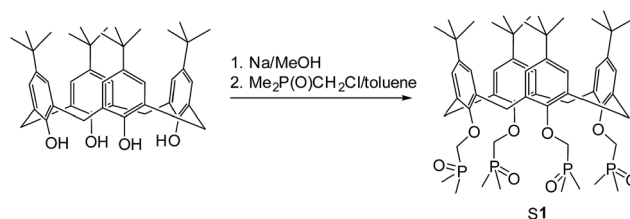

Fig. 3 log K values of La(III) vs. pK_a of the chelating extractants (see Table 2).
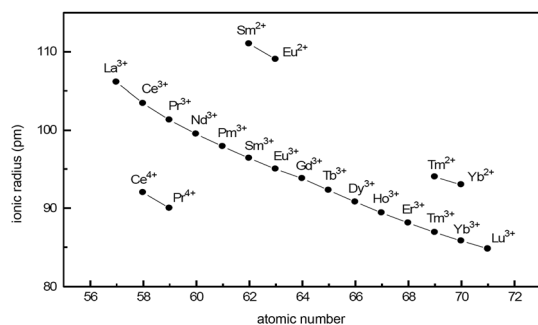
Fig. 4 Ionic radius (Ln^{3+}) vs. atomic number, Z.
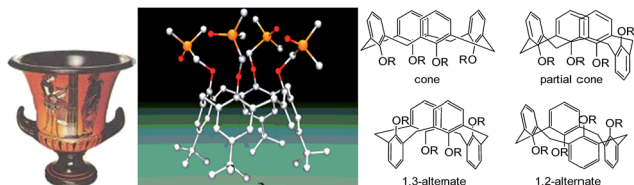
Fig. 5 Chalice. Structure of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis-(dimethylphosphinoylmethoxy)calix[4]arene[55] and different calix[4]arene conformations.

this chain prevents the benzene units from rotating inside the calixarene cavity.

The unique molecular architecture of calix[n]arenes (n = 4–20, macrocycles made up of n phenolic units) makes them a suitable platform for construction of host neutral molecules especially with an even number of cycles (n = 4, 6, 8; simple one-pot preparation in good to excellent yields, Scheme 2) cyclic that can selectively bind a variety of guest substrates through introduction of suitable fragments on the upper or lower rim,[55] Scheme 2. Calixarenes generally have high melting points, high chemical and thermal stability, low solubility and low toxicity.

There are two basic features to modify these unique three-dimensional structures with almost unlimited derivatization abilities: introduction of variable substituents and additional functional groups both at the lower or "wide" hydrophilic (OH side) and upper or "narrow" hydrophobic (alkyl branch side) rims, *i.e.* a versatile scaffold for the fabrication of a multi-purpose "lab on a macrocycle",[56–67] Fig. 6. The chemical structures of several calixarenes are presented in Fig. 7. Calixarenes structural properties combined with ligands containing phosphorus pendant arms at the lower rim have led to a substantial enhancement of lanthanoids and actinoids extraction effectiveness and selectivity, as consequence their implementation became very exploratory research topic in the extraction chemistry.[53] Depending on the nature of the ligating groups, on the dimension of the macrocyclic scaffold and on the hydrophobicity, calixarenes have shown immense selectivity in the separation of alkaline and alkaline earth ions, heavy metals and f-elements.[68–71] Furthermore, rigid stereochemistry of macrocyclic structures makes them highly selective as the complexation

which are in dynamic equilibrium, are possible (cone, partial cone, 1,2-alternate, and 1,3-alternate). But they can be locked by placing a bulkier substituent than ethyl group, as consequence

Scheme 2 Synthesis of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis-(dimethylphosphinoylmethoxy)calix[4]arene.

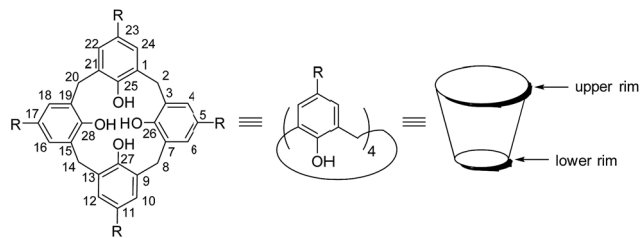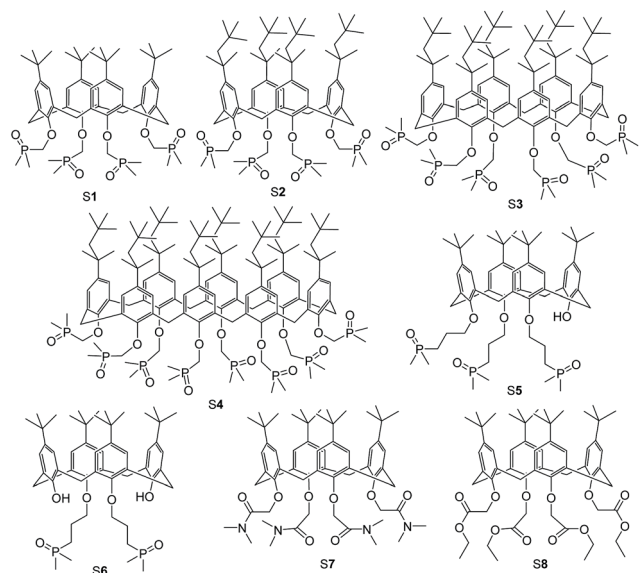Fig. 6 Molecular structure of calix[4]arenes.

Fig. 7 Chemical structures of selected calixarenes.

Fig. 8 Distribution ratio *vs.* $C(HNO_3)$ for the extraction of La(III), Eu(III) and Am(III) with the corresponding calixarene shown below. Drawn from data reported in ref. 75.

constant is rather high due to the better geometric matching between the metal ion and the set of donor centers of the calixarene matrix. Ludwig and co-workers[72] were concluded that the cavity size, the position and kind of donor groups, and the ligand hydrophobicity have a pronounced impact on the extraction power and selectivity. Some are better extractants for lanthanoids than TOPO (tri-*n*-octylphosphine oxide) or CMPO (*N*,*N*-diisobutylcarbamoylmethyl)octylphosphine oxide already used in the nuclear waste management.[68,73,74] It was established during the years that compounds possessing P═O group like phosphonates, phosphines and phosphine oxide derivatives, have shown high affinity for f-elements.[69]

The comparable extraction level or even superior to those of "classical" CMPO of calix[4]arenes bearing –$(CH_2)_n$–NH–C(O)–CH_2–P(O)–Ph_2 functions can be reached with ligand concentrations of 10^{-3} M or less under conditions relevant for the treatment of technical nuclear waste streams. Fig. 8 shows the results for the extraction of La^{3+}, Eu^{3+} and Am^{3+} into *o*-nitrophenyl hexyl ether as a function of the concentration of HNO_3 in the source phase.[75] So, no influence on the *D* values can be seen for higher acid concentrations.

The histograms given in Fig. 9 shows the extraction properties of three calixarene tetraphosphine oxides (S9, S10 and S11) dissolved in ionic liquid towards Eu^{3+}, Am^{3+} and UO_2^{2+} and
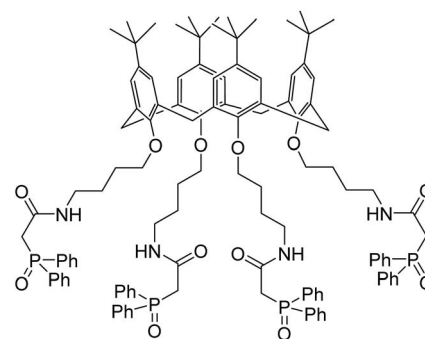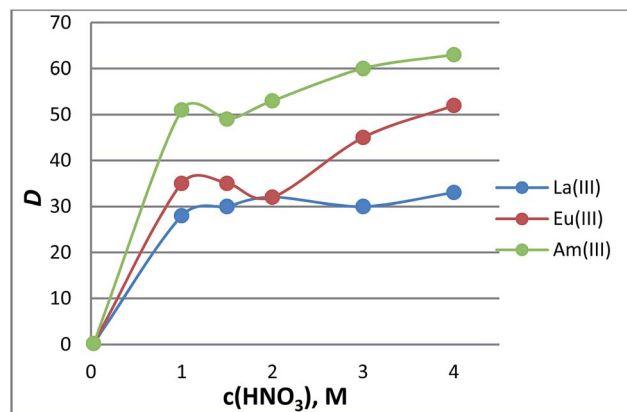
their superiority over industrial ligand, trioctylphosphine oxide, especially the high noticeable selectivity of S9 in UO_2^{2+} case.[76]

