Review

Assessment of the Equilibrium Constants of Mixed Complexes of Rare Earth Elements with Acidic (Chelating) and Organophosphorus Ligands

Maria Atanassova

Department of General and Inorganic Chemistry, University of Chemical Technology and Metallurgy, 8 Kliment Okhridski Blvd., 1756 Sofia, Bulgaria; ma@uctm.edu

Abstract: A survey of the experimental equilibrium constants in solution for the mixed complexes of 4f ions with acidic (chelating) and O-donor organophosphorus ligands published in the period between 1954 and 2022 is presented. These data are widely used in both analytical and solvent extraction chemistry. Important data evaluation criteria involved the specification of the essential reactions, process conditions and the correctness of techniques and calculations used, as well as appropriate equilibrium analysis of experimental data. Higher-quality data have been evaluated, compiled and presented herein, providing a synoptic view of the unifying theme in this area of research, i.e., synergism.

1. Introduction

According to the IUPAC Red Book *Nomenclature of Inorganic Chemistry*, the 15 elements from La (atomic number $Z = 57$) to Lu ($Z = 71$) should be named the 4f elements or lanthanoids (collective abbreviation, Ln). However, this term has not been widely adopted by the scientific community, which still favors "lanthanides" or "rare earths" (REs: Sc, Y and the lanthanoids). In fact, the rare earth elements are the lifeblood of many of today's high-tech industries owing to their outstanding chemical properties and they are widely regarded as a critical resource for the 21st century. For a long time, rare earths remained laboratory curiosities, although Carl Auer von Welsbach (1858–1929) initiated some important applications when he took out patents for the famous Auer mantle for gas lamps (1891) and for flint stones (1903), subsequently founding two companies (1898) that are still active today [1,2]. There is no doubt that the properties of these metals and their compounds have been understood more quantitatively with the improvement of research tools and technologies today.

Research investigations of the coordination complexes of the 4f metal ions have been stimulated by their exceptional properties and their applications in solvent extraction, which were widely applied in the 20th century to meet the needs of the pure metals. Liquid-liquid extraction (LLE) is a key process in metal refining and stands at the frontiers between organic synthesis and analytical, physical, coordination and green chemistry. It is the only industrial technology for intra-group separation of the rare earth elements [3–9]. In the LLE of metal-containing species, the two liquids should be sufficiently immiscible in order to produce two distinct phases when mixed in any proportion. In practice, one of the phases is almost invariably aqueous, whereas the other one is an organic diluent containing more than one substance ("solvent" = diluent + extractant + modifier . . .) [10]. Thus, the organic phase is usually a complicated solution of one or more organic liquids containing one or more extractants and possibly modifiers of various kinds, as well as a diluent. Modern extraction chemistry focuses on supramolecules with organophosphorus

ligating groups and, from the other side, the chemical engineering aspect pertaining to design new extractants, which are mainly used in organic (volatile) molecular diluents [11]. During the years, many IUPAC technical reports have been published concerning the equilibrium data of the metal complexes formed in solution using only one complexation reagent, but not those of synergic systems, i.e., combinations of two organic molecules. Although these tabulated forms of presenting the stability constants for metal complexes are useful generally, the number of combinations of metals, various ligands, different ionic media and temperatures are so large that very often even for simple systems, data for specific sets of experimental conditions are frequently absent [12].

This report aims to analyze the stability constants of 4f-metal-ion complexes in solution, relevant to proposed mixtures of acidic (chelating) molecules and O-donor organophosphorus ligands. These constants have wide potential applications in materials science, extractive metallurgy, metal recycling, industrial wastewater treatment, radioactive waste storage, etc. Reliable quantitative knowledge of these constants is especially important for optimizing the operation of new LLE systems at pilot and industrial scales. The report focuses on LLE systems that have been successfully employed for lanthanoid separations, which will help researchers to select the best options from among the many possibilities. Furthermore, collection and analyses of these data may facilitate the development of general rules that will assist in the intelligent design of the next generation of solvent systems, for example, incorporating ionic-liquid compounds as diluents or extractants. On the other hand, sustained interest in improving nuclear fuel reprocessing procedures and growing concern regarding the effects of actinoids in nuclear wastes have provided continuing motivation for studying the complexation and separation behavior of the f-family elements. In addition, safety and pollution concerns about the large volumes of contaminated diluents produced by means of traditional liquid-liquid separation processes have driven improvements in extraction efficiency and the development of innovative chemical technologies. The replacement of molecular diluents with ionic liquids (ILs), for example, is a particularly interesting direction of research [13–21]. The main contribution to date has likely been the improvement of the state of the art concerning concepts of classical solvent extraction through the transfer of knowledge with regard to the use of ionic liquids as innovative diluents in a separation field of 4f and 5f ions. The design of more efficient macrocyclic ligands containing chelating/phosphinoyl moieties also appears to be a promising objective. In other words, stereo-chemical features, reaction kinetics, conformational changes, and ligand field stabilization have also been shown to be relevant factors in specific cases. As the complexation of acidic ligands relies on their deprotonation form, a few classes of organic compounds have been included in this context in order to clarify the impact of their operational pH window, i.e., β-diketones, 4-acylpyrazolones, 4-acylisoxazolones and a few organic acids. To exploit the chelation effect and to enhance significantly the solvent extraction of 4f ions, multicoordinate compounds such as calixarenes are compared here to some well-known and widely usable organophosphorus ligands in the role of synergistic agents.

This report provides an exhaustive overview of the relevant literature for the period 1954–2022, although some Chinese and Japanese papers have been omitted due to difficulties in obtaining translations.

2. Synergism in the Liquid-Liquid Extraction of Metal Ions

An important milestone in the improvement of the solvent extraction processes was the discovery of the synergistic effect. Synergism occurs when two ligands used in conjunction display a better extraction efficiency than would be expected from the simple addition of their individual effects [22–27]. The adjective recommended in the IUPAC Golden Book is "synergic" but most scientists prefer "synergistic". The first thorough study of this phenomenon was carried out by Blake et al., who found that UO_2^{2+} can be extracted synergistically with a mixture of dialkylphosphoric acid and a neutral organophosphorus reagent, with the extraction being ten to one hundred times greater than that obtained with

either extractant alone [28–30]. Over the years, a thorough investigation of this phenomenon has shown that synergism is most effective when an acidic (HL) and a neutral (S) ligand are used together, although other combinations are also possible. Owing to the diversity of extractants, a classification proposed by Healy has been widely adopted. This scheme groups synergistic extractant systems as follows: acidic (anionic) plus neutral ligands; two acidic extractants; cationic plus neutral molecules; cationic plus anionic compounds; and two cationic reagents. Generally, the acidic/neutral duo is the simplest and best understood to date and is often very effective. For example, the synergistic enhancement of the extraction of trivalent actinoids and lanthanoids is up to 10^8 and this is one of the reasons for the great interest shown in synergistic research on this particular class of metals, i.e., f-elements. The nature of the metal cation always plays an important role in solvent extraction processes. Metal ions involved in synergistic solvent extraction processes, such as the 4f and 5f ions, typically have coordination numbers at least twice their charge. In general, the solution chemistry of the trivalent transplutonium elements strongly resembles that of the trivalent lanthanoids [31]. However, the actinoids tend to interact more strongly with soft donor atoms (sulfur, chloride, nitrogen) than the analogous lanthanoids. In order to separate individual actinoids lighter than Am from each other, or from the lanthanoids, separation systems sensitive to the oxidation state of the metal ion are sufficient [32]. Furthermore, if the ionic radius of the central metal ion is too small, the attachment of a new additional second ligand may become impossible for the formation of mixed species.

In synergistic systems, the acidic (chelating) compound (HL) typically deprotonates to form an anionic ligand L^- that can chelate with the metal ion, M^{n+}, whereas the neutral ligand or, in other words, the synergistic agent S, replaces any remaining water molecules from the coordination shell of the neutral complex, enhancing its solubility in the organic phase. This process can be expressed as:

$$M^{n+} + nHL + xS \rightleftharpoons ML_n \cdot S_x + nH^+ \tag{1}$$
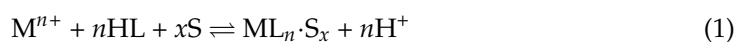
The main differences between weaker chelating agents and those containing phosphoric acid units are: (i) the much larger synergistic affect potentially possible with the latter; (ii) the higher values of their association constants, and (iii) the fact that their complexes are mostly monomeric in the organic (extracting) solution [28]. The most fruitful development in this field stemmed from a publication by Irving and Edgington [33], who indicated the following conditions required for the synergistic extraction of metal ions:

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

The second molecule (synergist) must be capable of displacing any residual coordinated water from this formally neutral complex, thereby rendering it less hydrophilic (Figure 1).
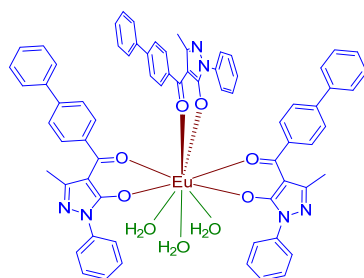
Figure 1. Neutral complex formed by the Eu (III) ion with 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one.

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

The maximum coordination numbers of the metal and the geometry of the ligands must be favorable.

No standard method for quantification of the phenomenon has been agreed upon and any approach should be clearly defined in a given situation (IUPAC Gold Book [34]). The synergistic effect can be represented by the synergistic coefficient (SC), defined by Taube and Siekierski as SC = log $[(D_{1,2}/D_1 + D_2)]$ (1), where D_1, D_2 and $D_{1,2}$ denote the distribution ratios of a metal ion between the organic and aqueous phase, containing one of the extractants and their mixture [35]. By definition, the distribution ratio (*D*) in liquid-liquid distribution, according to IUPAC Golden Book, is the ratio of the total analytical concentration of a solute in the extract (regardless of its chemical form) to its total analytical concentration in the other phase. In equations relating to aqueous/organic systems, the organic phase concentration is, by convention, the numerator and the aqueous phase concentration the denominator. In the case of the stripping ratio, the opposite convention is sometimes used but should then be clearly specified. In other words, the extraction is synergistic when SC > 0 and antagonistic when SC < 0 [22,23]. For instance, some researchers, mainly from Asia, have used different expressions [36].

Synergism, as a phenomenon in solvent extraction chemistry, has been interpreted as being due either to the replacement of water molecules bound to the metal ion by a more strongly binding ligand (S) or to the expansion of the metal-ion coordination shell to include such ligands [37]. For example, the addition of the first molecule of S completely dehydrates the chelated complex [Nd(TTA)$_3$(H$_2$O)$_2$] (where TTA$^-$ is the anion of thenoyltrifluoroacetone) established in the dry benzene diluent. In both models, the adduct increases the interaction of the complexed metal ion with the organic diluent. Many values of log*K*, ΔH and ΔS have been reported for the reaction:

$$M(TTA)_n + S \rightleftharpoons M(TTA)_n \cdot S \tag{2}$$

where S = tributylphosphate (TBP) or trioctylphosphine oxide (TOPO) with the coordinated water, if any, omitted. However, only the Nd(TTA)$_3$ system gives evidence for the addition of more than one molecule of S (TBP or TOPO) in comparison to UO$_2^{2+}$ and Th^{4+}. For all the reactions studied in [37], ΔH was negative. However, ΔS ranged from -60 to $+127$ J·mol^{-1}·K^{-1}. Negative entropy changes are associated with dry diluent systems involving the addition of a ligand (adduct) to the chelated complexes Th(TTA)$_4$ and Nd(TTA)$_3$·S. Synergism was also found to result primarily from the large positive entropies caused by the dehydration resulting from the addition of an adduct to 4-benzoyl-3-mehyl-1-phenyl-pyrazolin-5-one (HPMBP) f-complexes [38]. Both the enthalpy and entropy changes suggest little or no dehydration in the reaction for Th(PMBP)$_4$ with TOPO molecules in the organic phase, whereas it is probably the major factor in these two values for other studied f-ions such as UO$_2^{2+}$, Y, Gd and Nd. Water determinations indicate that the metal-ion/PMBP complexes are less hydrated than the corresponding TTA complexes, which is probably due to increased solvation by the diluent in use, nitrobenzene. The larger dielectric constant (34.8) of nitrobenzene (cf. 2.3 for benzene) seems to decrease the synergistic reaction, in agreement with the interpretation of synergism as being related largely to the increased non-polar character of the metal-extractant-adduct complex [38]. The following species were found to be formed in nitrobenzene used to extract f-ions from aqueous solutions with *I* = 0.1 mol dm^{-3} NH$_4$NO$_3$: UO$_2$(PMBP)$_2$·TOPO, Th(PMBP)$_4$·TOPO, Y(PMBP)$_3$·TOPO·H$_2$O, Gd(PMBP)$_3$·2TOPO, Nd(PMBP)$_3$·*x*TOPO, *x* = 1, 2 [38]. Synergism is found to result primarily from the large, positive entropies caused by the dehydration resulting from the addition of adducts to the PMBP complexes:

$$M(PMBP)_n + xS \rightleftharpoons M(PMBP)_n \cdot xS \tag{3}$$
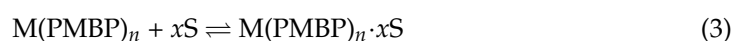
3. General Physicochemical Properties of Chelating and O-Donor Organo-Phosphorus Ligands

Nowadays, molecular design has produced likely multicenter ligands possessing higher extraction efficiencies with various structural backbones. For instance, powerful and selective extractants are essential components for efficient metal ion recovery and separation processes. Many types of acidic chelating compounds, mainly those with fluorinated or O-donor organophosphorus substituents, have been used successfully for the solvent extraction of metal ions from aqueous solution, including separation of the 4f and 5f ions. Such lipophilic reagents must have certain physicochemical properties. These include [39,40] (i) the formation of stable (preferably chelated) complexes with the target metal ion(s); (ii) discrimination against competing species present in the aqueous phase; (iii) maintaining good phase compatibility (sparing mutual solubility) with the organic diluent; (iv) easy partitioning from the aqueous medium; (v) the smooth release of the target metal under suitable conditions (essential for stripping procedures); and (vi) good integrity, i.e., resistance to degradation under realistic technological conditions. Additionally, the ideal ligand should be inexpensive and conform to the twelve principles of green chemistry with regard to sustainability [41,42]. Furthermore, it should consist only of C, H, O and N atoms (the "CHON principle") [40], making it fully combustible to gaseous products after use. To this, one should add somehow the ideal of specificity, as noted in [43]. The hope of achieving this goal was temptingly proffered after the introduction of Tschugaeff's dimethylglyoxime as a reagent for nickel by Brunck in 1907 [44]. Nonetheless, such a goal is rarely attained through a lucky chance, despite the progress in the field of analytical chemistry, nowadays. Unfortunately, as noted above, molecules containing F and P usually have better coordination abilities, especially towards the f-block ions [45]. On the other hand, the acid dissociation constant of the chelating agent is an important physicochemical parameter that is needed to estimate its application as an extractant [46]. The so-called S-criteria required for this process consist of selectivity, strength, speed, separation, solubility, stability, safety, synthesis, and a system [47,48].