2.3 Calixarenes in the role of synergistic agent during solvent extraction of 4f-elements

The investigations devoted to the synergistic solvent extraction including these macromolecules with the aim to create a synergistic effect, enhancing the efficiency and selectivity are not so numerous, but very divergent. Mixtures of two neutral cyclic compounds, a series of crown ethers (dicyclohexano (DC18C6), dibenzo (DB18C6), 18-crown-6 (18C6), benzo-15-crown-5 (B15C5)) and *p-tert*-butylcalix[4]arene, exhibit synergistic effects in the extraction of alkali ions (Na, K, Rb, Cs) in dichloroethane.[77] The extractions including DC18C6 lead to the formation of the most stable ion pair complexes, whatever the size and nature of the s-ion. The synergistic extraction of Fe^{3+} and La^{3+} with *p-tert*-butyl-calix[8]arene octacarboxylic acid (H_8L) and tributyl phosphate (TBP) (0.1 M KNO_3, $CHCl_3$) was carried out by Zhiliang and co-workers[78] aiming high-efficient separation of lanthanum from various impurities. The published extractability data of La^{3+} with H_8L are represented in Table 3. The provided results showed that TBP has led to a significant synergistic effect on the Fe^{3+} extraction but surprisingly not for La^{3+}. As a host, H_8L can provided 8 possible coordination sites to guest ions such as La (radius of 0.115 nm much bigger than that of Fe (0.064 nm)), which might be included in the
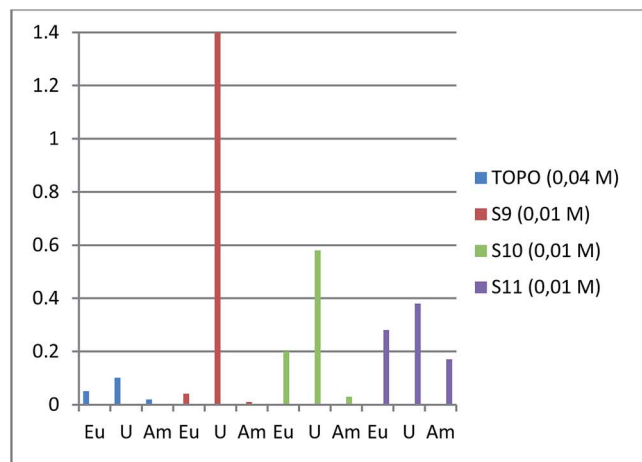
Fig. 9 Extraction of Eu^{3+}, UO_2^{2+}, Am^{3+} from HNO_3 (0.3 M) into N-butyl-N-methylimidazolium Tf_2N using the ligands TOPO, S9, S10 and S11. D-distribution ratios data from ref. 76.
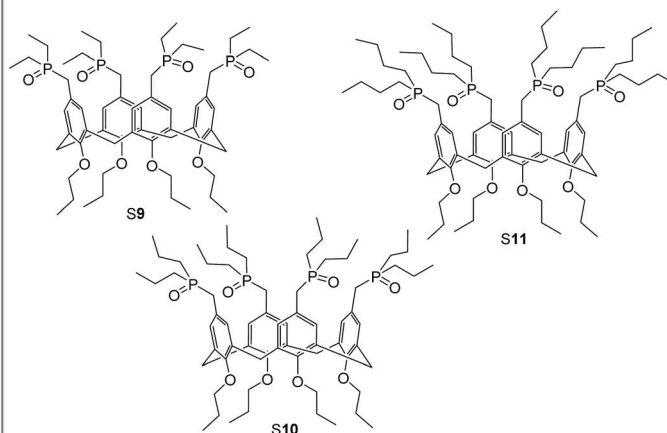
Table 3 Extractability data of La^{3+} with H_8L according ref. 78

pH	3.40		3.61	3.93	4.23
E, %	55.8		58.7	64.8	69.4
$C(H_8L) =$	$C(La^{3+}) =$		30 °C	For 12 h	
1.1×10^{-4} M	1.2×10^{-4} M				

Fig. 10 Molecular structures of $^tBu[4]CH_2COOH$ (H_4A) and primary amine N1923 (RNH_2).[79]

Fig. 11 Molecular structures of calix[4]resorcinarenes.[80]

coordination space of the upper rim, resulting to inability of TBP to take part in the formation of mixed complex. So, the authors' explanation is that the relatively bigger size of H_8L for Fe^{3+} ions may allow TBP molecules to participate in the synergistic extraction.

Li *et al.*[79] have concluded that a dramatic increase of the extractability of mixture of calix[4]arene carboxyl derivative and the primary amine N1923 (Fig. 10) might be due to a kind of acid–base intermolecular cooperative effect of $-CH_2=O(OH)$ and RNH_3Cl, which facilitated the formation of more stable lanthanoid complexes $LnClNa_2H_4A_2(RNH_3Cl)$. The addition of sodium ions (μ = 0.1 M, NaCl) into the aqueous phase for keeping the ionic strength enhanced the extractability of rare earth elements applying alone and in combination with the amine molecule as well. It is said that the cyclic tetramer calix[4]arene carboxyl derivative preferentially extracts sodium ions at first and then the sodium-loaded ligand extracts Ln(III) as a "pre-organized" extractant.[79]

Kuznetsova *et al.*[80,81] have studied the extraction of some f-ions (La, Pr, Yb, Lu, Ho, Eu, Am) with calix[4]resorcinarene or its alkylaminomethylated derivatives (dimethylamino-, piperidyl- and trimethylammonium moieties), (4×10^{-4} M, Fig. 11) in the presence of 1,10-phenanthroline (8×10^{-4} M) in n-heptanol. It was found that the synergistic effect is due to the formation of outer-sphere complex between the cation $[Ln(phen)_2]^{3+}$ and deprotonated forms of the calix[4]resorcinarene, $[H_5L]^{3-}$ *i.e.* dissociation of three protons from H_8L, and it was also established that the calix[4]resorcinarene's derivatives are more effective than its unsubstituted form. This effect was explained by the additional negative charge on the "rim" due to the intramolecular proton transfer from hydroxyl to basic
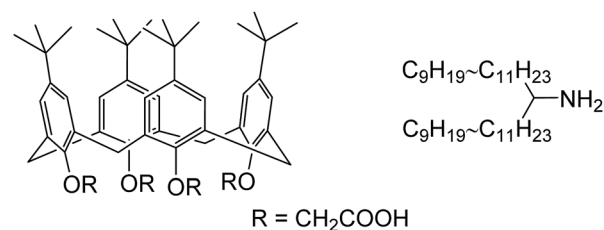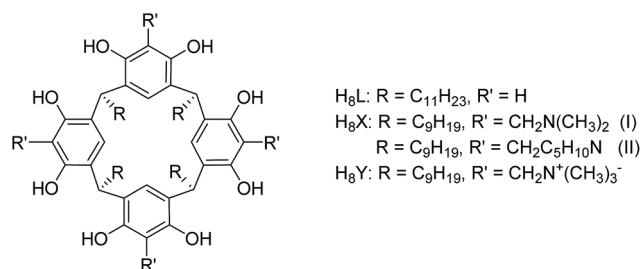
alkylamino-groups of the "host". The reported values of the extraction extent are more than 93% for La, Pr, Yb and Lu with H_8L–phen mixture at the pH region 6.6–6.9 with 0.0016 KOH equivalent quantities added to the organic phase *i.e.* a molar ratio H_8L : KOH = 1 : 4. H_8X itself also does not extract 4f-ions. In the presence of 1,10-phen the extraction occurs under the same concentration conditions (molar ratio Ln : H_8X : phen = 1 : 1 : 2) as H_8L but in more acidic media.

Tributylphosphate (TBP) was added to the *para-tert*-octylcalix[4]arene (both with concentration 2.4×10^{-4} M) in $CHCl_3$ in order to enhance the uranyl extraction.[82] The authors reported that TBP extracted only 11% under the experimental conditions applied but caused a significant synergistic effect increasing the extraction from 48% (calixarene alone) to 96%.

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The replacement of methylene bridges of calix[n]arene by sulfur atoms leads to an enlargement of the cavity and a possible coordination to specific metal ions controlled by the oxidation state of sulfur.[53] A synergistic effect with mixtures of three conformers (cone, partial cone and 1,3-alternate) of thiacalix[4]arene (four sulphur atoms instead of methylene groups) and dicarbollide in the solvent extraction of typical nuclear fusion products, Eu, Sr and Cs from diluted nitric acid into chlorobenzene was observed by Kyrš et al.[83] The plots of D values of all metals tested versus the varying concentration of one extractant keeping the concentration of the other extractant constant invariably exhibit maxima, interpreted as the result of an existence of several extracted species in the extract.[83] It is also relevant to remark that a synergistic effect of almost six orders of magnitude occurs in the extraction of europium from nitrate medium with mixtures of calix[4]arene and dicarbollide.[84] Highest synergistic D ratios were obtained with chlorobenzene as other 9 diluents were also tested. Similar to the work carried out by Kyrš and co-workers,[83] Macerata et al. presented investigation on the mechanism of the synergistic action of combinations calixarene/Co-dicarbollide (1×10^{-2} and 1.5×10^{-2} M, respectively) for La(III) extraction: nitrobenzene/HNO$_3$, pH 4.5, Fig. 12.[85]

A systematic attempt has been made by Atanassova and co-researchers to investigate the synergistic solvent extraction of lanthanoids with chelating molecule/calixarene combinations.[27–29,43–46,86–88] Various types of compounds, which belong to the two cyclic chemical families, Fig. 7, have been studied in order to examine the role of the chemical structure on the 4f-complexation.

2.4 Studying the possible interactions between 4-acylpyrazolones and calixarene molecule as a particular case (S1 and S5)

The possible direct interaction between the synergist and coordinated chelating molecule used for solvent extraction of metals is an important problem.[4,7,89–95]

The formation of an association product may occur effectively removing the free reagents from the extraction organic phase system. The interaction between acidic extractants, which belong to the pyrazolone family and neutral calixarene molecules (S1, S5) were studied at different molar ratios (respectively 1 : 2, 1 : 1, and 2 : 1) in chloroform by NMR experiments in few

papers.[24,45,46] The spectra show that no substantial interactions between the components of the extracting systems occur in the organic phase independently on the extractants' proportions. The NMR spectra of HPMFBP, for example correlate with pure enol forms possessing strong C=O···HO hydrogen bond. The signals in the spectra (^{1}H, ^{13}C, ^{31}P, ^{19}F) of the individual compounds and their mixtures possess the same chemical shifts, which is an indication that the presence of calixarene S1 in the organic phase as co-extractant does not cause conformational changes in pyrazolone molecules. This observation is confirmed by ROESY experiments. Only weak interactions between CH$_3$-3 of HL and t-Bu methyls and one of the bridged methylene protons of calixarene were detected (Fig. 13), while no cross peaks between the neighbouring to the complexing centres protons, calixarene P–CH$_3$ and P–CH$_2$ groups and pyrazolone aryls, were registered. For that reason, it can be concluded that the molecules are assembled in the space with HPMFBP CH$_3$-3 close to the upper rim of calixarene.[24]

HPMFBP interactions study with trialkylphosphine oxides (tributyl (TBPO), trioctyl (TOPO) and triphenyl (TPPO) phosphine oxides) and tributylphosphate (TBP) has shown that phosphorylated at the narrow rim calix[4]arene, S1 behaves similarly to TBP most probably due to the electronic effect of the calixarene oxygen or/and steric hindrance.[96]

A comparison between the studied systems permits to suggest that the free OH groups of S6 are involved in the interactions with pyrazolone chelating arm (HPMTFBP),[45] while pyrazolone phosphinoyl units of S5 do not participate.[24]