In fact, many β-diketones are commercially available at high purity [49]. A β-diketone molecule behaves as a monobasic acid, as the hydrogen on the α-carbon in its β-diketone form or the enol proton of the β-keto-enol form (Figure 2), and can readily dissociate over an appropriate pH range. The simplest of the β-diketones, acetylacetone, forms neutral chelates with about 60 metal ions [50]. Its solubility in neutral aqueous solution at 25 °C is 1.92 mol dm^{-3} [51], and this increases with increasing ionic strength and acidity of the aqueous phase, probably due to a shift of the enol-keto equilibrium. However, the purity of the used organic compounds must be sufficient for accurate determination of the equilibrium constant, as they are much less soluble in aqueous solutions. An example of the keto-enol tautomerism of a typical β-diketone is shown in Figure 2 [52].
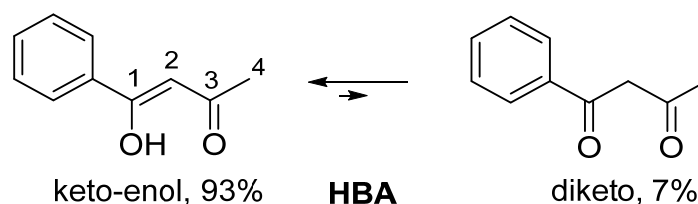
Figure 2. Tautomeric forms of benzoylacetone (HBA) in CDCl$_3$ in equilibrium at room temperature.

Thenoyltrifluoroacetone (HTTA), an unusual coordination compound, was introduced by Calvin and Reid in 1947 and has been extensively exploited as an extractant, particularly for lanthanoid elements [17,25]. Its most striking feature is the fact that the trifluoromethyl group gives it a high acidity in the enol form, which is very useful for extracting various metal ions at relatively low pH. In addition to acting as "scavengers" for a whole range of cations in Periodic Table, it is possible to devise solvent systems which are particularly

efficient for target metals. There have been innumerable papers describing the application of this preferable molecule during the years [53].

Acylpyrazolones have been known since the end of the 19th century. The acylpyrazoles are α-substituted β-dicarbonyl compounds with acid dissociation constants (pK_a = 2.5 to 4) that are much lower than 2-thenoyltrifluoroacetone [54–57]. The 4-acylpyrazol-5-ones, first studied by Jensen [56], are among the most widely exploited O-donors. An advantageous, fast and efficient protocol was developed in 1959 by Jensen [58], which has practically no concurrence and has been intensively exploited up to the present day (Figure 3). They have attracted attention because of their lower pK_a values (cf., conventional β-diketones), good extracting and separating abilities, and the intense colors of their complexes. Aroyl pyrazolones have displayed great complexing and extracting abilities towards the 4f and 5f elements and other metal ions. These abilities were found to be strongly dependent on the location and nature of the substituent(s) in the aromatic ring of the acyl group, which influence the electronic, steric and solubility parameters of the ligand.
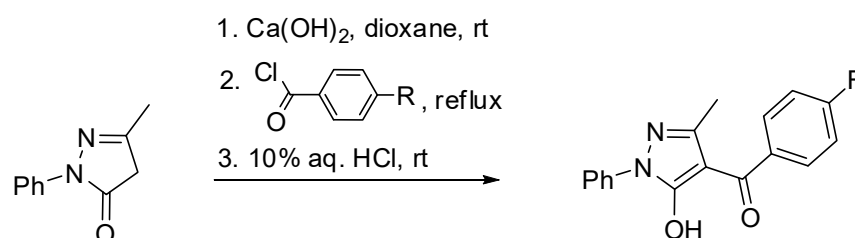
Figure 3. Selective C-acylation of 3-methyl-1-phenyl-pyrazol-5-one.

The very low pK_a value (1.23) makes 4-acyl-5-isoxazolones an interesting class of β-diketones for the extraction and separation of metal ions from strong acid media [59,60]; see Figure 3 in [53].

Tri-*n*-butyl phosphate (TBP, $(CH_3CH_2CH_2CH_2O)_3PO$, Figure 4) is an inexpensive ester of phosphoric acid and *n*-butanol. It is an excellent solvent extractant for various metal ions and has a good chemical stability and high selectivity. It has high boiling (289 °C) and melting points (−80 °C), a density of 0.977 g·cm^{-3} and a viscosity of ~3 cP at 25 °C. Its solubility in water or in 1 mol dm^{-3} nitric acid is low, ~400 ppm. As a matter of fact, the potential of TBP as a metal extractant was demonstrated in the 1940s as part of the Manhattan Project in the USA [61]. A 15–40 wt.% solution of TBP in kerosene or dodecane is widely used in the liquid-liquid extraction of uranium, plutonium and thorium from spent uranium nuclear fuel rods, following dissolution in nitric acid, as a part of a nuclear reprocessing process known as PUREX [62,63].
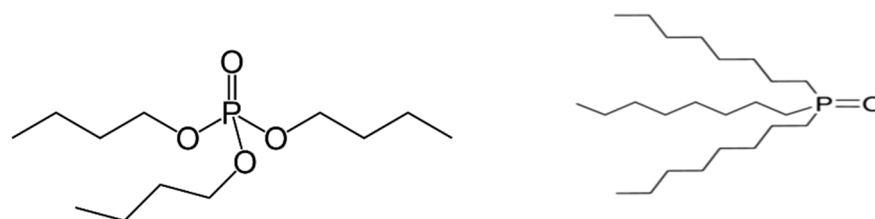
Figure 4. Chemical structure of tri-*n*-butyl phosphate (TBP) and trioctylphosphine oxide (TOPO).

Compared with other ligands, such as β-diketones, TBP is moderately powerful when used alone. Its affinity for metal ions is derived from its phosphoryl group, forming O-bonded coordinate links: $(C_4H_9O)_3P=O \rightarrow M$.

Another interesting organophosphorus extractant is trioctylphosphine oxide (a PIN trioctyl-λ^5-phosphanone) ($(C_8H_{17})_3PO$, TOPO; see Figure 4). Phosphine oxides (designation σ^{4}λ^5) have the general structure $R_3P=O$, with formal oxidation state V. The coordination number is designated by σ. The valency, or total number of bonds attached to phosphorus,

is described by λ. The high lipophilicity and the strongly electron-donating character of the oxygen moiety are the key properties of this ligand [64,65]. In the latest item of a long series of papers accumulating over several years, the simple replacement of O by S or N by P, and other attempts to exploit steric hindrance in various ways, have not met with much success.

　　　Calixarenes are supramolecules, first produced in the laboratory of Adolf von Baeyer in Berlin in the year 1872 [66]. Their oligomeric nature was delineated in the 1970s by Gutshe [66], who gave the compounds their currently accepted name (Gr: calyx meaning vase or chalice, and arene indicating the presence of aryl moieties) [22]. Calixarenes generally have high melting points, high chemical and thermal stability, low solubility and low toxicity. The introduction of substituents and functional groups on both the lower or "wide" hydrophilic (OH) and upper or "narrow" hydrophobic (hydrocarbon) rims allows almost unlimited structural modification, which can be used to create neutral host molecules that can selectively bind guest substrates, Figure 5 [67–69]. The chemical structures of some calixarenes are presented in Figure 6. In general, calixarenes containing phosphorus pendant arms on the lower rim have substantially improved extraction efficiencies and selectivity with regard to lanthanoids and actinoids [6], whereas other variants have shown good selectivity for separating alkali and alkaline-earth ions and various heavy metals.
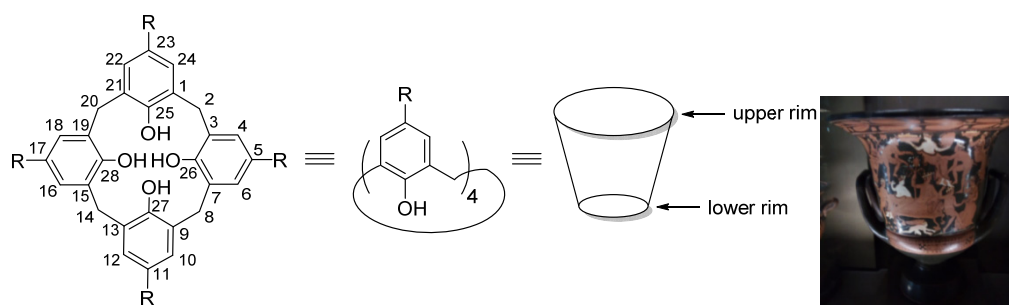

Figure 5. Molecular structure of calix[4]arenes.
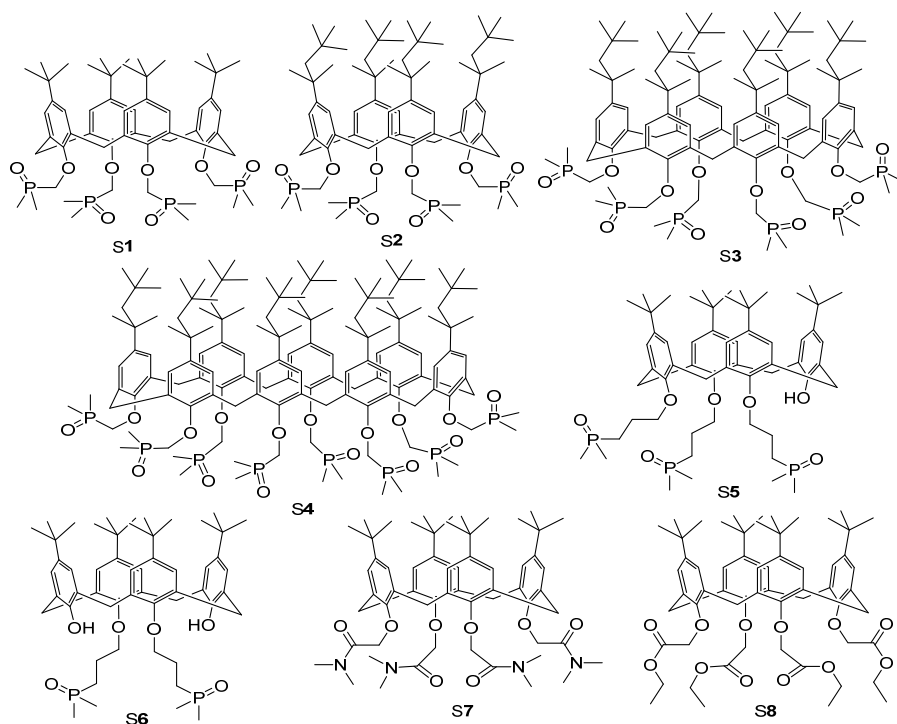
Figure 6. Chemical structures of several selected calixarenes.

Several commonly used compounds in solvent extraction chemistry and their abbreviations are provided in Table 1.

Table 1. Several ligands considered in this study.

IUPAC Ligand Name [a]	Acronym	Other Names [b]
2,4-pentanedione	HA	acetylacetone
1-phenyl-1,3-butanedione	HBA	benzoylacetone
4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione	HTTA	2-thenoyltrifluoroacetone
4,4,4-trifluoro-1-phenyl-1,3-butanedione	HBFA	benzoyltrifluoroacetone
	HFTA	froyltrifluoroacetone
1,1,1-trifluoro-2,4-pentdione	HTAA	trifluoroacetylacetone
4-benzoyl-3-mehyl-1-phenyl-pyrazolin-5-one	HPMBP, HP	1-phenyl-3-mehyl-4-benzoyl-pyrazol-5
3-methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-one	HPMTFBP	
3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one	HPMPBP	
3-methyl-4-(4-methylbenzoyl)-1-phenyl-pyrazol-5-one	HPMMBP	
4-(4-fluorobenzoyl)-3-methyl-1-phenyl-pyrazol-5-one	HPMFBP	
4-benzoyl-3-phenyl-5-isoxazolone	HPBI	4-benzoyl-3-phenyl-5-isoxazolone
	HQ	8-hydroxyquinoline
tri-*n*-butyl phosphate	TBP	tributyl phosphate
tri-*n*-butylphosphine oxide	TBPO	tributylphosphine oxide
tri-*n*-octylphosphine oxide	TOPO	
	TPPO	triphenylphosphine oxide
dihexyl-N,N-diethylcarbamoylmethyl phosphonate	CMP	
N,N-diisobutyl-2-[octyl(phenyl)phosphoryl]acetamide	CMPO	octyl(phenyl)-N,N-diisobutylcarbaoylmethyl phosphine oxide
5,11,17,23-*tert*-butyl-25,26,27,28-tetrakis(dimethylphosphinoylmethoxy)calix[4]arene	S1	
5,11,17,23-tetra(para-*tert*-octyl)-25,26,27,28-tetrakis(dimethylphosphinoylmethoxy)calix[4]arene	S2	
5,11,17,23,29,35-hexa(1,1,3,3-tetramethyl-butyl)-37,38,39,40,41,42-hexakis(dimethylphosphinoylmethyleneoxy)-calix[6]arene	S3	
5,11,17,23,29,35,41,47-octa(1,1,3,3-tetramethylbutyl)-49,50,51,52,53,54,55,56-octakis(dimethylphosphinoylmethyleneoxy)cali[8]arene	S4	
5,11,17,23-tetra-*tert*-butyl-25,26,27-tris(dimethylphosphinoylpropoxy)-28-hydroxy-calix[4]arene	S5	

Table 1. *Cont.*

IUPAC Ligand Name [a]	Acronym	Other Names [b]
5,11,17,23-tetra-*tert*-butyl-25,27-bis(dimethylphosphinoylpropoxy)-26,28-dihydroxy-calix[4]arene	S6	
5,11,17,23-*tert*-butyl-25,26,27,28-tetrakis(2-dimethylamino-2-oxoethyl)calix[4]arene	S7	*tert*-butylcalix[4]arene tetrakis(N,N-dimethylacetamide)
5,11,17,23-*tert*-butyl-25,26,27,28-tetrakis(2-ethoxy-2-oxoethyl)calix[4]arene	S8	4-*tert*-butylcalix[4]arene-tetraacetic acid tetraethyl ester
methyltri-*n*-octylammonium chloride, tricaprylylmethylammonium chloride	QCl, QClO$_4$	Aliquat 336
di-*n*-butyl sulfoxide	DBSO	dibutyl sulfoxide
3-(2-ethylhexylsulfinylmethyl)heptane	B2EHSO	bis-2-ethylhexyl sulfoxide
2*H*-chromen-2-one		coumarin, 1,2-benzopyrone, 1-benzopyran-2-one
naphtalen-1-ol		α-naphtol, 1-hydroxynapthalene
2-[2-(dioctylamino)-2-oxoethoxy]-N,N-dioctylacetamide	TODGA	N,N,N′,N′-tetraoctyldiglycilamide

Note: [a] Names in accordance with IUPAC recommendations. [b] In this report, the names that were mostly frequently encountered in the literature are used.

4. Presentation of Equilibrium Data and Some Abbreviations Used

First, it must be stressed that organic extractants facilitate the transfer of the metal ions from the aqueous to organic phase in solvent extraction chemistry. Since its discovery, a great deal of interest has been focused on the synergism in the extraction of metal ions by β-diketones [30]. 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, i.e., the organic phase. In aqueous solutions, acetylacetone is a weak acid in equilibrium with hydrogen ions and with enolate ions:

$$C_5H_8O_2 \rightleftharpoons C_5H_7O_2{}^- + H^+ \tag{4}$$

The dissociation constant of the acid HA can be defined as:

$$K_a = \frac{[A^-][H^+]}{[HA]} \tag{5}$$

but for convenience is usually presented in logarithmic form: $pK_a = -\log_{10}K_a$. For instance, IUPAC has recommended that the pK_a values for acetylacetone in aqueous solution at 25 °C are 8.99 ± 0.04 ($I = 0$), 8.83 ± 0.02 ($I = 0.1$ mol dm^{-3} NaClO$_4$) and 9.00 ± 0.03 ($I = 1.0$ mol dm^{-3} NaClO$_4$) [50]. It is desirable that internationally agreed-upon nomenclature, symbols, and units be used.

The distribution of acetylacetone between an organic diluent and an aqueous phase can be described as

$$D_{HA} = [HA]_o/[HA] + [A^-] = K_{D(HA)}/(1 + K_a[H^+]^{-1}), \tag{6}$$

where $K_{D(HA)} = [HA]_o/[HA]$ and "o" indicates the organic phase species.

Distribution constants decrease with an increase in the ionic strength and the acidity of the aqueous phase in accordance with the increasing solubility of molecules in aqueous electrolyte solutions, e.g., $\log K_{D(HA)}$ between water and chloroform at 25 °C at $c_{HA} \leq 0.1$ mol dm^{-3}: 1.38 ± 0.02 (I = 0.001 mol dm^{-3}), 1.37 ± 0.01 (I = 0.1 mol dm^{-3}) and 1.25 ± 0.03 (*I* = 1.0 mol dm^{-3}) [50].

For instance, the solvent extraction process of trivalent lanthanoid ions (Ln^{3+}) with the chelating ligand (HL) alone and with an additional ligand, i.e., a synergist (S), can be represented by Equilibria 1–5 presented in [53]. The equilibrium constants K_L, $K_{L,S}$ and $\beta_{L,S}$ are usually given by the expressions described in [53] (6–10). The equilibrium constants K_L, $K_{L,S}$ and $\beta_{L,S}$ are concentration constants and are based on the assumption that the activity coefficients of the species do not change significantly under the experimental conditions employed. This means that the activity coefficients were kept (approximately) constant during measurements. Such constants are strictly valid only in the chosen electrolyte at the stated ionic strength. In other words, ***I*** symbolizes the ionic strength. A variety of ionic strengths, most ranging from 0.1 (the most widely used) to 1.0 mol dm^{-3} of mainly background 1:1 electrolytes (e.g., NaCl, NaClO$_4$, NaNO$_3$), have been utilized. Ideally, the electrolyte used should not introduce any impurities to the solutions and should not react with the species under study [70]. Thus, the medium should keep the activity coefficients effectively constant.

The analyte (metal species, M) distributes itself between the two liquids according to its hydrophobic/hydrophilic character:

$$D = \frac{[M]_{(o)}}{[M]_{(aq)}} \cdot \frac{V_{(aq)}}{V_{(o)}} \tag{7}$$

where V_{aq} and V_o are the volumes of the two liquid phases. The ratio expresses the total (analytical) concentration of a solute in the extract (regardless of its chemical form) to its total (analytical) concentration in the other phase (aqueous). It is usually difficult under analytical conditions to work outside the range of phase ratios from 0.2 to 5.0, and a procedure that requires exceptionally small or large phase ratios is to be questioned. Of course, with a phase ratio of unity, the completeness of extraction should be 99.9%, at an error of less than 0.1%. This means a distribution ratio of $\geq 10^3$ [71].

Generally speaking, the synergistic solvent extraction of lanthanoids has usually been studied using "slope analysis", a traditional and effective method of obtaining both stoichiometric and equilibrium constant information about the extraction process [53,59,72, 73]. Some limitations of slope analysis arise from side reactions in the aqueous [74–78] or organic phases and to the interaction between extractants (Figure 7).
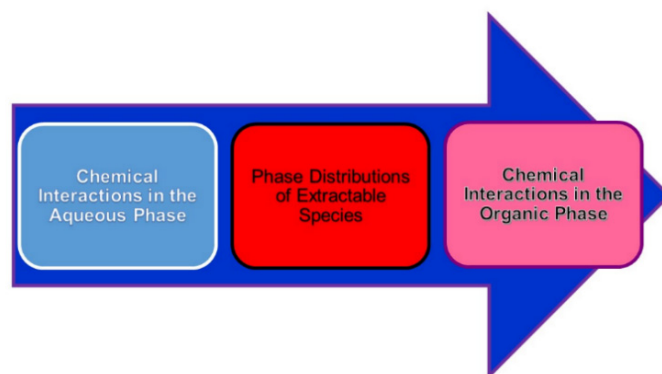
Figure 7. Process of solvent extraction.

Based on a study by Sekine [75–78], we may conclude that some chelate complexes in the aqueous phase (e.g., HTTA, dioctylhydrogenophosphate/CHCl$_3$, CCl$_4$) or the extraction of any mixed chelate complexes (examples: HTTA-TBP, HTTA-methylisobutylketone) are

negligible under the applied experimental conditions. Metal ions in the aqueous phase of course also form complexes with the extracting chelating ligand, HL, which has been distributed between the organic phase into the aqueous phase, and thus the aqueous chelate complexes my cause a systematic error in the calculated stability constants [79]. This deviation would be decreased with the use of the synergistic solvent extraction system because the adduct formation of the chelate complexes in the organic phase makes metal extraction several times higher, and so one can obtain a certain distribution ratio of the metal at a lower $[HL]_{(o)}/[H^+]$ [79]. The slope analysis 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 of interaction between them, which will reduce the concentrations of free ligands and was found to result in a particularly antagonistic effect [23,80]. It can be assumed that this type of association between the reagents would decrease both of their concentrations in the organic phase and thus their availability for chelate extraction and further for adduct formation, and this should decrease the overall synergistic enhancement [81].

In this context, the distribution of six β-diketone compounds (acetylacetone, benzoylacetone, trifluoroacetylacetone, benzoyltrifluoroacetone, thenoyltrifluoroacetone, hexafluoroacetylacetone) between hexane, benzene, carbontetrachloride or chloroform and 0.1 mol dm^{-3} aqueous perchlorate solutions has been measured in the presence of TOPO [82]. The distribution ratio was, in many cases, enhanced by the presence of TOPO in the organic phase; this was explained in terms of the association of β-diketone and TOPO:

$$HL_{(o)} + S_{(o)} \rightleftharpoons HL\cdot S_{(o)} \text{ or } HL_{(o)} + 2S_{(o)} \rightleftharpoons HL\cdot 2S_{(o)}$$

The association constants were greater when the β-diketone was stronger as an acid and also in the following order of diluents: $CHCl_3 < CCl_4 < C_6H_6 < C_6H_{14}$ [82]. When the diluent is chloroform, the association is observed only between hexafluoroacetylacetone and TOPO. With the other tested β-diketones, a slight decrease in the distribution ratio with an increase in the TOPO concentration has been distinguished.

It should be noted that there are quite a few new ideas that have appeared in the literature recently, with a significant impact in the field of metal solvent extraction [83–90], but here the classic scientific developments are considered.

5. Data Evaluation Criteria

As a whole, the reliability of published equilibrium constants for the formation of complexes by various ligand combinations with 4f metal ions has been evaluated here using the criteria adopted in previous IUPAC publications in this area [91–97] and also summarized in [53]. Thus, *recommended* values are normally based on a comparison of at least two independent high-quality publications that meet these established requirements. These are the usual criteria for the selection of published data that are used for the grouping of "*recommended*" and "*provisional*" values. Nevertheless, experimental data were examined initially on the basis of these criteria and grouped first into two categories: "accepted" and "rejected". Of the data that passed the preliminary acceptance criteria, those that exhibited the best agreement normally were averaged, rounded and, depending on the standard deviations (s.d.), their mean values were regarded as **recommended** (**R**): s.d. ≤ 0.05 log units for metal complexes (M + L, H + ML, or M + HL) or **provisional** (**P**): $0.05 < $ s.d. ≤ 0.2 log units. Unfortunately, for most of the metal + ligand(s) combinations that are the focus of this study, comparison of results from two or more independent research groups under the same experimental conditions was rarely possible. A good example is the two more or less independent publications concerning solvent extraction studies applying 4-benzoyl-3-phenyl-5-isoxazolone (HPBI) in $CHCl_3$, but using different electrolytes—0.1 mol dm^{-3} $NaClO_4$ [98] and 0.1 mol dm^{-3} 2-morpholinoethanesulfonic acid (MES) buffer [60]—and with different determined log$K$ values for La^{3+} (-1.33 ± 0.05; -11.34 ± 0.1) and Lu^{3+} (0.70 ± 0.05; 0.73 ± 0.1), respectively. However, such a comparison

was possible only for frequently used extractants, such as chelating compounds, and was also limited to some 4f ions, so strictly following the above criterion would leave a large number of equilibrium constants unassessed. Therefore, an attempt was made to extend the assessment to equilibrium constants published by one author/research team that were not determined independently by other different scientists [99,100].

In consequence, data from a single study have also been **recommended** (**R**, s.d. ≤ 0.05 log units) if (i) there was no doubt concerning the adequacy of the experimental and calculation procedures or (ii) the results were in **R**-level agreement with either the recommended values for similar cations (e.g., the trivalent lanthanoid ions) or with values for the same constant for the same cation, but under slightly different experimental conditions (e.g., temperature, ionic strength). The reliability of the data was normally revealed through careful examination and even the recommended values cannot be regarded as "final" ones, but rather as a data source that is helpful for providing practical guidelines because there is no guarantee of a lack of misprints and errors. Therefore, even the critically evaluated data have to be treated routinely with care and prudence because after all, errors cannot be excluded a priori.