2.5 Synergistic solvent extraction of lanthanoids using mixtures of chelating extractant and calixarenes i.e. acidic/neutral system

2.5.1 Solvent extraction equilibria: mechanism.
Extraction from aqueous solutions into organic diluents can be achieved

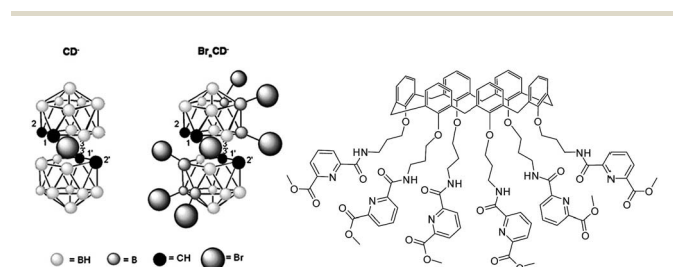**Fig. 12** The molecular structures and atom numbering of calix(1), Co-dicarbollide (CD) and Co-bromodicarbollide (Br$_6$CD).[85] Reproduced from ref. 85 with permission from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry.
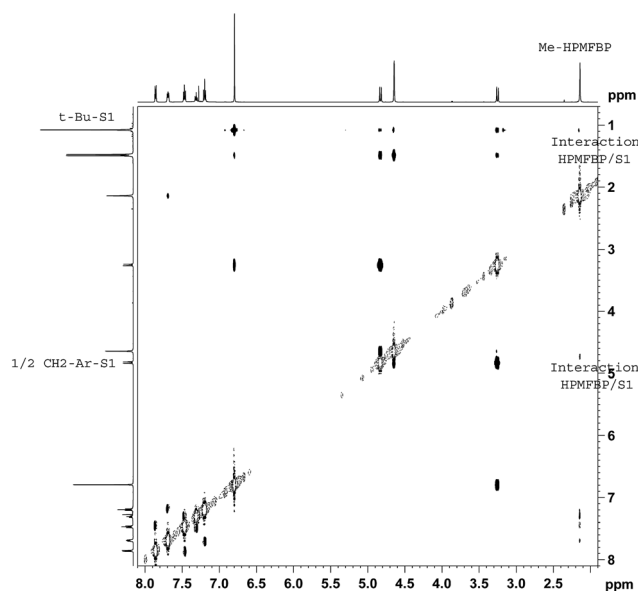
Fig. 13 A part of the ROESY spectrum of HPMFBP : S1 2 : 1 mixture in deuterochloroform.[24] ©2012 Elsevier.

through different chemical reactions but usually the overall net reaction was written.[16] An initial step in data analysis is to develop an equation that explain the extraction data in a quantitative manner and presents chemical modeling of solvent extraction process of metal complex as well as how this model can be used to obtain equilibrium constants.

The involvement of one molecule of the phosphorus containing calix[4]arene in the synergistic species when trivalent lanthanoids are extracted with chelating extractants from 4-aroyl-3-methyl-1-phenyl-pyrazol-5-one's family (HP,[43] HPMFBP and HPMMBP,[24] HPMTFBP[45] or HPPMBP[46]) have been established independently from the number of the macrocycles, calix[4]arene, calix[6]arene and calix[8]arene, fragments on the upper[88] or lower rim.[43,44,88] The complexes with the same stoichiometry $LnL_3 \cdot S$ have been confirmed with combinations including HTTA and 4-*tert*-butylcalix[4]arene-tetraacetic acid tetraethyl ester (S8)[29] and HPBI and *tert*-butylcalix[4]arene tetrakis(*N,N*-dimethylacetamide (S7)).[87]

The extraction data of La^{3+} ions with HPMTFBP–S5 combination were presented in Fig. 14 as an example of implemented slope analysis method.[45]

The equation for the reaction involving synergistic species 1 : 3 : 1 ratio (metal : chelating ligand : synergist) is:

$$Ln^{3+}_{(aq)} + 3HL_{(o)} + S_{(o)} \rightleftharpoons [LnL_3S]_{(o)} + 3H^+_{(aq)} \quad (16)$$
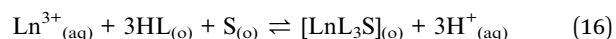
The synergistic mixed complexes (1 : 3 : 2) containing two molecules of synergistic agent, phosphorus-containing *p-tert*-butylcalix[4]arene (S1) have also been formed in the organic phase during extraction when chelating ligands HTTA and HPBI are applied. It was also found that the composition of the extracted species is $[Ln(TTA)_3S_2]$, where S is *tert*-butylcalix[4]arene tetrakis(*N,N*-dimethylacetamide), S7.[28] The lanthanoid extraction can be expressed by the following equation in these cases:

$$Ln^{3+}_{(aq)} + 3HL_{(o)} + 2S_{(o)} \rightleftharpoons [LnL_3S_2]_{(o)} + 3H^+_{(aq)} \quad (17)$$
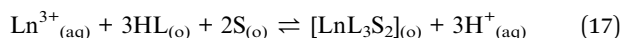
A variety of 5f-ions (Ac^{3+}, Th^{4+}, UO_2^{2+}, Am^{3+}, Cf^{3+}, Pu^{4+}, Np^{4+}) were extracted from aqueous nitric or perchloric solutions as adduct chelates incorporating one or two molecules of the oxo-donor ligands with fluctuate basicities *viz.* TOPO, TBP, di-*n*-butyloctanamide, di-*n*-octyl sulfoxide, methylisobutylketone.[35–38,52,97–99]

It is known that the major factor in synergism is an increase in hydrophobic character of the extracted metal complex upon addition of the synergistic agent. So, the transformation of the self-adduct into mixed complex $LnL_3 \cdot S$ according to eqn (5) when 4-acylpyrazolones are applied cannot contribute to a large increase in its stability in the organic phase as both $LnL_3 \cdot HL$ and $LnL_3 \cdot S$ do not contain water molecules in the coordination sphere. On the other hand, the formation of the complex $Ln(TTA)_3 \cdot S$ in the organic phase (eqn (4)) is connected with the replacement of all water molecules from the coordination sphere of $La(TTA)_3(H_2O)_n$.[18] This results in a much higher stability of the mixed complex $Ln(TTA)_3 \cdot S$ (as compared to the chelate $Ln(TTA)_3$). This suggestion is supported by thermodynamic data which show that a major part of the energy is spent in releasing the water molecules from the chelate.[100]

High coordination numbers (CN, varying from 6 to 12) with ligands adopting geometries that minimize interligand repulsion are the norm for lanthanoids. There are some examples for CNs 3 to 5 with bulky ligands.[13] Owing to the high positive charge, large ionic radii, hard Lewis acid character and the ionic nature of the Ln^{3+}–ligand bonds, Ln ions tend to form complexes with high coordination numbers and flexible coordination geometries.[12] While the CNs observed in solid complexes may reflect the values for the complexes in solution, such an assumption must be approached with some caution. It was found that in the presence of phosphorus-containing calix[4]are, S1, the lanthanoids have been extracted as $Ln(TTA)_3 \cdot 2S$, while in solid state complex $[Eu(TTA)_2 \cdot S]^+Cl^-$ was isolated.[27] The established species extracted in the organic phase are not inclusion complexes. Different composition of the mixed complexes obtained in solution during liquid–liquid extraction and in solid state is probably due to the different experimental conditions applied. In solution, complexes involving two molecules of synergist $Ln(PBI)_3 \cdot 2S$, S1[86] and $Ln(TTA)_3 \cdot 2S$, S7[28] have been also established but at the same time the isolated
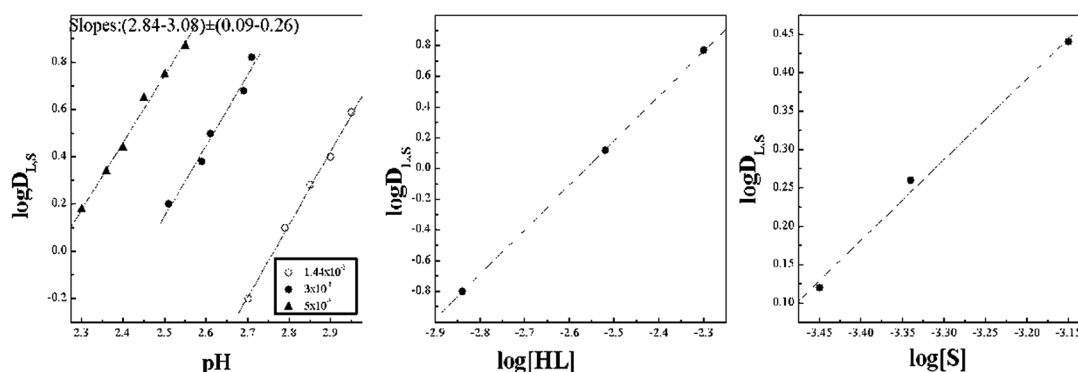
Fig. 14 log $D_{L,S}$ vs. pH for La(ɪɪɪ) extraction with HL–S5 at [S] = 7×10^{-4} mol dm^{-3} in IL(1-butyl-3-methylimidazolium-bis(trifluoromethanesulfonyl)imide). log $D_{L,S}$ vs. log[HL] (3 concentrations) for La(ɪɪɪ) ion extraction at [S] = 7×10^{-4} mol dm^{-3} and pH = 2.50, slope 0.98 ± 0.06. log $D_{L,S}$ vs. log[S] (3 concentrations) for La(ɪɪɪ) ion extraction at [HL] = 3×10^{-3} mol dm^{-3} and pH = 2.60, slope 1.04 ± 0.12. ref. 45 ©2014 Royal Society of Chemistry.

complexes contained only one molecule of the co-extractant. There are cases, of course, when the chemical composition is identical: solution/solid state.[87,88] It is also relevant to remark that there is no change in the symmetry of ligand S2 upon coordination and all resonances of S2 remain in the same form as for free ligand, which indicates uniform interaction of all P=O with Eu^{3+} ion, i.e. the complex has CN = 10 (six oxygen atoms from three bidentate L^- anions and four dentate S ligand), Fig. 15. The ^{31}P NMR spectra of $EuP_3 \cdot S2$ complex at different temperature consist of a single resonance, which supports the conclusion of uniform interaction of all P=O with Eu^{3+} ion, Fig. 16.[88]