In a similar way, a **provisional (P)** ranking was given to some results from single papers if they showed **P**-level agreement with other researchers for at least one different 4f cation. A provisional designation was also assigned to those data in good agreement with independent studies, even if the evaluators noted some deviations from the necessary rigor. In a few cases, values from a single publication that fit the general trend within P-level results have also been treated as provisional. For this reason, "P" can be assigned for good quality papers of which the results have not been confirmed: $0.05 <$ s.d. ≤ 0.2 log units. For instance, most of the uncertainties reported in the literature reflect analytical and numerical precision, but do not include systematic errors.

In this work equilibrium constants were in all cases simply taken from the original source. Our primary aim was to choose and recommend of the best value of each constant, taking into account the precision and care with which experiments have been performed [100].

The criteria for assigning equilibrium data as "*recommended*" or "*provisional*", based partly on those used in previous IUPAC critical reviews [91–95,97], will be left to be categorized by the reader. The term "indicative" (**I**) implies a value that the present authors consider to be reasonable, somehow below *provisional* but above *rejected*, or at least the best available, but which has not been substantiated by independent studies under the same experimental conditions and therefore has a level of uncertainty. For a more explicit discussion and definition of terms, see [97–101].

It should be stressed that the formulation of uniform criteria for ligands of different chemical natures and denticities is not possible. The same treatments have been used in some scientific papers that do not have evident errors but which contain gaps in the description of some important experimental details, and hence the data are to be regarded as informatory. Some research papers with data that were rejected contained important Supplementary Information (normally spectroscopic) that could be helpful in future research investigations. Thus, all the references, including some with doubtful or partial data, are listed in the notes below tables in each section devoted to the particular ligand(s), and the metal cations under study. It is advisable for the reader to use provisional constants obtained under well-identified experimental conditions because, in spite of the numerous studies recommended values could be offered in only a few cases, taking into account the diversity of ligands. However, data that were unacceptable at first glance have not been listed in the Tables. References that are cited (see Supplemental Material) but not included in the Tables also include:

- Communications with possibly correct data, but inadequate or poor descriptions of experimental conditions;
- Communications that reviewers could not access in the original version;

- Publications from the same research group as that of a cited study with stability constant data that completely duplicate the data in the cited study;
- Publications that need further independent evaluation (this situation includes the cases where two independent research groups offer data that formally met the requirements stated above, but owing to some hidden systematic errors exhibit very large numerical discrepancies);
- Publications that provide data for conditions that contrast with those used to obtain other data (e.g., high or low temperatures, "unusual" ionic strengths, mixed diluents, overly complicated metal mixed ligand complexes, effective or conditional stability constants, etc.). Another obvious reason for this is associated with an inadequate description of chemical equilibria in a particular solvent extraction system, especially implementing ionic liquids compounds;
- Publications that present only enthalpy values (e.g., [102]); and
- Publications that present only *D* values (e.g., [103]).

The purity of reagents and diluents and the procedures for purification should be given in all papers. The ligand combinations were considered in order of increasing complexity. Information on the experimental conditions used in papers selected for evaluation is provided after each table. The averaged equilibrium constants (with standard deviations in parentheses) and their evaluation categories are tabulated, together with the most important experimental information (medium, temperature) and the references that contributed to the mean value listed in the table. When the average value was derived from data obtained in different media, symbols such as Na/KCl or KCl/NO$_3$ are used. The evaluators did not adjust stability constants to a uniform ionic strength or medium. When buffer solutions are used, complex formation may occur between the metal ions of interest and the buffer components. The data listed represent an average (mean) of those reported in the accepted publications. Critically evaluated data are presented in Tables 2–8. Based on this conjecture, in Tables 2–8, the assigned uncertainty for each "accepted" datum of $\log_{10}K$ reported originally by the authors represents a 95% confidence level. The tables summarize data up to the end of July 2022. For each extractant combination and its established 4f complexes, distribution equilibrium constants, as well as appropriate extraction constants, are recorded. Note that all outlined metal complexes (placed in the columns titled *equilibrium* in Tables 2–8) obtained due to the reactions described in this document refer to those established in the organic solutions. For each synergistic solvent extraction system, information is provided for the chemical reaction, the equilibrium constant, the temperature (°C or "rt"—room temperature, which is assumed to fall within the range from ca. 20 °C to 35 °C), the composition of the aqueous and the organic phases, the homogeneous equilibria involving the acid dissociation of the main extractant in the aqueous phase, and of course the reference to the original published source. The organic diluent used must be specified [104]. Concentrations are expressed in mol dm^{-3}. It is important that the total concentrations of the metal ion(s), ligand(s) and hydrogen ions should be within ranges that are relevant to the particular equilibria. In other words, beyond certain concentration ranges, additional equilibria may need to be taken into consideration [60]. All stability constants are reported in terms of concentrations. This means that activity coefficients were assumed to be constant throughout the measurements. As noted above, this means that the reported constants are valid only at the stated ionic strength in the medium selected. The specific analytical technique (spectrophotometric, inductively coupled plasma atomic emission spectrometry, etc.) used for measurements are not included [50,105].

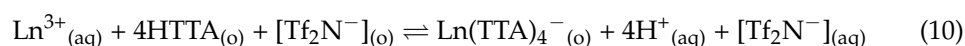## 6. Combination of β-Diketone and Organophosphorus Ligands

As a matter of fact, the synergistic enhancement of metal-ion extraction has been studied most extensively using thenoyltrifluoroacetone (HTTA) ligands and various organic phosphate esters. Some important findings, valid for organic molecular diluents [106,107] as well as for ILs [53], have been summarized already.

In the data compilation tables, the calculated references obtained in an ionic liquid environment can also been seen. The very limited set of equilibrium constant data concerning metal extraction in ILs raise the hope of obtaining much greater extraction efficiencies of metals and increased selectivity at the same time. In order to highlight the ionic character of such compounds, the ILs are noted as [Cat$^+$][Ani$^-$]. As regards the most typical IL family, imidazolium cations are denoted as [C$_\mathbf{n}$C$_\mathbf{m}$im$^+$] for *n*-alkyl-*m*-alkylimidazolium, whereas the anion [(CF$_3$SO$_2$)$_2$N$^-$] (bis(trifluoromethylsulfonyl) imide, [Tf$_2$N$^-$]) has been by far the most frequently investigated one (see Figure S2 in the Supplementary Material). For instance, the ionic character of IL compounds has an essential influence on the extraction process of metallic species from the aqueous phase and the reaction mechanisms are often quite different, without analogs in volatile organic compound (VOC)-based systems. Although metals generally exist in the form of neutral hydrophobic complexes in molecular liquids (Equation (8)), charged metallic entities that are highly soluble in an IL phase may pertain to this ionic solvation environment (Equation (10)). In contrast, electroneutrality is an important principle as only neutral complexes may enter the hydrophobic molecular organic layer. Therefore, an ion exchange mechanism is perhaps one of the most relevant metal extraction models in which ILs are used as diluents. Furthermore, component ions of the ILs—cations or anions—can be transferred to the aqueous phase, permitting ion exchange mechanisms and including them in the chemical equilibrium reactions [16,17]. Thus, the extraction equilibria in the two liquid phases—molecular or ionic—and the extraction constants of the neutral and anionic complexes of 4f ions formed with the sole use of HTTA can be expressed as follows:

$$Ln^{3+}{}_{(aq)} + 3HTTA_{(o)} \rightleftharpoons Ln(TTA)_{3(o)} + 3H^+{}_{(aq)} \tag{8}$$
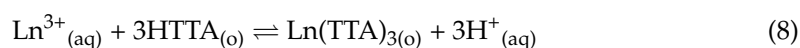
$$K = \frac{[Ln(TTA)_3]\left[H^3\right]}{[Ln^{3+}][HTTA]^3} \tag{9}$$

whereas in an IL media [C$_1$C$_n$im$^+$][Tf$_2$N$^-$],

$$Ln^{3+}{}_{(aq)} + 4HTTA_{(o)} + [Tf_2N^-]_{(o)} \rightleftharpoons Ln(TTA)_4{}^-{}_{(o)} + 4H^+{}_{(aq)} + [Tf_2N^-]_{(aq)} \tag{10}$$

$$K = \frac{[Ln(TTA)_4^-]\left[H^4\right][Tf2N]}{[Ln^{3+}][HTTA]^4[Tf2N]} \tag{11}$$

To avoid overweight and to assist the reader, the expression of the extraction constants (log*K*) for most of the cited cases (Tables 2–8) can be found in [53].

It is important at present to point out the efforts undertaken to exploit the most favorable features of this liquid media, especially for the combined used of two ligands for metal complexation in solution. The complexity of the multiple possible mechanisms occurring during synergistic solvent extraction is the key factor to consider here [17,108,109]. Although still less explored as a scientific topic, several valuable examples can be found in the open literature. Unfortunately, an attempt to calculate equilibrium constants has been made for the cases of two molecular ligands dissolved in ILs, among the infinite possible combinations, as shown in Figure 8.

A survey of the data is presented in Table 2. Data in the tables are first ordered according to the target 4f ion, followed by the applied ionic strength (*I*) and the type of metal complex extracted in the organic phase, and within each category the data are sequenced in line with the applied diluents. Water of solvation in some metal chelates is omitted for the sake of simplicity.

Table 2. Recommended and provisional (noted as "P") data for synergistic systems of thenoyltrifluoroacetone with an organophosphorus ligand for the solvent extraction of trivalent lanthanoids.

Cation	I (mol dm^{-3})	Diluents	Equilibrium	Log$K$	Refs.
Eu		cyclohexane	Eu(TTA)$_3$	−7.66 [P]	[110]
			Eu(TTA)$_3$·2TBP	1.78 [P]	
^{152,154}Eu	0.1 NaClO$_4$	*n*-hexane	Eu(TTA)$_3$·TBP	5.87 [P]	[111]
		n-heptane		6.27 [P]	
		cyclohexane		6.08 [P]	
		methylenechloride		3.32 [P]	
		chloroform		3.40 [P]	
		benzene		4.70 [P]	
		CCl$_4$		5.05 [P]	
		bromoform		3.66 [P]	
		toluene		4.84 [P]	
		isopropylbenzene		4.98 [P]	
		chlorobenzene		4.48 [P]	
		o-dichlorobenzene		4.30 [P]	
		n-hexane	Eu(TTA)$_3$·2TBP	10.78 [P]	
		n-heptane		11.14 [P]	
		cyclohexane		1.96 [P]	
		methylene chloride		5.24 [P]	
		chloroform		5.20 [P]	
		benzene		8.00 [P]	
		CCl$_4$		8.40 [P]	
		bromoform		5.62 [P]	
		toluene		7.98 [P]	
		isopropylbenzene		8.56 [P]	
		chlorobenzene		7.26 [P]	
		o-dichlorobenzene		7.20 [P]	
Ce	1 NaClO$_4$	CCl$_4$	Ln(TTA)$_3$	−3.89 ± 0.10 [P]	[112]
Pr				−3.74 ± 0.10 [P]	
Nd				−3.45 ± 0.09 [P]	
Pm				−2.92 ± 0.07	
Sm				−3.06 ± 0.10 [P]	
Gd				−2.44 ± 0.07	
Tb				−2.48 ± 0.04	
Dy				−2.56 ± 0.06	
Ho				−2.39 ± 0.05	
Er				−2.23 ± 0.05	
Tm				−2.01 ± 0.07	
Yb				−1.79 ± 0.04	
Lu				−1.62 ± 0.04	

Table 2. *Cont.*

Cation	I (mol dm^{-3})	Diluents	Equilibrium	Log$K$	Refs.
Y				-2.32 ± 0.09 [P]	
Pr				-0.59 ± 0.06	
Nd				-0.55 ± 0.08	
Pm				-0.17 ± 0.07	
Sm				0.05 ± 0.06	
Gd				0.14 ± 0.07	
Tb				0.04 ± 0.05	
Dy				0.03 ± 0.08	
Ho				0.09 ± 0.07	
Er				-0.16 ± 0.1 [P]	
Tm				-0.17 ± 0.13 [P]	
Yb				-0.33 ± 0.11 [P]	
Lu				-0.67 ± 0.16 [P]	
Y				-0.24 ± 0.11 [P]	
Sc	0.1 NaClO$_4$	CHCl$_3$	Sc(TTA)$_3$	-1.30 [P]	[113]
Sc	0.1 NaClO$_4$	CHCl$_3$	Sc(acac)$_3$	-6.35 [P]	[113]
Sc	1 NaClO$_4$	CCl$_4$	Ln(TTA)$_3$	-0.81 [P]	[114]
La				-10.95 [P]	
Eu				-8.57 [P]	
Lu				-7.43 [P]	
Sc	1 NaClO$_4$	CCl$_4$	Ln(TTA)$_3 \cdot$TBP	3.44 [P]	[114]
La				4.83 ± 0.27 [P]	
Eu				5.15 ± 0.013	
Lu				5.69 ± 0.05	
La			Ln(TTA)$_3 \cdot$2TBP	9.33 ± 0.11 [P]	
Eu				8.89 ± 0.08	
Lu				6.67 ± 0.29 [P]	
Eu	0.1 NaClO$_4$	CHCl$_3$	Eu(TTA)$_3 \cdot$TBP	3.63 [P]	[115]
			Eu(TTA)$_3 \cdot$2TBP	5.40 [P]	
		CCl$_4$	Eu(TTA)$_3 \cdot$TBP	5.36 [P]	
			Eu(TTA)$_3 \cdot$2TBP	8.96 [P]	
		CHCl$_3$	Eu(TTA)$_3 \cdot$TOPO	5.40 [P]	
			Eu(TTA)$_3 \cdot$2TOPO	7.60 [P]	
		CCl$_4$	Eu(TTA)$_3 \cdot$TOPO	7.49 [P]	
			Eu(TTA)$_3 \cdot$2TOPO	12.26 [P]	
Tm		C$_6$H$_6$	Tm(TTA)$_3$	-6.96 [P]	[28]
			Tm(TTA)$_3 \cdot$TBP	-2.61 [P]	
			Tm(TTA)$_3 \cdot$TOPO	-0.01 [P]	
			Tm(TTA)$_3 \cdot$2TBP	-0.34 [P]	

Table 2. *Cont.*

Cation	I (mol dm^{-3})	Diluents	Equilibrium	Log$K$	Refs.
		cyclohexane	Tm(TTA)$_3$	-5.60 [P]	
			Tm(TTA)$_3$·2TBP	2.62 [P]	
			Tm(TTA)$_3$·2TOPO	5.72 [P]	
Eu		cyclohexane	Eu(TTA)$_3$	-7.66 [P]	
			Eu(TTA)$_3$·2TBP	1.78 [P]	
^{152,154}Eu	0.1 NaClO$_4$	pentane	Eu(TTA)$_3$·TOPO	8.71 [P]	[116]
		hexane		8.56 [P]	
		heptane		8.68 [P]	
		cyclohexane		8.40 [P]	
		isopropylbenzene		7.84 [P]	
		CCl$_4$		8.04 [P]	
		toluene		7.40 [P]	
		benzene		7.19 [P]	
		chloroform		4.95 [P]	
		chlorobenzene		6.97 [P]	
		methylene chloride		5.91 [P]	
		o-dichlorobenzene		7.21 [P]	
		bromoform		6.00 [P]	
			Eu(TTA)$_3$·2TOPO		
		pentane		6.37 [P]	
		hexane		6.40 [P]	
		heptane		6.08 [P]	
		cyclohexane:		6.06 [P]	
		isopropylbenzene		5.20 [P]	
		CCl$_4$		4.84 [P]	
		toluene		4.62 [P]	
		benzene		4.59 [P]	
		chloroform		2.73 [P]	
		chlorobenzene		4.37 [P]	
		methylene chloride		4.23 [P]	
		o-dichlorobenzene		4.45 [P]	
		bromoform		3.04 [P]	
^{169}Yb	1 NaNO$_3$	cyclohexane	Ln(TTA)$_3$·TOPO	2.4 ± 0.1 [P]	[117]
			Ln(TTA)$_3$·2TOPO	6.88 ± 0.04	
^{140}La			Ln(TTA)$_3$·TOPO	-0.3 ± 0.2	
			Ln(TTA)$_3$·2TOPO	4.67 ± 0.07	
La	0.2 NaClO$_4$	benzene	Ln(TTA)$_3$	-10.25 ± 0.01	[118]
Ce				-9.04 ± 0.01	
Pr				-8.41 ± 0.02	
Nd				-8.33 ± 0.02	

Table 2. *Cont.*

Cation	I (mol dm^{-3})	Diluents	Equilibrium	Log$K$	Refs.
Sm				-7.99 ± 0.02	
Eu				-7.79 ± 0.02	
Gd				-7.70 ± 0.01	
Tb				-7.21 ± 0.01	
Dy				-6.98 ± 0.02	
Ho				-6.88 ± 0.01	
Er				-6.69 ± 0.01	
Tm				-6.55 ± 0.01	
Yb				-6.43 ± 0.01	
La			Ln(TTA)$_3 \cdot$2TPPO	-3.34 ± 0.01	
Ce				-3.14 ± 0.01	
Pr				-2.99 ± 0.01	
Nd				-2.94 ± 0.01	
Sm				-2.72 ± 0.01	
Eu				-2.65 ± 0.01	
Gd				-2.60 ± 0.01	
Tb				-2.54 ± 0.01	
Dy				-2.50 ± 0.01	
Ho				-2.46 ± 0.01	
Er				-2.42 ± 0.02	
Tm				-2.40 ± 0.01	
Yb				-2.36 ± 0.02	
La	0.1–1 (Na,Li)Cl 0.01 acetate buffer	[C$_1$C$_4$im$^+$][Tf$_2$N$^-$]	Ln(TTA)$_3$	-7.48 ± 0.07	[119]
Nd				-6.21 ± 0.09 [P]	
Eu				-5.51 ± 0.03	
Dy				-5.29 ± 0.07	
Lu				-4.94 ± 0.06	
La	0.1–1 (Na,Li)Cl 0.01 acetate buffer	[C$_1$C$_4$im$^+$][Tf$_2$N$^-$]	Ln(TTA)$_4$$^-$	-10.02 ± 0.06	[119]
Nd				-8.37 ± 0.09 [P]	
Eu				-8.14 ± 0.05	
Dy				-7.22 ± 0.08	
Lu				-7.78 ± 0.15 [P]	
La	0.1–1 (Na,Li)Cl 0.01 acetate buffer	[C$_1$C$_4$im$^+$][Tf$_2$N$^-$]	Ln(TTA)$_3 \cdot$2TOPO	-0.74 ± 0.18 [P]	[119]
Nd				0.65 ± 0.17 [P]	

Table 2. *Cont.*

Cation	I (mol dm^{-3})	Diluents	Equilibrium	Log$K$	Refs.
Nd			Ln(TTA)$_2$·2TOPO	3.00 ± 0.09 [P]	
La			Ln(TTA)$_2$·3TOPO	4.60 ± 0.05	
Nd				5.55 ± 0.15 [P]	
Eu				7.22 ± 0.07	
Dy				7.69 ± 0.05	
Lu				8.08 ± 0.07	
Lu			Ln(TTA)·3TOPO	8.27 ± 0.14 [P]	

Additional notes in Supplementary Material.

At four different concentrations of TBP (3, 10, 30 and 80 mmol dm^{-3}) and 0.2 mol dm^{-3} HTTA the distribution ratios (D) vs. Z have been plotted, showing a gradual change and the tetrad effect involved in the synergistic extraction process [112]. When the complex Ln(TTA)$_3$·TBP [112] is formed, the corresponding K value is roughly six orders of magnitude larger than the extraction constant without a synergist in the solvent system. It can be seen that the value for Lu(TTA)$_3$ chelate (-1.62) obtained in CCl$_4$ at 1 M NaClO$_4$ differs very much from the value of -7.43 published in [114] and thus it can be regarded as strongly doubtful and can be used only as informative additional data. On the other hand, the choice of a molecular diluent is very important not only for synergistic enhancement, but also for the effective separation of complexes with different compositions [116]. The tris-TTA chelate EuL$_3$ forms two types of synergistic adducts, EuL$_3$·TOPO and EuL$_3$·2TOPO. The adduct formation constants determined in approximately thirteen diluents are strongly diluent-dependent, e.g., logβ_{S2} = 15.08 in pentane, compared to 7.68 obtained in chloroform.

Furthermore, Aly et al. have found that almost all lanthanoids can be synergistically extracted usng a HTTA-TOPO mixture in benzene under comparable conditions and it has been reported that the separation factors as well as the synergistic coefficients change periodically in a manner directly related to the tetrad effect, the double-double effect and the so-called inclined-W effect [118]. That contribution was an extensive study on the solvent extraction of the whole 4f series, except two ions, Pm and Lu. In that work [118], the lanthanoid chelate, Ln(TTA)$_3$, gave an adduct of a general formula Ln(TTA)$_3$·2TPPO across the whole series:

$$Ln^{3+}_{(aq)} + 3HTTA_{(o)} + 2TPPO_{(o)} \rightleftharpoons Ln(TTA)_3 \cdot 2TPPO_{(o)} + 3H^+_{(aq)} \tag{12}$$
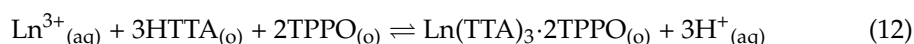
To date, no studies are available concerning the coordination of water molecules to the chelate or the mixed adduct. In many cases, it was suggested that the lighter members, i.e., La-Nd are mainly 9-coordinated, whereby the heavier representatives Gd-Lu are 8-coordinated in solutions.

Only ion exchange reactions of the extraction process of 4f ions are assessed in this work. The exact composition of complexes formed by ligand(s) is represented regularly in column four. No attempt was made here to form an opinion of the equilibrium constants for 5f ions, but some published results are presented in section Supplementary Material, as additional notes to Tables. A survey of the data using various β-diketones is presented in Table 3.
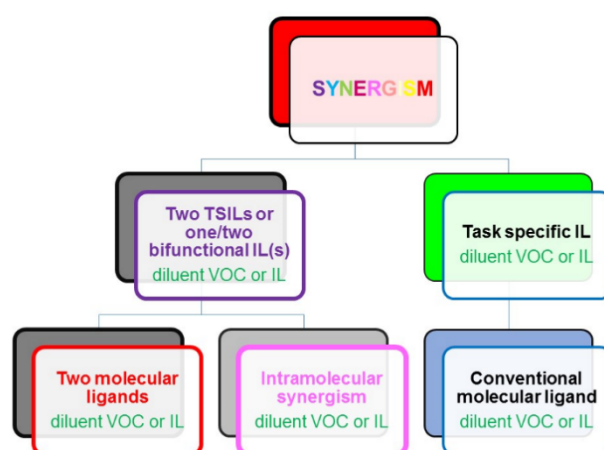
Figure 8. Evolution of the solvent extraction chemistry of 4f ions.

Table 3. Recommended and provisional data (noted as "P") for synergistic systems containing β-diketone and organophosphorus ligands used for the solvent extraction of trivalent lanthanoids.

Cation	I (mol dm^{-3})	Diluents	Equilibrium	log$K$	Refs.
Eu	0.1 NaClO$_4$	CHCl$_3$	EuL$_3$		[106]
			L: acetylacetone	−	
			L: benzoylacetone	−19 [P]	
			L: trifluoroacetylacetone	−	
			L: benzoyltrifluoroacetone	−9.47 [P]	
			L: froyltrifluoroacetone	−8.73 [P]	
			L: thenoyltrifluoroacetone	−8.68 [P]	
			EuL$_3$·TBP		
			L: acetylacetone	1.90 [P]	
			L: benzoylacetone	1.60 [P]	
			L: trifluoroacetylacetone	3.32 [P]	
			L: benzoyltrifluoroacetone	3.64 [P]	
			L: froyltrifluoroacetone	3.50 [P]	
			L: thenoyltrifluoroacetone	3.34 [P]	
			EuL$_3$·2TBP		
			L: acetylacetone	−	
			L: benzoylacetone	−	
			L: trifluoroacetylacetone	4.64 [P]	
			L: benzoyltrifluoroacetone	5.28 [P]	
			L: froyltrifluoroacetone	5.00 [P]	
			L: thenoyltrifluoroacetone	5.28 [P]	
	0.1 NaClO$_4$	C$_6$H$_6$	LnL$_3$, L: benzoyltrifluoroacetone		[120]
La				−11.6 [P]	
Eu				−8.9 [P]	
Tb				−8.8 [P]	
Lu				−7.7 [P]	
La			LnL$_3$·TBP	4.38 [P]	

Table 3. *Cont.*

Cation	I (mol dm^{-3})	Diluents	Equilibrium	log$K$	Refs.
Eu				4.55 [P]	
Tb				4.50 [P]	
Lu				4.70 [P]	
La			LnL$_3$·2TBP	7.80 [P]	
Eu				7.40 [P]	
Tb				7.30 [P]	
Lu				6.00 [P]	
La			LnL$_3$·TOPO	7.00 [P]	
Eu				6.85 [P]	
Tb				6.90 [P]	
Lu				7.50 [P]	
La			LnL$_3$·2TOPO	12.30 [P]	
Eu				11.70 [P]	
Tb				11.20 [P]	
Lu				−	
La	0.1 NaCl	C$_6$H$_6$	LnL$_3$; L: 4,4,4-trifluoro-1-(biphenyl-4-yl)butane-1,3-dione	-6.40 ± 0.05	[121]
Ce				-5.59 ± 0.05	
Pr				-5.17 ± 0.05	
Nd				-4.76 ± 0.05	
Sm				-4.36 ± 0.05	
Eu				-4.06 ± 0.05	
Gd				-3.75 ± 0.05	
La			LnL$_3$·2TOPO	1.82 ± 0.05	
Ce				2.57 ± 0.05	
Pr				2.92 ± 0.05	
Nd				3.12 ± 0.05	
Sm				3.33 ± 0.05	
Eu				3.50 ± 0.05	
Gd				3.76 ± 0.05	
La			LnL$_3$·2TBPO	-0.36 ± 0.05	
Ce				0.32 ± 0.05	
Pr				0.58 ± 0.05	
Nd				1.02 ± 0.05	
Sm				1.35 ± 0.05	
Eu				1.62 ± 0.05	
Gd				1.97 ± 0.05	
La			LnL$_3$·TPPO	0.92 ± 0.05	
Ce				1.09 ± 0.05	
Pr				1.35 ± 0.05	