Ramírez et al.[101] have obtained suitable (tetragonal crystals) for X-ray single diffraction with composition $[La(S1)(H_2O)_5]$, in which La(III) ion is not encapsulated into calixarene cavity and is coordinated by all four O(P) atoms. Zhao et al.[102] have prepared and characterized two complexes of La^{3+} and Eu^{3+} nine-coordinated with all four oxygen atoms from phosphinoxide ($-CH_2P(O)Ph_2$) substituted calix[4]arene as well four oxygen atoms from two bidentate nitrate anions and one oxygen atom from a water molecule ($[L \cdot La(OH_2)(NO_3)_{(2)}]NO_3$ and $[L \cdot Eu(OH_2)(NO_3)_2]NO_3 \cdot CH_3OH$, L = terakis(methylenediphenylphosphinoxide)calix[4]arene) and their crystal structures were determined by X-ray diffraction method showing that the coordination polyhedron is a single-capped square antiprism.
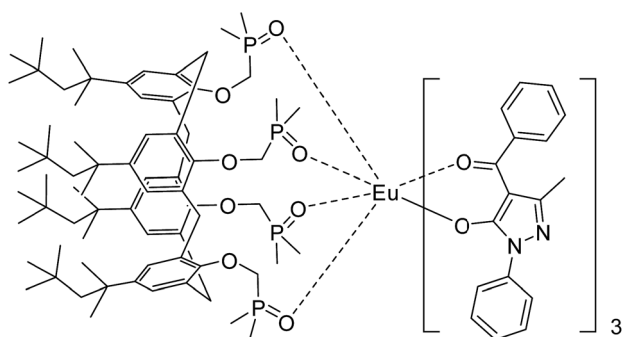

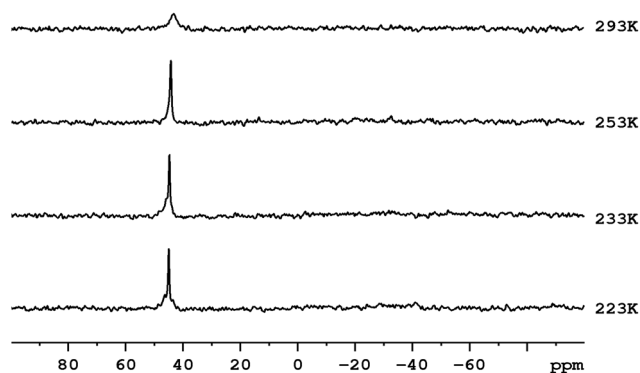Fig. 15 Proposed structure of the europium complex extracted in solution and in solid state, $EuP_3 \cdot S2$.[88]

Fig. 16 $^{31}P \{^1H\}$ NMR spectra of $EuP_3 \cdot S2$ complex at 223, 233, 253 and 293 K in CD_3OD.[88]

2.5.2 Critical evaluation of equilibrium constants of 4f-metal complexes in solution involving calixarenes. The extraction equilibrium constants of metal complexes in two-liquid phase systems are extremely important as relationships must often be found between such quantities and certain properties of both metal ion and ligands. The researchers have used them widely in the field of extraction, coordination, analytical and separation chemistry for estimating various interfering effects. There are limiting published data as only D values are reported usually, in the most referenced papers, so some difficulties have been experienced in the comparison data treatment as a serious restriction of a future evaluation work. The calculated equilibrium constants for the extraction of all lanthanoids with synergistic combination HTTA–S7 on the basis of eqn (3) are summarized in Table 4 as an example study. When all numerical values listed in Table 4 are compared, it is seen that the equilibrium constants, K, increase with increasing atomic number as already pointed out in Section 2.1. The great increase of the equilibrium constant value (approximately 11 orders of magnitude) was found by the addition of the synergist S7 to the system Ln^{3+}–HTTA. In order to compare the extraction efficiency of the system HTTA–S7 to that of the chelating extractant HTTA used alone, the pH_{50} values (values of pH where log D = 0, i.e., 50% of the solute is extracted; $pH_{0.5}$ or $pH_{1/2}$), corresponding to the extraction of the studied lanthanoids in the absence and in the presence of calix[4]arene are collected in Table 4. A difference between the pH_{50} values of 1.7–1.3 pH units can be detected. It has been found that some properties of 4f and 5f-ions and their complexes vary linearly with the total angular momentum, the L-values regarded as a reflection of f-electronic configuration.[12] Plots resembling a four segmented "inclined W" have been obtained for the whole series, where data were available.[28] The data found in the present study show that the linearity of the four segments to form "inclined W" is preserved too (Fig. 17).

Fig. 18 gathers the log $K_{L,S}$ values reported for 14 synergistic acidic/neutral systems by one research group mainly, is the superiority of the mixtures including 4-acylisoxazolone (HPBI) as a chelating ligand. This compound is relatively efficient at low acidity independently from the co-extractant.[23,53] Another significant point to be stressed for this series of ligand combinations is that the two systems HTTA–S1 and HTTA–S8 lead to not so magnify or strengthen lanthanoid extraction.

The established order of efficiency confirms the higher complexation performance of β-diketones containing a heterocyclic moiety compared to classical β-diketone derivatives. One has to point out the peculiar behaviour of the principal extractant in use and its essential role. Several classes of synthesized calixarenes bearing various moieties (ester, amide, phosphinoyl) have been tested for the extraction of lanthanoids. Among the eight molecules, Fig. 7, the highest log K values were obtained with phosphorus-containing p-tert-butylcalix[4]arene as a synergistic agent, following by amide and ester ligating groups at the lower rim (HTTA–S1, HTTA–S7, HTTA–S8, HPBI–S1, HPBI–S7).[27–29,86,87] Note that to enhance the effectiveness of extraction the simple change of diluent can be applied (HTTA–

Table 4 Values of the equilibrium constants K_T, $K_{T,S}$, and $\beta_{T,S}$ and synergistic coefficients for lanthanoids extraction with the HTTA–S7 mixture.[28] ©2011 Elsevier

| Ln^{3+}	$\log K_T$	$\log K_{T,S}$	$\log \beta_{T,S}$	pH$_{50}$ (HTTA)	pH$_{50}$ (HTTA–S7)	SC	S.F. (HTTA)
La	−10.50	1.29	11.79	4.89	3.16	5.19	3.2
Ce	−9.99	1.74	11.73	4.72	3.02	5.13	2.8
Pr	−9.53	1.90	11.43	4.57	2.97	4.83	1.5
Nd	−9.35	2.10	11.45	4.51	2.89	4.85	4.6
Sm	−8.68	2.38	11.06	4.29	2.80	4.46	1.0
Eu	−8.55	2.61	11.16	4.24	2.73	4.56	1.9
Gd	−8.40	2.78	11.18	4.19	2.66	4.58	2.0
Tb	−8.22	2.92	11.14	4.13	2.62	4.54	1.7
Dy	−7.98	3.03	11.01	4.05	2.59	4.41	1.3
Ho	−7.87	3.11	10.98	4.02	2.56	4.38	1.3
Er	−7.76	3.23	10.99	3.98	2.52	4.39	2.3
Tm	−7.40	3.33	10.73	3.86	2.49	4.13	1.8
Yb	−7.14	3.47	10.61	3.77	2.45	4.01	1.4
Lu	−6.99	3.60	10.59	3.72	2.41	3.99	
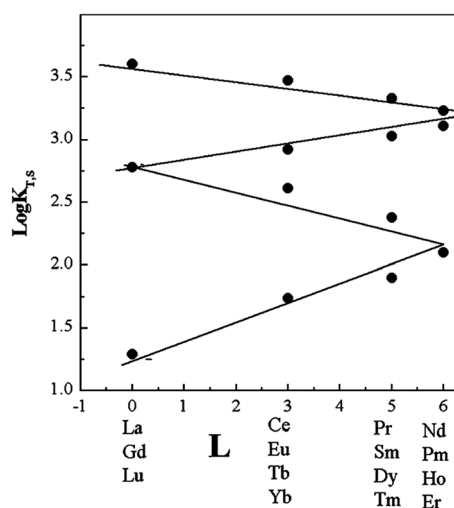
Fig. 17 $\log K_{T,S}$ *vs. L*, HTTA–S7.[28] ©2011 Elsevier.

S1 and HTTA–S7). An increase of the number of phenolic units from 4 to 8 in the molecular structure of *p-tert*-octyl-calix[*n*] arene does not cause any regular change in the extraction efficiency as the established order is 8 < 4 < 6.[44,88,103]

Surprisingly, 5,11,17,23-*tert*-octyl-25,26,27,28-tetrakis (dimethylphosphinoylmethoxy)calix[4]arene is a distinctly better co-extractant for trivalent lanthanoids than the *para-tert*-butylcalix[4]arene, although the ligating functions on the narrow rim are the same in the two molecules S1 and S2.[43,88]

2.5.3 The magnitude of synergistic enhancement induced by calixarenes. The term "synergism" is apprehended from biology in order to demonstrate the more strong influence of two or more pharmaceutical products taken together in comparison with the sum of their impact when they were used separately. A synergistic effect of almost six orders of magnitude occurs in the extraction of Eu^{3+} from 0.1 M HNO_3 with mixtures of thiacalix[4]arene ($C_{56}S_4H_{72}O_{12}$) and dicarbollide.[83] Maximum D values around 2000 and higher were obtained if the concentration ratio of the extractants is close to 2 : 1 respectively. Kurš

et al. also studied the influence of several metal nitrates (Li, Na, K, Ca, Sr, Ba, Co, Ni, Cu, UO_2, concentration range 0.001–0.1 M) on the europium extraction. The conditions are beneficial to Eu^{3+} and consequently it exhibits considerably higher D values than any other metal tested.[82] A significant difference between D values can be distinct 501 and 1441 using $CHCl_3$ and chlorobenzene and in order to obtain "the maximum D_{Eu} value" at equilibrium 1 h and 24 h shaking time was needed, respectively.