Table 3. *Cont.*

Cation	I (mol dm^{-3})	Diluents	Equilibrium	log$K$	Refs.
Nd				1.63 ± 0.05	
Sm				2.14 ± 0.05	
Eu				2.34 ± 0.05	
Gd				2.52 ± 0.05	
La	0.1 NaClO$_4$ 0.01 CH$_3$COONa	CHCl$_3$	LnL$_3$ L:2-trifluoroacetyl-cyclopentanone	−13.26 [P]	[122]
Pr				−11.80 [P]	
Eu				−10.81 [P]	
Ho				−10.34 [P]	
Yb				−9.62 [P]	
Pr			LnL$_3$; L:2-trifluoroacetyl-cyclohaxanone	−17.27 [P]	
Eu				−16.52 [P]	
Ho				−15.74 [P]	
Yb				−14.61 [P]	
Pr			LnL$_3$ L:2-trifluoroacetyl-cycloheptanone	−17.55 [P]	
Eu				−16.23 [P]	
Ho				−15.60 [P]	
Yb				−14.56 [P]	
La			ML$_3$·TOPO L:2-trifluoroacetyl-cyclopentanone	−6.19 [P]	
Pr				−5.52 [P]	
Eu				−5.25 [P]	
Ho				−4.41 [P]	
Yb				−4.48 [P]	
Pr			ML$_3$·TOPO L:2-trifluoroacetyl-cyclohaxanone	−11.51 [P]	
Eu				−10.68 [P]	
Ho				−9.22 [P]	
Yb				−8.25 [P]	
Pr			ML$_3$·TOPO L:2-trifluoroacetyl-cycloheptanone	−11.13 [P]	
Eu				−9.87 [P]	
Ho				−9.22 [P]	
Yb				−7.90 [P]	
La	0.1 NaCl	CHCl$_3$	LnL$_3$, L: HTTA	−11.06 ± 0.05	[123]
Nd				−10.12 ± 0.05	

Table 3. *Cont.*

Cation	I (mol dm^{-3})	Diluents	Equilibrium	log$K$	Refs.
Eu				-8.68 ± 0.05	
Ho				-8.56 ± 0.05	
Lu				-8.15 ± 0.05	
La	0.1 NaCl	CHCl$_3$	LnL$_3\cdot$2S; S: S1, (Figure 6)	-3.22 ± 0.06	
Nd				-1.89 ± 0.06	
Eu				-1.07 ± 0.06	
Ho				-0.50 ± 0.06	
Lu				0.08 ± 0.06	
La	0.1 NaClO$_4$	CCl$_4$	LnL$_3$; L: HTTA	-10.50 ± 0.05	[124]
Ce				-9.99 ± 0.05	
Pr				-9.53 ± 0.05	
Nd				-9.35 ± 0.05	
Sm				-8.68 ± 0.05	
Eu				-8.55 ± 0.05	
Gd				-8.40 ± 0.05	
Tb				-8.22 ± 0.05	
Dy				-7.98 ± 0.05	
Ho				-7.87 ± 0.05	
Er				-7.76 ± 0.05	
Tm				-7.40 ± 0.05	
Yb				-7.14 ± 0.05	
Lu				-6.99 ± 0.05	
La			LnL$_3\cdot$2S; S: S7, (Figure 6)	1.29 ± 0.05	
Ce				1.74 ± 0.05	
Pr				1.90 ± 0.05	
Nd				2.10 ± 0.05	
Sm				2.38 ± 0.05	
Eu				2.61 ± 0.05	
Gd				2.78 ± 0.05	
Tb				2.92 ± 0.05	
Dy				3.03 ± 0.05	
Ho				3.11 ± 0.05	
Er				3.23 ± 0.05	
Tm				3.33 ± 0.05	
Yb				3.47 ± 0.05	
Lu				3.60 ± 0.05	
La	0.1 NaClO$_4$	CCl$_4$	Ln(TTA)$_3\cdot$S; S: S8, (Figure 6)	-5.69 ± 0.05	[125]
Ce				-5.41 ± 0.05	
Pr				-5.22 ± 0.05	
Nd				-5.08 ± 0.05	
Sm				-4.84 ± 0.05	

Table 3. *Cont.*

Cation	I (mol dm^{-3})	Diluents	Equilibrium	log$K$	Refs.
Eu				-4.65 ± 0.05	
Gd				-4.50 ± 0.05	
Tb				-4.34 ± 0.05	
Dy				-4.15 ± 0.05	
Ho				-3.94 ± 0.05	
Er				-3.76 ± 0.05	
Tm				-3.59 ± 0.05	
Yb				-3.38 ± 0.05	
Lu				-3.28 ± 0.05	
La	1×10^{-2} buffer	[C$_1$C$_4$im$^+$] [Tf$_2$N$^-$]	Ln(ba)$_2^+$; L: benzoylacetone	-12.65 ± 0.05	[126]
Nd				-11.11 ± 0.08	
Eu				-10.85 ± 0.05	
Dy				-10.08 ± 0.08	
Lu				-9.68 ± 0.21	
La			LnL$_3$; L: benzoylacetone	-18.03 ± 0.03	
Nd				-16.69 ± 0.14	
Eu				-15.61 ± 0.06	
Dy				-15.35 ± 0.15	
Lu				-13.62 ± 0.13	
La	1×10^{-2} buffer	[C$_1$C$_4$im$^+$] [Tf$_2$N$^-$]	LnL$_2$(TOPO)$_2^+$ L: benzoylacetone	-5.69 ± 0.07	[126]
Nd				-3.93 ± 0.05	
Eu				-2.66 ± 0.06	
Dy				-1.93 ± 0.14	
La			LnL(TOPO)$_4^+$; L: benzoylacetone	3.85 ± 0.05	
Nd				5.37 ± 0.05	
Eu				6.01 ± 0.06	
Dy				7.11 ± 0.17	
Lu				9.26 ± 0.05	

Additional notes in Supplementary Material.

Overall, it has been reported that the synergistic effect is different when different inert organic diluents are applied and is usually larger when water has a smaller solubility in the organic diluent. The pH of 50% extraction increases in the following order of applied β-diketones [106]: TTA ≈ FTA < BFA < TAA < BZA < AA. Therefore, acetylacetone showed the lowest extraction of Eu(III), at less than 10%. The metal chelates with CH$_3$-group β-diketones did not form the second adduct, ML$_3$·2TBP, but the metal chelates with CF$_3$-group β-diketones formed this second adducts in solution. The substitution of a methyl group in acetylacetone or trifluoroacetone with a benzoyl, froyl or thenoyl group increases the possibility of good metal extraction, because the substitution increases the organophilic tendency of the molecules and prevents the formation of metal chelates in the aqueous phase. Moreover, β-diketones with one trifluoromethyl group extract metal ions from aqueous solutions at a lower pH than those without the CF$_3$-group.

The stability of rare earth benzoyltrifluoroacetone complexes decreases, but that of adducts increases, as the ionic radius increases in 4f series [120]. The maximum number of base synergistic molecules bonding to one molecule of the metal chelate is two, except in the case of lutetium adducts with TOPO ligands, in which the formation of secondary adducts is not observed. The log$K$ values for the synergistic mixture including *n*-hexyl alcohol with the formation of the species ML$_3$·S are listed herein as well—La: 1.95; Eu: 1.85; Tb: 1.85; Lu: 1.65. Thus, the studied organic bases form stable adducts with rare earth benzoyltrifluoroacetonates in the following order: 4-hexyl alcohol < TBP < TOPO. The value of pH$_{1/2}$ rises as the ionic radius of the central rare earth metal increases [120].

A great increase in the equilibrium constant value (approximately 11 orders of magnitude) was found with the addition of the synergist calixarene S7 molecule (see Figure 6 and Table 4) to the system Ln^{3+}–HTTA. In order to compare the solvent extraction efficiency of the HTTA-S7 system 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 was extracted; pH$_{0.5}$ or pH$_{1/2}$) were obtained, corresponding to the extraction of the studied lanthanoids in the absence and in the presence of calix[4]arene, with a difference between the pH$_{50}$ values of 1.7–1.3 pH units detected [22]. Outstanding SC results for the HTTA-S7/CCl$_4$ system (up to 10^5) were obtained [124], but the synergism drastically decreased upon a change in the synergistic agent with S8 [125]. The calculated SCs of Ln(III) ions of the HTTA-S8 combination [125] were in most cases approximately five times smaller than those in which the co-extractant was S1 [123]. As a whole, the interaction of adduct molecules with metallic ions depends strongly on the organic function in which the donor atom resides (i.e., on the charge density of the donor) [127]. In this sense, the influence of the synergistic agent used in the systems HTTA-S8 and HTTA-S7 on the degree of solvent extraction is clearly shown in Figure 9.
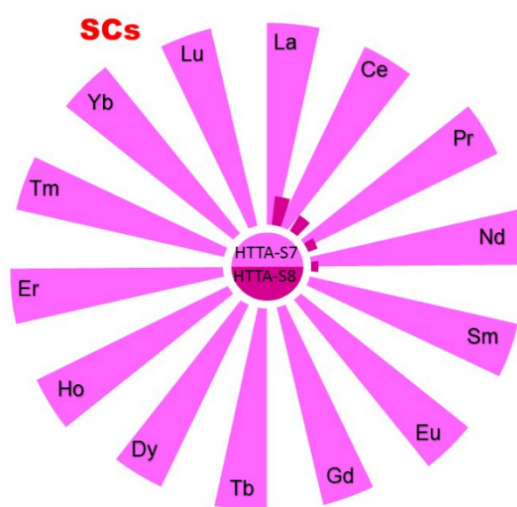
Figure 9. SC data visualization of the two solvent systems HTTA-S7 and HTTA-S8 with a Nightingale rose diagram.

On the other hand, it may be important to investigate various solvent systems in order to compare phosphorus-containing ligands with other synergistic agents (Figure 10). The superiority of the system involving calixarenes can be clearly seen, followed by crown ethers and the very popular ionic liquid Aliqut 336 [128,129]. Nonetheless, a large number of rare earths bearing phosphate minerals have been found in nature, thus indicating that 4f ions have a strong natural affinity towards phosphates.
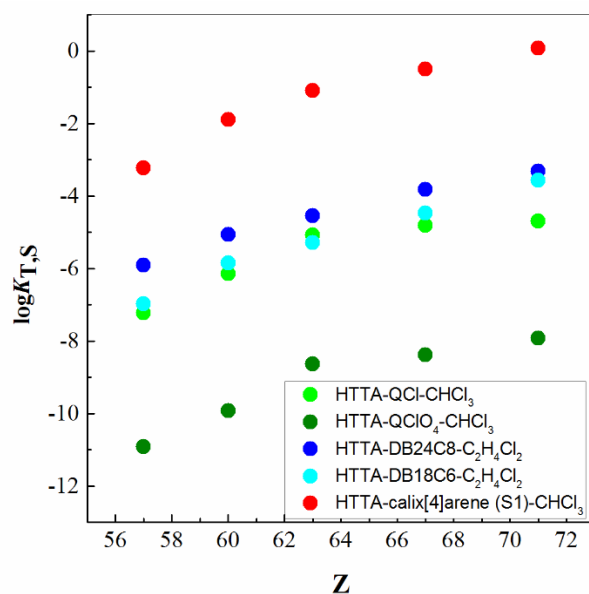
Figure 10. Comparison of synergistic solvent extraction systems for lanthanoids: $\log K_{T,S}$ vs. Z.

Table 4. Recommended data for the synergistic system of thenoyltrifluoroacetone and organophosphorus ligands when different temperatures were applied.

Cation	I (M)	Diluents/T °C	Equilibrium	$\log K$	Refs.
Eu	0.1 NaClO$_4$ and pH = 3.4	C$_6$H$_6$	Eu(TTA)$_3$	-7.22 ± 0.05	[130]
			Eu(TTA)$_3\cdot$TOPO	-0.63 ± 0.02	
			Eu(TTA)$_3\cdot$2TOPO	4.74 ± 0.02	
		10 °C	Eu(TTA)$_3\cdot$2TOPO	4.74 ± 0.02	
		25 °C		4.74 ± 0.02	
		35 °C		4.74 ± 0.02	
		45 °C		4.75 ± 0.03	
Tb			Tb(TTA)$_3$	-7.25 ± 0.05	
			Tb(TTA)$_3\cdot$TOPO	-0.93 ± 0.03	
			Tb(TTA)$_3\cdot$2TOPO	4.32 ± 0.02	
^{152,154}Eu [a]	0.1 chloroacetate buffer, pH 2.77	C$_6$H$_6$, 30 °C	Eu(TTA)$_3\cdot$2TBP	2.85 ± 0.07	[131]
		40 °C		2.67 ± 0.04	
		50 °C		2.54 ± 0.04	
		60 °C		2.27 ± 0.04	
		30 °C	Eu(TTA)$_3\cdot$2TOPO	3.30 ± 0.04	
		40 °C		2.95 ± 0.05	
		50 °C		2.89 ± 0.03	
		60 °C		2.77 ± 0.06	

Note: [a] Equilibrium constants for the organic-phase synergistic reactions are presented in Table 3, increasing in the following order: DPSO < TBP < TOPO (diphenyl sulfoxide) [131]. The obtained results indicate that the synergistic species extracted into the organic phase were of the type Eu(TTA)$_3\cdot$S and Eu(TTA)$_3\cdot$2S. In addition, thermodynamic parameters for the organic phase synergistic reactions of the Eu(III)$-$HTTA chelate with neutral oxo-donors were also given: Eu(TTA)$_{3(o)}$ + x S$_{(o)}$ $\rightleftharpoons$ Eu(TTA)$_3\cdot x$S$_{(o)}$, x = 1,2.