The three different conformers (cone, partial cone and 1,3-alternate) of the specific thiacalix[4]arene compound with identical chemical composition, Fig. 19, exhibit very differing extraction properties toward typical nuclear fusion products Eu, Sr, Cs, Ba and Co involving dicarbollide in the synergistic systems and chlorobenzene as a diluent.[83] The existence of synergic effect for Eu was confirmed by an isomolar series of extraction experiments with χ_C values between 0.3 and 0.65 (0.1 M HNO_3, $c_S = 0.033$). The D_{Eu} values obtained for rising χ_C were found to increase from 48 ($\chi_C = 0.3$) to a maximum of 150 ($\chi_C = 0.55$) and to decrease to 99 ($\chi_C = 0.65$).[83] But the type of the conformation does not influence the basic fact of the existence of a strong synergism for all extractable metals under suitable conditions. The cone conformer can presumably be used for extracting Eu with adequate selectivity over Sr and Cs, while 1,3-alternate conformer is more selective for Cs extraction.[83]

The results reported by He and co-researchers have revealed the existence of "double peak effect" of the relationship between the synergistic enhancement coefficients and the increasing atomic numbers of Lns, Fig. 20.[79] A "trough" was appeared in the figure, as the stabilization of synergistic extracted species takes a dominant role from La^{3+} to Eu^{3+}. But this stabilization is relatively smaller for $Z = 64$ because Gd^{3+} electrons in the $4f^7$ shell have been in half-full structure consequently the ligand's influence is usually smaller.

The addition of phosphorus-containing *tert*-butylcalix[4] arene, S1 to the systems with acylpyrazolones causes rather large enhancement between two and four orders of magnitude, Fig. 21. The conjunction of two actions, the chelating and macrocyclic effects could be the cause of it. It is seen from Fig. 21 that the synergistic enhancement is higher for
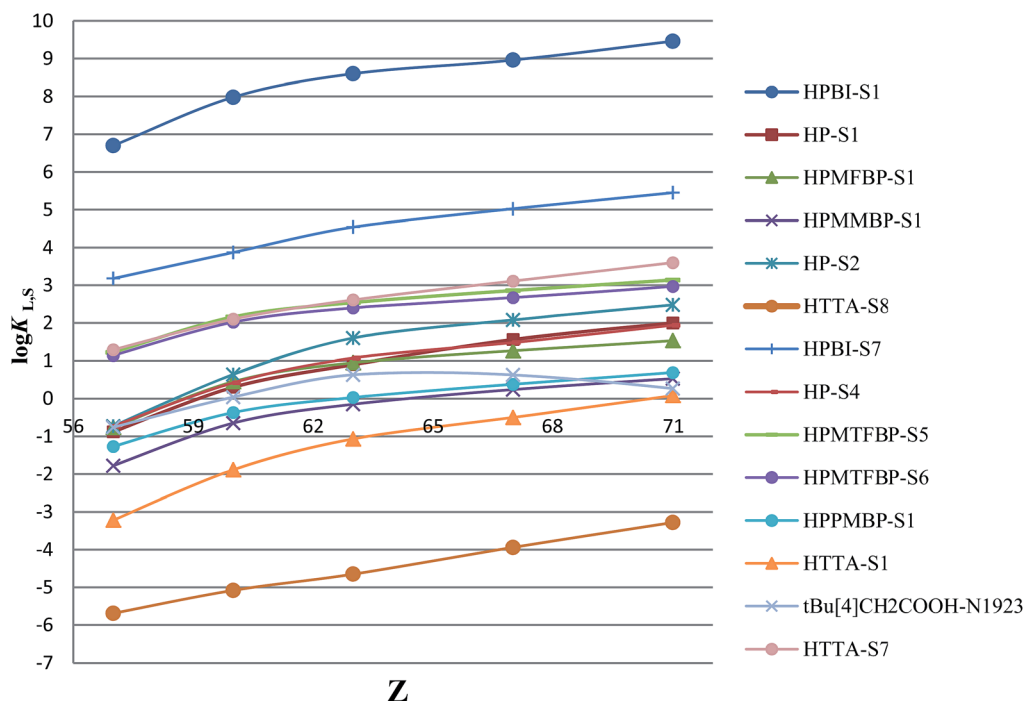
Fig. 18 log $K_{L,S}$ values *vs.* Z of some synergistic mixtures.[24,27–29,43–46,79,86–88]
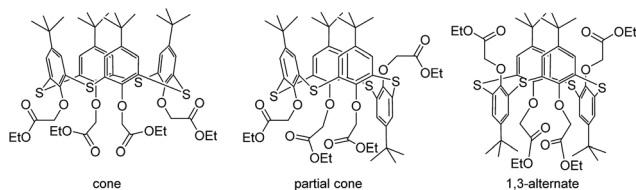
Fig. 19 5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-terakis[(ethoxycarbonyl)methoxy]-2,8,14,20-tetrathiacalix[4]arene.[83]

Fig. 21 Synergistic coefficients *vs.* atomic number (Z) of the systems applying 4-acylpyrazolones and S1: [HL] = 1.5×10^{-2} M, [S1] = 7×10^{-4} M.[24,43,46]

Fig. 20 Synergistic enhancement coefficients *vs.* atomic number, Z.[79]

a particular lanthanoid ion when 4-acylpyrazolone possessing $-C_6H_5$ radical is used as a chelating extractant. This is in accordance with some observation found that the weaker is the chelating extractant, higher is the synergism.[4,26] But the synergistic increase produced by the system HPMFBP–S1 is approximately one order of magnitude higher than HPMMBP–S1,

although the substitution of a fluorine atom in the four position of the benzoyl moiety in the acylpyrazolone structure improves the extraction efficiency better than the presence of methyl group (HPMMP).[24] The best extractions were acquired with the system HPBI–S1, when the difference of the values of K_I and $K_{I,S}$ is more than eight orders, the corresponding SCs are approximately 2.6.

It is clear from Table 5 that the synergistic factor of the trivalent 4f-ions increases a little bit with increasing the concentration of S1. It is also well known that the synergistic effect depends strongly on the choice of diluent.[87] The SCs for the system HPBI–S7 including CCl_4 are 2 orders of magnitude higher than the cases when $CHCl_3$ and $C_2H_4Cl_2$ were used.

The outstanding values of SCs result of HTTA–S7/CCl_4 system (up to 10^5) were obtained, Table 4,[28] but the synergism

Table 5 Synergistic enhancement factors of lanthanoids extracted with HPBI–S1 ([HPBI] $= 2.5 \times 10^{-3}$ mol dm^{-3}).[86]

Ln^{3+}	[S], (mol dm^{-3})	SC
La	7.5×10^{-4}	1.86
	1×10^{-3}	2.03
	2.04×10^{-3}	2.65
Eu	7.5×10^{-4}	2.30
	1×10^{-3}	2.54
	2.04×10^{-3}	3.16
Lu	7.5×10^{-4}	2.52
	1×10^{-3}	2.76
	2.04×10^{-3}	3.38

Fig. 22 Comparison of log K (HPBI–S7) for CHCl$_3$, C$_6$H$_6$, CCl$_4$ and C$_2$H$_4$Cl$_2$ to log K for C$_6$H$_6$ (1-La, 2-Nd, 3-Eu, 4-Ho, 5-Lu) from ref. 87 ©2011 American Chemical Society.

drastically decreases upon change of the synergistic agent with S8.[29] The calculated SCs of Ln(III) ions of HTTA–S8 combination[29] are in the most cases approximately 5 times smaller than those when co-extractant is S1.[27] So, the introduction of P=O functional group in the calixarene architecture leads to a significant increase in the extraction efficiency[45] and is preferable to be inserted in extractant molecules as a tactic with more conventional aspect of ligand design to tune its strength and selectivity.

2.6 Diluent effect on the synergistic solvent extraction

The diluents (solvent: a liquid or solid phase containing more than one substance, solvent = diluent + extractant + modifier…)[104] used are often classical ones and the choice can affect extraction as well as separation,[105] so when planning the system several factors can be taken into account regarding viscosity, polarity, solubility in water, flash and freezing points, price *etc.* This mini review offers a selected summarizing of literature systems concerning diluent effects in synergistic systems as an attempt to point out important evaluation steps of a successful extraction fundamental operation. Unfortunately, the poor solubility of calixarenes, especially tetraphosphorylated, excluding dichloromethane, chloroform or toluene is a barrier for their application. In almost the majority of cases, nitrophenyl alkyl esters were used as diluents for the extraction tests handled by CEA (Cadarache facility, France), because they are able to dissolve calixarenes at relatively high concentration.[53] The introduction of appropriate hydrophobic residues either at the wide or the narrow rim on the platform can allow a control of solubility in organic diluents or insolubility in aqueous phases. In order to overcome this disadvantage (bad solubility), the reorganization of long alkyl chain on the upper rim of the matrix or calixarene addition as synergistic agent (usually at lower concentrations) to the chelating systems seems very rational approach. The effect of the diluents on the metal extraction with HPBI–S7 combination is shown in Fig. 22. The comparison of log $K_{I,S}$ for C$_6$H$_6$ (various metals) with those of the other diluents shows that log–log plots describing the behavior of the metals and the diluents are almost parallel to one another. These regularities appear to be quite helpful to estimate equilibrium constants and to select suitable diluents. Since activity coefficients of solutes are very sensitive to the
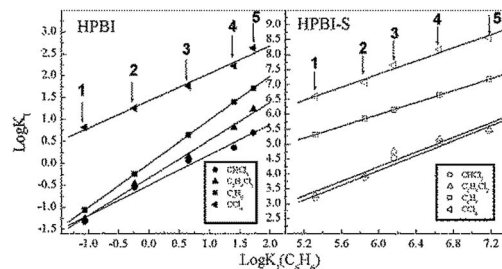
properties of diluent, effects of diluent on the liquid–liquid extraction have been quantitatively explained. For a given metal, the values of log $K_{I,s}$ increase in the order CHCl$_3$ < C$_2$H$_4$Cl$_2$ < C$_6$H$_6$ < CCl$_4$.[87] It can be concluded that as a whole the increase of the diluent solvating ability hinders the extraction process.

The distribution ratios of La, Eu, Er and Y increase with an increase in polarity of the diluent (nitrobenzene > 1,2-dichloroethane > dichloromethane > chloroform) during the metal extraction applying cone-5,11,17,23-tetra-*t*-butyl-25,26,27,28-tetrakis(diphenylphosphinoylmethoxy) calix[4]arene.[106]

A broader investigation on the dependence of the D values for the synergistic extraction of europium from nitric acidic solution (0.01 M) with total concentration of the two extractants of 0.033 M and molar ratio 2 : 3, thiacalix[4]arene (C$_{56}$S$_4$H$_{72}$-O$_{12}$) : cobalt dicarbollide (H(C$_2$B$_9$H$_8$Cl$_3$)$_2$Co) on the type of diluent was carried out by Kyrš *et al.* testing 17 molecular diluents.[84] Less noticeable D values were measured with butyl-, ethyl- and amyl acetate as well as no unambiguous with toluene, carbon tetrachloride, diisopropyl ether, dodecane, *n*-decane, butylbenzene or 1-chlorohexane, Table 6. It can be seen from the table that only diluents containing a polar group or atom (chlorine, fluorine or nitro-group) yield fairly high D. The synergistic effect is strongly diluent dependent and the highest D value was obtained applying chlorobenzene. Unfortunately, no evident correlation can be found concerning the diluents' characteristics such as dipole moment, polarizability and solubility parameter also proved of no avail.[84]

1-Heptanol appears to be a better diluent than dichloroethane on the extraction of Am(III) and Eu(III) nitrates from neutral or weakly acidic aqueous solutions (pH 4–6) with dimethylaminomethylated calix[4]resorcinolarene in combination with 1,10-

Table 6 Dependence of synergism on the type of the employed diluent[84]

Diluent	D_{Eu}
Chlorobenzene	992
o-Fluorotoluene	401
Trifluoronitrotoluene	36.7
1,2-Dichloroethane	34.7
Chloroform	34.4
Dichloromethane	32.6
o-Dichlorobenzene	3.6

phenantroline.[81] Additions of 1,10-phen to the organic phase decrease by 2–3 orders of magnitude the concentration of resorcinolarene required for efficient f-ion extraction showing synergism. The D_{Am} value grows from 0.01 to 0.1 and the Am content in the third phase appreciably decreases going from dichloroethane to 1-heptanol. Kuznetsova *et al.* reported that in the process approximately 50% of the f-elements appear in the third phase.[81]

The effect of molecular organic diluents on the extraction of all 15 4f-ions plus Y(III) from 3 M HNO_3 medium with 0.05 M solution of CMPO-functionalized ionic liquid (1-[3[[(diphenyl-phosphinyl)acetyl]amino]propyl]-3-tetradecyl-1*H*-imidazol-3-ium hexafluorophosphate) has been studied by another Russian research group.[107] These experiments have shown that the extractability increased in the order: nitrobenzene < 1,2-dichloroethane < chloroform < *o*-xylene with a decreasing solvating power of a diluent.

A major goal of the chemical and nuclear industries today is to search for safer alternatives to VOCs that can minimize diluent loss and air pollution induced by diluent evaporation. In recent years, there has been increasing interest in developing more "green" diluents to minimize the adverse impact on the environment. Ionic liquids exhibit advantageous physico-chemical properties and have demonstrated remarkable outstanding potential as diluents for extraction of valuable and precious metals and their applications in the separation chemistry can be considered as a "hot" research topic nowadays.[108–111] Dai and co-workers[112] in 1999 first discovered that highly efficient extraction of Sr^{2+} ions can be achieved when dicyclohexane-crown-ether is combined with ILs at pH = 4.1 and have made a significant contribution in this field.[113] It was demonstrated from the data that extraction efficacy in IL medium is remarkable, with such important advantage over conventional diluents, Table 7.

Most often fluorinated anions are chosen in the extraction systems because of their hydrophobic character, relatively low viscosity, tenability of cation, high persistency (hydrolysis of hexafluorophosphate), weak coordinating ability, addition of extractant or extra chemicals needed, but the loss of IL components to the aqueous phase by anion or cation exchange mechanism is an important shortcoming.[114–116] The established *D* value of Ag^+ ions for $[C_8mim][PF_6]$ is around 230-fold higher

than that for $CHCl_3$ when pyridinocalix[4]arene was applied as extractants by Shimojo and Goto[117] and provides enormously high extractability, Fig. 23.

Very important question arises: is this approach economically competitive ($[C_1C_4im][Tf_2N]$: 1140 EU kg^{-1}) and more environmentally benign[118] than the employment of traditional molecular diluents, VOCs? The main reason is due to their negligible flammability and volatility that they display as a result of their ionic character and this is a major advancement in the reduction of environmental footprint.[119]

Applying ILs is not a matter of simply replacing VOCs. Current works have revealed that liquid–liquid IL based systems, with their unique properties, show some intriguing differences over conventional systems used aliphatic molecules or aromatic class ones.[113,120] A NMR investigation on the possible interactions between a series of imidazolium based ILs (1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, $[C_1C_nim^+][Tf_2N^-]$, n = 4, 6, 8, 10) and some commonly applied in solvent extraction and separation science of 4f and 5f-ions acidic chelating and neutral extractants has been performed by analytical techniques as ^1H, ^{13}C, ^{19}F, ^{31}P NMR spectra and NOESY experiments.[121] The types and strengths of the solvent–solute interactions is necessary for a knowledge-based features concerning chemical solubility, reactivity and selectivity as ILs have a strong influence on the liquid–liquid metal extraction taking part in the extraction mechanism in comparison with traditional molecular diluents. Kurteva *et al.*[121] reported that no interactions occurred in chloroform solution independently on the length of the imidazolium alkyl chain and on the structure and acidity of the ligand. The use of ILs in the solvent extraction of metal ions increases the complexity of system chemistry in solution regarding the mechanism and the complexes built up during the process in the IL phase.[122,123]

As you can see from the results in the Table 8, the substitution of trifluoromethyl group with phenyl group in the 4-

Table 7 Distribution ratio of Sr^{2+} using molecular and ionic diluents[112]

Diluent	*D* without CE	*D* with CE
$[C_4C_1C_1im][PF_6]$	0.67	4.2
$[C_4C_1im][PF_6]$	0.89	24
$[C_2C_1C_1im][Tf_2N]$	0.81	4500
$[C_2C_1im][Tf_2N]$	0.64	11 000
$[C_3C_1C_1im][Tf_2N]$	0.47	1800
$[C_3C_1im][Tf_2N]$	0.35	5400
$C_6H_5CHCl_3$	0	0.76
$CHCl_3$	0	0.77

PF_6^-

R = C_4H_9 $[C_4mim][PF_6]$
R = C_6H_{13} $[C_6mim][PF_6]$
R = C_8H_{17} $[C_8mim][PF_6]$

$^tBu[4]CH_2Py$
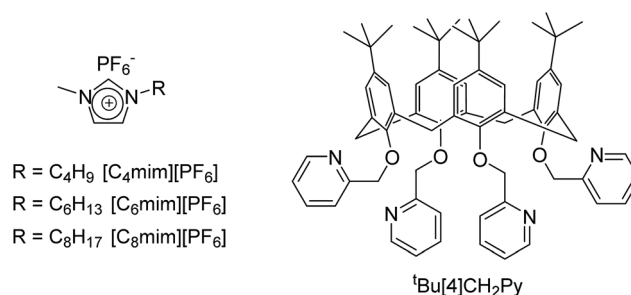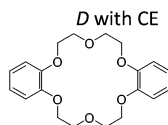
Fig. 23 Chemical structures of ILs and calix[4]arene.[117]

Table 8 Comparison of $CHCl_3$ and $[C_1C_4im^+][Tf_2N^-]$ when mixtures HPPMBP–S1 and HPMTFBP–S5 were used for La(III) extraction, Cl^- medium.[45,46]

System	$CHCl_3$			$[C_1C_4im^+][Tf_2N^-]$			
	log K_L	log $K_{L,S}$	SC	log K_L	log K_S	log $K_{L,S}$	SC
HPPMBP–S1	−6.21	−1.27	3.54	−2.16	3.38	3.44	2.45
HPMTFBP–S5	−3.24	1.22	3.13	−2.33	3.30	3.34	2.52

acylpyrazolone structure diminishes the extraction efficiency, the difference in equilibrium constant values of three logarithmic units were obtained when $CHCl_3$ is applied. The synergistic enhancements produced using this molecular diluent as organic media do not differ in great extent.[45,46] By contrast, in the IL, the calculated equilibrium values are more or less unchanged and the corresponding SC values are also similar. However, all ligand tested alone neutral (calixarenes) or acidic display a sensational enhancement of their individual extraction efficiencies in IL. A moderate decrease of synergism is observed in IL and as a consequence, the presence of a second extractant does not seem as compulsory as it is in chloroform to improve extraction efficiency *i.e.* SCs.

The observed synergistic extraction mechanism in the two systems, Table 8, is identical but different for the conventional systems using chelating extractant alone: self-adduct in $CHCl_3$ (eqn (2)) and chelate complex (eqn (1)) in IL are formed.[45,46] In summary, synergistic rules for acidic/neutral couples in IL medium are a little bit different from those already accepted in molecular diluents till now, considering the negligible impact of the chemical structure of investigated ligands on individual extraction efficiencies and synergistic extraction.

2.7 Selectivity of lanthanoids as a consequence of the synergistic extraction

The separation of metallic ions owing to economic concern has occupied the attention of *Homo sapiens* for many eons continue to be an important environmental goal of modern life as well.[124–126] Diversification of the use of REs in high-technology products not to mention security inks and counterfeiting tags,[13] accelerated their need as industrial demand is steadily increasing in the last few decades. The total request is expected to grow from 128 000 tons in 2011 to 225 000 tons in 2020 ($7 \div 10\%$/yr). The REs (counting as one) are high on the list of fourteen critical or strategic elements classified by European Union. Due to the exceedingly close chemical properties of lanthanoids, separating them from one another was an extremely difficult task for the chemists (long time they were thought to be a single element) and this is one of the most complicated separation in inorganic chemistry.[53,100,127] Liquid–liquid extraction for rare earth separation was proposed by Fischer in 1937.[128] Solvent extraction is the only industrial technology for rare earth separation and some methods for the subsequent selectivity from each other contain up to (one thousand) 1000 steps.