7. Combination of 4-Acyl-Pyrazolones and Organophosphorus Ligand

A survey of the data is presented in Table 5.

The substituent effect of several 1-phenyl-3-methyl-4-acylpyrazol-5-ones on the adduct formation between their europium and scandium chelates and TOPO ligands in C_6H_6 was studied [132]. It was found that europium acylpyrazolonates react with TOPO to form an adduct of the type $EuL_3 \cdot S$ for an aliphatic group and the $EuL_3 \cdot 2S$ type for aromatic and trifluoromethyl groups. The stability of adducts increases in the following order: aliphatic < aromatic < trifluoromethyl. A steric effect of the terminal group on adduct formation was observed for 2-, 3- and 4-methyl-substituted benzoylpyrazolonates of europium, and especially scandium. In the typical β-diketonate system, the stability of adducts formed increases in the following order: aliphatic groups (e.g., acetylacetonate, dipivaloymethane) < aromatic groups (e.g, benzoylacetone, dibenzoylmethane), trifluoromethyl groups (e.g., trifluoroacetylacetone, thenoyltrifluoroacetone). Similarly, the adducts formed with unfluorinated 4-aliphatic-substituted pyrazolones are expected to be less stable than those formed with 4-aryl- or 4-trifluoromethyl-substituted pyrazolones. This is reflected by the reaction of one mole of TOPO with one mole of europium chelate to form an $EuL_3 \cdot S$ adduct for the aliphatic-substituted pyrazolone system. The general trend indicating that the synergistic effect increases in the order described above can also be applied to the present system, i.e., the trifluoromethyl group strongly withdraws electrons between the metal ion and acylpyrazolone, whereas an aromatic group gives a resonance effect to π-electrons of the chelate ring. Accordingly, when an alkyl group replaces the aromatic or trifluoromethyl group, the interaction between the metal and the ligand may weaken, and the residual coordinating power of the metal may increase. Thus, such a situation would be favorable for adduct metal formation [132].

Table 5. Recommended and provisional (noted as "P") data for the synergistic system of 4-acyl-pyrazolone and organophosphorus ligands for the solvent extraction of trivalent lanthanoids.

Cation	I (mol dm^{-3})	Diluents	Equilibrium	log$K$	Refs.
Eu	0.1 NaClO$_4$	C_6H_6	EuL$_3$ L: 1-phenyl-3-methyl-4-acylpyrazol-5-one		[132]
			R: phenyl (see Figure 4)	−4.50 [P]	
			R: 2-chlorophenyl	−2.55 [P]	
			R: 2,4-dichlorophenyl	−2.28 [P]	
			R: 4-chlorophenyl	−3.45 [P]	
			R: 2-methylphenyl	−3.12 [P]	
			R: 3-methylphenyl	−3.90 [P]	
			R: 4-methylphenyl	−4.32 [P]	
			R: 2-naphthyl	−3.75 [P]	
			R: cyclohexyl	−6.00 [P]	
			R: *n*-heptyl	−6.00 [P]	
			R: methyl	−6.12 [P]	
			R: trifluoromethyl	−2.61 [P]	
Sc	0.1 NaClO$_4$	C_6H_6	EuL$_3$ 2-methylphenyl	−4.26 [P]	[132]
			R: 3-methylphenyl	−3.54 [P]	
			R: 4-methylphenyl	−3.12 [P]	

Table 5. *Cont.*

Cation	I (mol dm^{-3})	Diluents	Equilibrium	log$K$	Refs.
La	0.1 NaClO$_4$	CHCl$_3$	LnL$_3$ L: 1-phenyl-3-methyl-4-(trifluoroacetyl)-5-pyrazolone	−6.18 [P]	[133]
Pr				−4.98 [P]	
Eu				−3.78 [P]	
Ho				−3.36 [P]	
Yb				−3.15 [P]	
La			LnL$_3$·2TOPO	4.20 [P]	[133]
Pr				5.19 [P]	
Eu				6.06 [P]	
Ho				6.08 [P]	
Yb				5.68 [P]	
La			LnL$_3$·CMPO	1.47 [P]	[133]
Pr				2.61 [P]	
Eu				3.43 [P]	
Ho				3.54 [P]	
Yb				3.42 [P]	
La			LnL$_3$·MBDPO (methylenebis)(diphenylphosphine oxide)	3.81 [P]	[133]
Pr				4.89 [P]	
Eu				5.64 [P]	
Ho				5.52 [P]	
Yb				5.34 [P]	
La			LnL$_2$(ClO$_4$)·2MBDPO	8.10 [P]	[133]
Pr				8.96 [P]	
Eu				9.36 [P]	
Ho				8.74 [P]	
Yb				8.15 [P]	
^{140}La [a]	0.01 chloroacetate buffer pH = 2.7	xylene	ML$_3$·HL L: 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5	−4.41 ± 0.09	[134]
^{152,154}Eu				−2.11 ± 0.04	
^{177}Lu				−1.86 ± 0.04	
^{140}La	0.01 chloroacetate buffer pH = 2.7		ML$_3$·CMPO L: 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5	−0.49 ± 0.01	[134]
^{152,154}Eu				1.75 ± 0.04	
^{177}Lu				1.92 ± 0.04	
La [b]	0.01 chloroacetate buffer solutions, pH = 2.70	xylene	ML$_3$·HL L: 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5	−4.41 ± 0.09 [P]	[135]
Eu				−2.11 ± 0.04	
Lu				−1.86 ± 0.04	

Table 5. *Cont.*

Cation	I (mol dm^{-3})	Diluents	Equilibrium	log$K$	Refs.
La	0.01 chloroacetate buffer solutions, pH = 2.70	xylene	ML$_3$·CMP L: 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5	-0.76 ± 0.01	[135]
Eu				1.42 ± 0.01	
Lu				1.27 ± 0.01	
^{147}Nd	0.01 chloroacetate buffer pH = 2.7	CHCl$_3$	LnL$_3$ L: 1-phenyl-3-methyl-4-trifluoroacetl-pyrazolone-5	1.98×10^{-4}	[136]
^{152,154}Eu				1.11×10^{-3}	
^{177}Lu				2.74×10^{-3}	
^{147}Nd			LnL$_3$·TPPO	1.49×10^{1} [(mol dm^3)$^{-1}$]	[136]
^{152,154}Eu				1.5×10^{2} [(mol dm^3)$^{-1}$]	
^{177}Lu				4.7×10^{2} [(mol dm^3)$^{-1}$]	
^{47}Nd			LnL$_3$·2TPPO	9.30×10^{1} [(mol dm^3)$^{-2}$]	
^{152,154}Eu				5.47×10^{5} [(mol dm^3)$^{-2}$]	
^{177}Lu				2.7×10^{6} [(mol dm^3)$^{-2}$]	
Lu	0.1 NaClO$_4$	C$_6$H$_6$	LuL$_3$ L: ortho-substituted 1-phenyl-3-methyl-4-aroyl-5-pyrazolones		[137]
			1-phenyl-3-methyl-4-benzoylpyrazol-5-one	-3.90 [P]	
			1-phenyl-3-methyl-4-(2-toluoyl)pyrazol-5-one	-2.67 [P]	
			1-phenyl-3-methyl-4-(2-methoxybenzoyl)pyrazol-5-one	-3.36 [P]	
			1-phenyl-3-methyl-4-(2-trifluoromethylbenzoyl)pyrazol-5-one	-2.31 [P]	
			1-phenyl-3-methyl-4-(2-fluorobenzoyl)pyrazol-5-one	-2.85 [P]	
			1-phenyl-3-methyl-4-(2-chlorobenzoyl)pyrazol-5-one	-1.74 [P]	
			1-phenyl-3-methyl-4-(2-bromobenzoyl)pyrazol-5-one	-2.16 [P]	
			1-phenyl-3-methyl-4-(2,6-difluorobenzoyl)pyrazol-5-one	-2.58 [P]	
Lu	0.1 NaClO$_4$	C$_6$H$_6$	LuL$_3$·TOPOL: ortho-substituted 1-phenyl-3-methyl-4-aroyl-5-pyrazolones		[137]
			1-phenyl-3-methyl-4-benzoylpyrazol-5-one	6.69 [P]	

Table 5. *Cont.*

Cation	I (mol dm^{-3})	Diluents	Equilibrium	log$K$	Refs.
			1-phenyl-3-methyl-4-(2-toluoyl)pyrazol-5-one	6.50 [P]	
			1-phenyl-3-methyl-4-(2-methoxybenzoyl)pyrazol-5-one	6.03 [P]	
			1-phenyl-3-methyl-4-(2-trifluoromethylbenzoyl)pyrazol-5-one	6.70 [P]	
			1-phenyl-3-methyl-4-(2-fluorobenzoyl)pyrazol-5-one	7.06 [P]	
			1-phenyl-3-methyl-4-(2-chlorobenzoyl)pyrazol-5-one	6.65 [P]	
			1-phenyl-3-methyl-4-(2-bromobenzoyl)pyrazol-5-one	6.58 [P]	
			1-phenyl-3-methyl-4-(2,6-difluorobenzoyl)pyrazol-5-one	6.97 [P]	
Lu	0.1 NaClO$_4$	C$_6$H$_6$	LuL$_3$·2TOPO L: ortho-substituted 1-phenyl-3-methyl-4-aroyl-5-pyrazolones		[137]
			1-phenyl-3-methyl-4-benzoylpyrazol-5-one	2.15 [P]	
			1-phenyl-3-methyl-4-(2-toluoyl)pyrazol-5-one	1.52 [P]	
			1-phenyl-3-methyl-4-(2-methoxybenzoyl)pyrazol-5-one	2.43 [P]	
			1-phenyl-3-methyl-4-(2-trifluoromethylbenzoyl)pyrazol-5-one	1.49 [P]	
			1-phenyl-3-methyl-4-(2-fluorobenzoyl)pyrazol-5-one	2.22 [P]	
			1-phenyl-3-methyl-4-(2-chlorobenzoyl)pyrazol-5-one	1.85 [P]	
			1-phenyl-3-methyl-4-(2-bromobenzoyl)pyrazol-5-one	1.71 [P]	
			1-phenyl-3-methyl-4-(2,6-difluorobenzoyl)pyrazol-5-one	2.48 [P]	
La [c]	0.1 NaClO$_4$	C$_6$H$_6$	ML$_3$ L: ortho-substitited 4-aroylpyrazol-5-ones		[138]
			1-phenyl-3-methyl-4-benzoylpyrazol-5-one	-7.29 ± 0.03	
			1-phenyl-3-methyl-4-(2-toluoyl)pyrazol-5-one	-6.48 ± 0.09 [P]	
			1-phenyl-3-methyl-4-(2-methoxybenzoyl)pyrazol-5-one	-7.05 ± 0.11 [P]	
			1-phenyl-3-methyl-4-(2-trifluoromethylbenzoyl)pyrazol-5-one	—	
			1-phenyl-3-methyl-4-(2-fluorobenzoyl)pyrazol-5-one	-6.33 ± 0.08	

Table 5. *Cont.*

Cation	I (mol dm^{-3})	Diluents	Equilibrium	log$K$	Refs.
			1-phenyl-3-methyl-4-(2-chlorobenzoyl)pyrazol-5-one	-5.64 ± 0.10 [P]	
			1-phenyl-3-methyl-4-(2-bromobenzoyl)pyrazol-5-one	-5.46 ± 0.01	
			1-phenyl-3-methyl-4-(2,6-difluorobenzoyl)pyrazol-5-one	-5.85 ± 0.06	
La	0.1 NaClO$_4$	C$_6$H$_6$	ML$_3$·TOPO / ML$_3$·2TOPO L: ortho-substitited 4-aroylpyrazol-5-ones		[138]
			1-phenyl-3-methyl-4-benzoylpyrazol-5-one	$6.40 \pm 0.06 /$ 3.70 ± 0.08	
			1-phenyl-3-methyl-4-(2-toluoyl)pyrazol-5-one	$5.97 \pm 0.08 /$ 3.65 ± 0.09	
			1-phenyl-3-methyl-4-(2-methoxybenzoyl)pyrazol-5-one	$5.52 \pm 0.04 /$ 3.73 ± 0.04	
			1-phenyl-3-methyl-4-(2-trifluoromethylbenzoyl)pyrazol-5-one	$-$	
			1-phenyl-3-methyl-4-(2-fluorobenzoyl)pyrazol-5-one	$6.41 \pm 0.05 /$ 3.73 ± 0.06	
			1-phenyl-3-methyl-4-(2-chlorobenzoyl)pyrazol-5-one	$5.68 \pm 0.09 /$ 3.82 ± 0.11 [P]	
			1-phenyl-3-methyl-4-(2-bromobenzoyl)pyrazol-5-one	$5.67 \pm 0.09 /$ 3.68 ± 0.11 [P]	
			1-phenyl-3-methyl-4-(2,6-difluorobenzoyl)pyrazol-5-one	$6.07 \pm 0.06 /$ 3.82 ± 0.08	
Sc	0.1 NaClO$_4$	C$_6$H$_6$	ML$_3$ L: ortho-substitited 4-aroylpyrazol-5-ones		[138]
			1-phenyl-3-methyl-4-benzoylpyrazol-5-one	3.48 ± 0.04	
			1-phenyl-3-methyl-4-(2-toluoyl)pyrazol-5-one	4.32 ± 0.05	
			1-phenyl-3-methyl-4-(2-methoxybenzoyl)pyrazol-5-one	3.39 ± 0.04	
			1-phenyl-3-methyl-4-(2-trifluoromethylbenzoyl)pyrazol-5-one	4.20 ± 0.04	
			1-phenyl-3-methyl-4-(2-fluorobenzoyl)pyrazol-5-one	3.63 ± 0.03	
			1-phenyl-3-methyl-4-(2-chlorobenzoyl)pyrazol-5-one	4.20 ± 0.04	
			1-phenyl-3-methyl-4-(2-bromobenzoyl)pyrazol-5-one	4.35 ± 0.02	
			1-phenyl-3-methyl-4-(2,6-difluorobenzoyl)pyrazol-5-one	3.69 ± 0.04	