One of the important processes in the management of nuclear wastes is the intra- and inter group separation of 4f and 5f elements.[129] The separation Ans/Lns is a key challenge, due to the similar chemical behavior of the two families.[130,131] Lanthanoids, which account for about one third of the fission products are strong neutron-absorbing elements. CEA, France, was launched the idea of implementing calixarenes for selective extraction of radionuclides from radioactive waste.[53] Today separation chemists were provided to work with a rich and enticing array of formidable and fancy ligands including calixarene molecules with great specificity and practicality.[132] The

metal separation can be assessed using separation factors (the denotation SF followed by an index telling the elements is commonly used) given by the ratio of the D values of the different metals. Furthermore, the selectivity can be calculated as a difference in the $pH_{D=1}$ values among the two ions. According to IUPAC nomenclature the separation factor is denoted α, which symbol is not often used to avoid misinterpretation as alpha-radiation. When the metals form the same type of complexes with a given combination of extractants, the separation factors can be determined as $SF = K_{(Z+n)}/K_{(Z)} = D_{(Z+n)}/D_{(Z)}$ as well.

A mission oriented was the work of Delmau *et al.*[133] reporting the synthesis of calix[4]arenes substituted by acet-amidophosphine oxide groups at their wider (upper) rim and its excellent extraction efficiency and pronounced selectivity for f-elements from highly acidic media. $D_{Am/Eu} = 10.2$ is probably one of the highest ever observed under the studied conditions (4 M $NaNO_3$, 0.01 M HNO_3, $CHCl_3$). Kuznetsova and co-researchers have chosen dimethylaminomethylated resorcinolarene (Fig. 11) as extractant for Eu and Am due to the fact that the presence of alkylaminogroups enhances its affinity for "softer" 5f ions (in terms of Pearson's concept).[81] The growth of the $SF_{Am/Eu}$ observed with increasing the extractant concentration from 0.00125 M (SF = 0.6) *via* 0.005 M (SF = 2.2) to 0.01 M (SF = 4.5) was accompanied by an increase in the metal content in the third phase (dichloroethane). The same trend, extracted ion in the third phase, was also seen as the concentration of $NaNO_3$ was increased from 2 to 4 M, the Am/Eu separation factor increases from 2.2 to 7.5. 1,10-Phenanthroline added to the organic phase exhibits a synergistic effect in f-ions extraction and influence the selectivity with appreciably higher $SF_{Am/Eu} = 12$ at pH 4.8 in 1-heptanol.[84] Kyrš *et al.*[83] have been prone to claim the existence of an empirically observed congruency between efficient synergistic extraction and favourable Eu separation from other long-lived fission products *i.e.* Sr and Cs with maximum SFs close to 10 (extraction conditions in isomolar series 0.2 M HNO_3, $\chi_C = 0.3$–0.6, $c_S = 0.033$ mol dm^{-3}). The authors' conclusion for this useful coincidence is that for lower acidities and higher c_S values more favorable SFs can be achieved.

The calculated SFs for all adjacent 4f-ions with HTTA alone and HTTA–S7 systems are given in Tables 4 and 9.[28] A significant loss of separation selectivity is observed across the 4f-series due to the cation radii decrease of approximately 20% from La to Lu, Fig. 4. The SFs between La and other lanthanoids are very high, Table 9, but it is not typical lanthanoid. The synergistic extraction makes the separation of metals worse, as compared with the chelating ligand only, is generally accepted suggestion by scientists. This effect seems to be related to the present compiled results.

The comparison of the data for separation factors obtained using the proposed synergistic systems including calix[n]arenes, Table 10, shows that the selectivity for light lanthanoids is better in the following two cases HP–S2 and HTTA–S1. It needs to be paid attention to the conditions under which the calculated SFs listed in Table 9 are obtained. A significant difference (3.5 times) was obtained for Eu/La pair changing S2 with S1 *i.e.* different upper rim functionalized synergist. The superiority of

Table 9 Values of separation factors between the adjacent lanthanoid elements obtained using mixture HTTA–S7.[28] ©2011 Elsevier

SF	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
La	2.8	4.1	6.4	12.3	20.8	30.9	42.6	54.9	66.0	87.1	109.6	151.3	204.2
Ce		1.4	2.3	4.4	7.4	10.9	15.1	19.4	23.4	30.9	38.9	53.7	72.4
Pr			1.5	3.0	5.1	7.5	10.4	13.4	16.2	21.3	26.9	37.1	50.1
Nd				1.9	3.2	4.7	6.6	8.5	10.2	13.5	16.9	23.4	31.6
Sm					1.6	2.5	3.4	4.4	5.4	7.0	8.9	12.3	16.5
Eu						1.5	2.0	2.6	3.2	4.2	5.2	7.2	9.7
Gd							1.4	1.7	2.1	2.8	3.5	4.8	6.6
Tb								1.3	1.5	2.0	2.5	3.5	4.7
Dy									1.2	1.5	1.9	2.7	3.7
Ho										1.3	1.6	2.3	3.1
Er											1.2	1.7	2.3
Tm												1.3	1.8
Yb													1.3

Table 10 Separation factors of lanthanoids using various synergistic mixtures[a]

		SF		
Synergistic system	Diluent	Eu/La	Lu/La	Lu/Eu
HP–S1	$CHCl_3/Cl^-$	60.3	758.5	12.5
HPMFBP–S1	$CHCl_3/Cl^-$	52.5	199.5	3.8
HPMMBP–S1	$CHCl_3/Cl^-$	42.6	204.2	4.7
HPPMBP–S1	$CHCl_3/Cl^-$	19.9	91.2	4.6
HPMTFBP–S5	$CHCl_3/Cl^-$	20.8	83.2	3.9
HPMTFBP–S6	$CHCl_3/Cl^-$	18.2	67.6	3.7
HPBI–S1	$CHCl_3/Cl^-$	79.4	575.4	7.3
HTTA–S1	$CHCl_3/Cl^-$	141.3	1.9×10^3	14.1
HP–S2	$CHCl_3/Cl^-$	213.7	1.6×10^3	7.6
HP–S3	$CHCl_3/Cl^-$	16.5	120.2	7.2
HP–S4	$CHCl_3/Cl^-$	63.1	467.7	7.4
HPBI–S7	$CHCl_3/ClO_4^-$	22.9	186.2	8.1
HTTA–S7	CCl_4/ClO_4^-	20.8	204.2	9.7
HTTA–S8	CCl_4/ClO_4^-	10.9	257.1	23.4
$^tBu[4]CH_2COOH$[79]	$CHCl_3/Cl^-$	10.9	10.6	
$^tBu[4]CH_2COOH$–N1923 (ref. 79)	$CHCl_3/Cl^-$	24.7	10.9	0.44
HPMFBP–TBP[96]	C_6H_6/Cl^-	109.6	831.7	7.6
HPMFBP–TOPO[96]	C_6H_6/Cl^-	46.7	199.5	4.3
HPMFBP–TBPO[96]	C_6H_6/Cl^-	54.9	263.0	4.7
HPMFBP–TPPO[96]	C_6H_6/Cl^-	24.5	95.49	3.8
HP–DBCMPO[42]	Toluene/Cl^-	~44.6	~29.5	~0.66
HPBI–bipy[134]	$CHCl_3/ClO_4^-$	263.0	1.5×10^3	5.62
HPBI–phen[134]	$CHCl_3/ClO_4^-$	27.5	177.8	6.45
HTTA–bipy[134]	$CHCl_3/ClO_4^-$	4×10^3	7.7×10^3	18.6
HTTA–phen[134]	$CHCl_3/ClO_4^-$	3.3×10^3	3.8×10^4	11.74
HPBI–MDOAHClO4 (ref. 138)	C_6H_6/ClO_4^-	8.7×10^2	10.9×10^3	12.6
HPBI–TDDAHClO4 (ref. 138)	C_6H_6/ClO_4^-	1.4×10^2	5.2×10^3	36.3
HPBI–QClO4 (ref. 26)	C_6H_6/ClO_4^-	54.9	1.1×10^3	20.9
HTTA–QClO4 (ref. 135)	C_6H_6/ClO_4^-	2.3×10^3	6.3×10^3	2.7
HTTA–DB24C8 (ref. 136)	1,2-Dichloroethane/Cl^-	22.4	380.4	16.9
HTTA–DB18C6 (ref. 136)	1,2-Dichloroethane/Cl^-	50.4	2.5×10^3	51.3
HTTA–TOPO[137]	$[C_1C_4im][Tf_2N]/Cl^-$	~10.0	~63.0	~6.3
HNTA–TOPO[137]	$[C_1C_4im][Tf_2N]/Cl^-$	~10.0	~63.0	~6.3
HBA–TOPO[137]	$[C_1C_4im][Tf_2N]/Cl^-$	~190.0	~3.8×10^4	~199.5

[a] Notes: DBCMPO = dibutyl-(N,N-dibutylcarbamoylmethoxymethyl)phosphine oxide, HNTA = 2-naphthoyltrifluoroacetone, bipy = 2,2′-bipyridine, QClO4 = Aliquat 336, MDOAHClO4 = methyldioctylammonium perchlorate, TDDAHClO4 = tridodecylammonium perchlorate.

the synergistic mixture HP–S2 over HP–S1 on the selectivity can be seen from Fig. 24, in which the calculated SFs of systems HP// HP–S1(S2) have been plotted for the four lanthanoid pairs vs. their atomic number, Z. The influence of an empty (f^0), half-filled (f^7) and full f-subshell (f^{14}) on the selectivity is clearly demonstrated in Fig. 24.
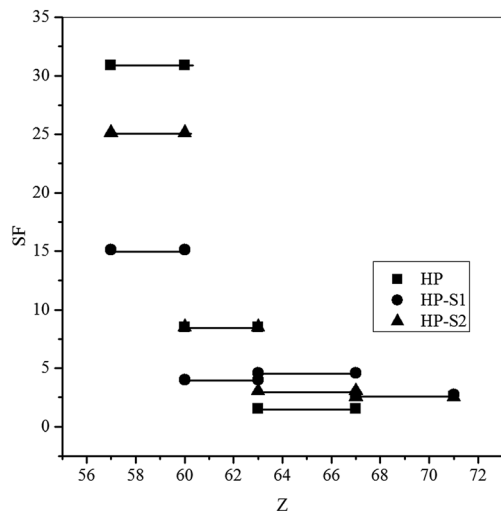
Fig. 24 SFs of lanthanoid pairs *vs. Z*.[88] ©2015, Taylor & Francis.

The number of the phenol units in the calixarene's molecule also has impact on the 4f-separation. When octylcalix[*n*]arenes were applied the SFs of Eu/La pair diminish in the order 4 > 8 > 6, with very noticeable influence. The various substituted 4-acylpyrazolones and **S1** as co-extractant caused also small quantitative changes in SFs of the above mentioned pair.

Changing the chelating extractant HPBI with HTTA in combination with the same synergistic agent, **S7** leads to similar selectivity of light Lns. This fact can be explained taking into account the type of diluent used polar-$CHCl_3$ and nonpolar-CCl_4, respectively. The mixture of $^tBu[4]CH_2COOH$–N1923 facilitates Eu/La selectivity in the same order but much better in comparison when $^tBu[4]CH_2COOH$ is applied alone.[79] This mixture of acid–base coupling extractants is not only a stronger synergistic system for the middle rare earths extraction but also for the extraction selectivity of La and other 4f-ions (SFs of Eu, Gd, Tb, Dy, Ho, Er/La pairs ≈ 23).[79]

It is noteworthy to mention that HTTA–**S7** mixture, which has poor extraction efficiency, exhibits a better selectivity for heavier lanthanoids, Table 9. The separation values of Lu/Eu pair produced by the systems HP(HTTA)–**S1** are very similar. The selectivity of these two elements remains almost constant (around 7) using HPBI–**S1**(**S7**) or HTTA–**S7** as well as combinations HP(**S1**, **S3**, **S4**). The various *para*-substituents (–F, –CH_3, –CF_3, –C_6H_5) of 4-acylpyrazolone molecule didn't influence the selectivity of Lu/Eu in great extent in combination with **S1** or **S5** and **S6**: the calculated values are between 4.7 and 3.7. The extraction ability and selectivity is a pair of contradictory elements, *i.e.* usually good extraction efficiency was not accompanied with marked selectivity. The synergistic lanthanoid extraction with **S1** increase in the order HTTA < HP < HPBI, while at the same time the SFs decrease, Table 8. So, the separation becomes poorer as the extractability increases, and the selectivity decreases with increasing the extractant acidity *i.e.* pK_a value.

The comparison of selectivity data procured with calixarene molecules with those found for assorted combinations of Eu/La,

Lu/La and Lu/Eu pairs, Table 10, and dissimilar organic media exposes to view that the systems including macrocyclic co-extractant combine high synergistic enhancement with good selectivity especially for heavier lanthanoid pair, Lu/Eu. The integration of high molecular ammonium salts favors the 4f-intra group selectivity but in these cases the extraction mechanism leads to the formation of anionic mixed complexes.[26,135,138] Appreciable metals split-up unveil the insertion of ionic liquid in chelating/neutral extractants duo (HBA–TOPO: $SF_{Lu/La} = 3.8 \times 10^4$).[137]

It has to be pointed out that the two calixarene compounds C4 and C5 (10^{-3} M, NPHE), Fig. 25, display relatively lower separation ability, $SF_{Eu/La} < 1$.[53] The most striking is the notable decrease of Eu/La refinement exhibited by C5, which differs from C4 only by the replacement of H with CH_3 unit on the nitrogen atom of amide. This gives a clear demonstration of preferability to manipulate with calixarenes as synergistic agents. In the work of Galletta and co-researchers[139] the lipophilic dicarbollide anion Br-Cosan (cesium commo-3,3-cobalta-bis(8,9,12 tribromo-1,2 dicarba-*closo*-dodecarborane)ate (1-)) was chosen as a suitable synergistic species in order to improve the ligand performance of hexakis(3-*N*-picolone-amidepropyloxy)calix[6]arene (Fig. 26) in 2-nitrophenylhexyl ether (NPHE) as organic medium. Experimental results indicate that at pH ≥ 2 a strong synergistic effect takes place and at higher acidity the ligand

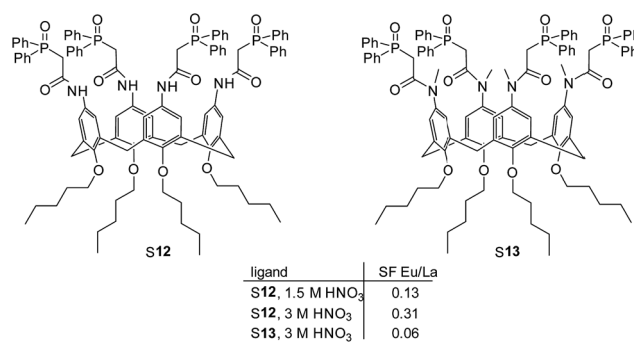| ligand	SF Eu/La
S12, 1.5 M HNO_3	0.13
S12, 3 M HNO_3	0.31
S13, 3 M HNO_3	0.06

Fig. 25 Structural formulas of ligands **S12** and **S13**.[53]

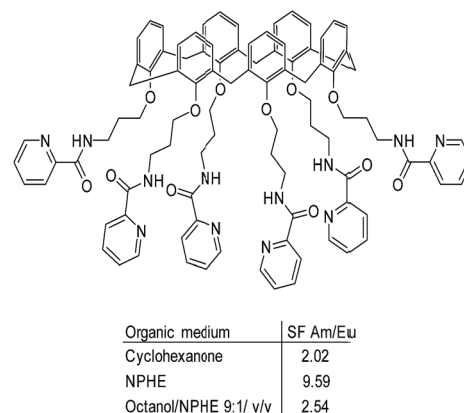| Organic medium	SF Am/Eu
Cyclohexanone	2.02
NPHE	9.59
Octanol/NPHE 9:1/ v/v	2.54

Fig. 26 Molecular structure of the ligand hexakis(3-*N*-picoline-ami-depropyloxy)calix[6]arene, (PAR4).[139]

protonation dramatically affects the efficiency and selectivity as well. 2-Nitrophenyl hexyl ether is the best screening organic diluent by the authors, taking into account its excellent properties from the viewpoints of calixarene solubility, ligand extracting and selective capabilities inducing separation value of 9.59 of the pair Am/Eu, Fig. 26.

For the first time, a spectacular high separation factor (SF) value has been reported of >3000 for Am^{3+} over Eu^{3+} using methyl derivative of N-donor ligand (bis(5,6-dialkyl-1,2,4-triazinyl)pyridine) in ionic liquid medium ($[C_n mim][Tf_2N]$, $n =$ 2, 3, 4, 6 or 8).[140] The obtained results by Mohapatra and co-workers may have a great significance in the mutual separation of trivalent Ans/Lns as a different scientific approach applying unconventional organic media instead of designing new "remarkable" molecules. What will choose the organic and separation scientists?

4. Conclusions and outlook

Solvent extraction is a distinguished process for metal refining that stands at the frontier between organic synthesis, analytical, physical, coordination, green chemistry and modeling and is the only industrial technology for rare earth separation in the 21st century. This review is focused on the synergistic solvent extraction of 4f-block elements and the role of molecular design of chelating ligands and calixarenes, in order to ensure the increase ion withdrawn and achieve better selectivity, when using these whimsical compounds together. In the above discussion, numerous examples have been given to illustrate the impact of the chemical composition and the characteristics of aqueous and organic media on metal ion extraction to achieve a desired extraction and separation. For years, tremendous efforts have been put on the ligand design based on structural refinements in a given chemical family in order to achieve better extraction efficiency. This is particularly true when extractants operate in molecular diluents, where the stability and selectivity of complex formation can be controlled by ensuring appropriate functional groups ($-CF_3$ for example),[19,45,137] that undoubtedly meet the requirements of the target metal. The coordination chemistry of lanthanoids in solution or in solid state as well, is a great challenge and there is also ambiguity defining the exact structure of the formed large assemblies, although the composition of the extracted species is determined as mixed adducts in most cases. The application of calixarenes as synergistic agents results in an outstanding extraction performance in all studied cases in the scientific literature. So far most of the works on solvent extraction of 4f and 5f-ions involves phosphorus-containing calixarenes. Such synergistic effect is strongly diluent dependent and is not influenced significantly on the type of macrocyclic conformation. In addition, with atomic number's increment and lanthanoid contraction, the 4f ionic radii decrease but the hydration becomes stronger and the metal ion chelation is hampered, in consequence, the synergistic coefficients decrease across the series, (Table 4, Fig. 20).[79] However, the field of synergistic solvent extraction and separation applying supramolecules is still far from to be fully explored and interpreted. This is a major lacuna in the field since few researchers attempted this step. The importance of various factors, which favor the extraction enhancement, remains not well clearly defined and explained, especially the use of ionic liquids as organic media. Applying ILs is not a matter of solely substitution of VOCs. The lanthanoids' extraction behavior in the IL medium is not influenced neither qualitatively nor quantitatively by the nature of the 4-acylpyrazolone substituents.[45,46] On the other hand, in molecular diluents, the separation becomes poorer as the extractability increases. It has also been observed for acidic ligands that the selectivity decreases with increasing extractant acidity, *i.e.* lower pKa values. Moreover it was shown that diluent plays a crucial role. The research today focuses on the optimization of the extraction systems and the most reasonable thing to do this is to perform a careful diluent screening. The very limited set of data concerning synergism in ILs raise the hope to much greater extraction efficiencies accompanied with increased selectivity at the same time. An ideal target for future investigation might be the synthesis of ionic diluents, in which the extraction process could operate in a similar way as in molecular one, regarding mechanism,[141] or why not using ionic liquid compounds as a synergistic agents in appropriate combination in conventional molecular diluents, as was already successfully done with Aliquat 336.[9,26,135,142–144] In summary, whenever possible, IL-aqueous solutions should be the preferred choice for adaptation to increasing stringent environmental requirements.

Acknowledgements

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