Table 5. *Cont.*

Cation	I (mol dm^{-3})	Diluents	Equilibrium	log$K$	Refs.
Sc	0.1 NaClO$_4$	C$_6$H$_6$	ML$_3$·TOPO / ML$_3$·2TOPO L: ortho-substitited 4-aroylpyrazol-5-ones		[138]
			1-phenyl-3-methyl-4-benzoylpyrazol-5-one	2.81 ± 0.41/ 3.66 ± 0.41 [P]	
			1-phenyl-3-methyl-4-(2-toluoyl)pyrazol-5-one	2.84 ± 0.22/ 3.19 ± 0.22 [P]	
			1-phenyl-3-methyl-4-(2-methoxybenzoyl)pyrazol-5-one	2.71 ± 0.22/ 3.29 ± 0.22 [P]	
			1-phenyl-3-methyl-4-(2-trifluoromethylbenzoyl)pyrazol-5-one	3.38 ± 0.06/ 2.91 ± 0.06	
			1-phenyl-3-methyl-4-(2-fluorobenzoyl)pyrazol-5-one	3.90 ± 0.08/ 3.04 ± 0.09 [P]	
			1-phenyl-3-methyl-4-(2-chlorobenzoyl)pyrazol-5-one	3.78 ± 0.05/ 2.75 ± 0.06	
			1-phenyl-3-methyl-4-(2-bromobenzoyl)pyrazol-5-one	3.66 ± 0.03/ 2.54 ± 0.04	
			1-phenyl-3-methyl-4-(2,6-difluorobenzoyl)pyrazol-5-one	4.23 ± 0.05/ 2.78 ± 0.06	
La	0.1 NaCl	C$_6$H$_6$	LnL$_3$·HL L: 4-(4-fluorobenzoyl)-3-methyl-1-phenyl-pyrazol-5-one	−4.74 ± 0.05	[64]
Nd				−2.76 ± 0.05	
Eu				−2.37 ± 0.05	
Ho				−2.06 ± 0.05	
Lu				−1.58 ± 0.05	
La	0.1 NaCl	C$_6$H$_6$	LnL$_3$·2TOPO L: HPMFBP	4.60 ± 0.05	[64]
Nd				5.68 ± 0.05	
Eu				6.27 ± 0.05	
Ho				6.62 ± 0.05	
Lu				6.90 ± 0.05	
La	0.1 NaCl	C$_6$H$_6$	LnL$_3$·2TPPO L: HPMFBP	3.58 ± 0.05	[64]
Nd				4.46 ± 0.05	
Eu				4.97 ± 0.05	
Ho				5.30 ± 0.05	
Lu				5.56 ± 0.05	
La	0.1 NaCl	C$_6$H$_6$	LnL$_3$·2TBP L: HPMFBP	0.33 ± 0.05	[64]
Nd				1.45 ± 0.05	
Eu				2.37 ± 0.05	
Ho				2.83 ± 0.05	
Lu				3.25 ± 0.05	

Table 5. *Cont.*

Cation	I (mol dm^{-3})	Diluents	Equilibrium	log$K$	Refs.
La	0.1 NaCl	C$_6$H$_6$	LnL$_3$·2TBPO L: HPMFBP	1.96 ± 0.05	[64]
Nd				3.23 ± 0.05	
Eu				3.70 ± 0.05	
Ho				4.12 ± 0.05	
Lu				4.38 ± 0.05	
Nd	1 NaNO$_3$	CHCl$_3$	4-sebacoylbis(1-phenyl-3-methyl-5-pyrazolone)	−5.64 ± 0.04	[139]
Eu				−5.21 ± 0.03	
Tm				−4.79 ± 0.04	
Nd			TOPO	−2.90 ± 0.03	
Eu				−2.36 ± 0.02	
Tm				−1.15 ± 0.03	
Nd			TBP	−4.32 ± 0.02	
Eu				−3.76 ± 0.03	
Tm				−2.80 ± 0.02	
Nd			CMPO	−2.92 ± 0.02	
Eu				−2.40 ± 0.03	
Tm				−1.60 ± 0.02	

[a] The corresponding log$K$ values calculated for the extraction of the americium species AmL$_3$·HL and AmL$_3$·CMPO are −2.38 ± 0.05 and 1.55 ± 0.03 [134]. The data obtained when the bis(2-ethylhexyl) sulfoxide (B2EHSO) ligand was applied as a synergistic agent were also published for the complexes ML$_3$·B2EHSO or ML$_3$·2B2EHSO: La(III), −2.49 ± 0.05 and −0.14 ± 0.01; Eu(III), −0.35 ± 0.01 and 1.26 ± 0.02; Lu(III), 0.24 ± 0.01 and 2.19 ± 0.03; Am(III), −0.49 ± 0.01 and 1.13 ± 0.02 [134]. Separation factors for Eu/La, Lu/Eu and Eu/Am pairs with HPMBP alone, HPMBP−CMPO and HPMBP−B2EHSO mixtures were also calculated as ca. 202, 18 and 1.9; 174, 1.5 and 1.6; and 25, 8.5 and 1.3, respectively. [b] The synergistic mixture HL-CMP (dihexyl-N,N-diethylcarbamoylmethylphosphate) provides about 3- to 20-fold enhancement during the extraction process [135]. The possible interaction between the chelating agent and the neutral donor in the organic phase was additionally analyzed: HPMBP$_{(o)}$ + CMP$_{(o)}$ ⇌ HPMBP·CMP$_{(o)}$. The trivalent lanthanoids, i.e., La, Eu and Lu, are found to be extracted from 0.01 mol dm^{-3} chloroacetate buffer solutions as ML$_3$·HL-type self-adducts with 1-phenyl-3-mehyl-4-benzoyl-pyrazol-5 alone and in the presence of CMP as ML$_3$·CMP into xylene. The equilibrium constants for Am(III) are −2.38 ± 0.08 with HL and 1.23 ± 0.01 with the combination of two ligands. [c] The substituent effect of ortho-substituted 4-aroyl derivatives of 1-phenyl-3-methylpyrazol-5-one on the adduct formation reaction between their scandium or lanthanum chelates and a neutral ligand TOPO in benzene was studied using a liquid-liquid distribution system [138]. The published results indicate that Sc(III) can be extracted in a much lower pH region than La(III) and the difference in the log$K$ values between these two ions is about 10. On the contrary, the synergistic effect of Sc(III) is much smaller than that of La(III). The established order of the steric hindrance in the adduct formation reaction with two TOPO molecules is Lu > La > Sc. The steric hindrance is determined by tree factors, (1) the bulkiness of the substituent, (2) the proximity of the neutral ligand to the metal chelate and (3) the crowdedness of ligands around the central ion [138]. Additional notes in Supplementary Material.

Moreover, the calculated values of logK_L for 3-methyl-1-phenyl-4-(4-trifluoromethyl-benzoyl)-pyrazol-5-one are approximately 1.50, 1.20 and 0.9 logarithmic units higher than those obtained with 3-methyl-4-(4-methylbenzoyl)-1-phenyl-pyrazol-5-one (HPMMBP), 3-methyl-4-benzoyl-1-phenyl-pyrazol-5-one (HP) and 3-methyl-1-phenyl-4-(4-trifluoromethyl-benzoyl)-pyrazol-5-one (HPMFBP), respectively (Table 6). This difference is due to the fact that this HL reagent is a slightly stronger acid (pK_a = 3.40) than HPMMBP (pK_a = 4.02), HP (pK_a = 3.92) and HPMFBP (pK_a = 3.52). Therefore, the acidity of the extracting agent is increased by the electron-withdrawing effect of the fluorinated group, and the extracting agent can be used to extract metal ions from more acidic aqueous solutions, so the equilibrium values increase as the pK_a value decreases, as shown in Figure 11.

**Table 6.** Recommended data for the synergistic solvent systems of 4-acyl-pyrazolone and calixarenes.

Cation	I (mol dm^{-3})	Diluents	Equilibrium	log$K$	Refs.
La	0.1 NaCl	CHCl$_3$	LnL$_3$·HL L: HPMBP	-5.84 ± 0.05	[140]
Nd				-4.35 ± 0.05	
Eu				-3.42 ± 0.05	
Ho				-3.24 ± 0.05	
Lu				-2.83 ± 0.05	
La			LnL$_3$·S S: S1, (Figure 6)	-0.88 ± 0.05	
Nd				0.30 ± 0.05	
Eu				0.90 ± 0.05	
Ho				1.56 ± 0.05	
Lu				2.00 ± 0.05	
La [a]	0.1 NaCl	CHCl$_3$	LnL$_3$·S L: HPMBP; S: S4, (Figure 6)	-0.73 ± 0.07	[141]
Nd				0.42 ± 0.07	
Eu				1.07 ± 0.07	
Ho				1.48 ± 0.07	
Lu				1.94 ± 0.07	
La	0.1 NaCl	CHCl$_3$	LnL$_3$·S L: HPMBP; S: S2, (Figure 6)	-0.73 ± 0.05	[142]
Nd				0.64 ± 0.05	
Eu				1.60 ± 0.05	
Ho				2.08 ± 0.05	
Lu				2.48 ± 0.05	
La	0.1 NaCl	CHCl$_3$	LnL$_3$·S L: HPMBP; S: S3, (Figure 6)	2.15 ± 0.05	[143]
Nd				2.93 ± 0.05	
Eu				3.37 ± 0.05	
Ho				3.76 ± 0.05	
Lu				4.23 ± 0.05	
La	0.1 NaCl	CHCl$_3$	LnL$_3$·HL L: HPMFBP	-5.16 ± 0.05	[144]
Nd				-3.91 ± 0.05	
Eu				-3.37 ± 0.05	
Ho				-2.84 ± 0.05	
Lu				-2.62 ± 0.05	
La			LnL$_3$·S S: S1, (Figure 6)	-0.77 ± 0.05	
Nd				0.45 ± 0.05	
Eu				0.95 ± 0.05	
Ho				1.26 ± 0.05	

Table 6. *Cont.*

Cation	I (mol dm^{-3})	Diluents	Equilibrium	log$K$	Refs.
Lu				1.53 ± 0.05	
La			LnL$_3 \cdot$HL; L: HPMMBP	-6.12 ± 0.05	
Nd				-4.17 ± 0.05	
Eu				-3.89 ± 0.05	
Ho				-3.37 ± 0.05	
Lu				-3.12 ± 0.05	
La			LnL$_3 \cdot$S; S: S1, (Figure 6)	-1.78 ± 0.05	
Nd				-0.65 ± 0.05	
Eu				-0.15 ± 0.05	
Ho				0.24 ± 0.05	
Lu				0.53 ± 0.05	
La	0.1 NaCl	CHCl$_3$	LnL$_3 \cdot$HL;L:HPMTFBP	-3.24 ± 0.05	[145]
Nd				-2.74 ± 0.05	
Eu				-2.47 ± 0.05	
Ho				-1.88 ± 0.05	
Lu				-1.62 ± 0.05	
La			LnL$_3 \cdot$S; S: S5, (Figure 6)	1.22 ± 0.05	
Nd				2.16 ± 0.05	
Eu				2.54 ± 0.05	
Ho				2.86 ± 0.05	
Lu				3.14 ± 0.05	
La			LnL$_3 \cdot$S; S: S6, (Figure 6)	1.14 ± 0.05	
Nd				2.02 ± 0.05	
Eu				2.40 ± 0.05	
Ho				2.67 ± 0.05	
Lu				2.97 ± 0.05	
La	0.1 NaCl	CHCl$_3$	LnL$_3 \cdot$HL L: HPMPBP	-6.21 ± 0.05	[146]
Nd				-5.84 ± 0.05	
Eu				-5.57 ± 0.05	
Ho				-4.97 ± 0.05	
Lu				-4.58 ± 0.05	
La			LnL$_3 \cdot$S; S: S1, (Figure 6)	-1.27 ± 0.05	
Nd				-0.37 ± 0.05	
Eu				0.03 ± 0.05	
Ho				0.38 ± 0.05	
Lu				0.69 ± 0.05	

Note: [a] An increase in the number of phenolic units from 4 to 8 in the molecular structure of calixarene p-*tert*-octyl-calix[n]arene does not cause any regular change in the extraction efficiency as the established order is as follows: 8 < 4 < 6 [141–143]. 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 para-*tert*-butylcalix[4]arene in combination with the same chelating ligand, although the ligating functions on the narrow rim are the same in the two synergistic molecules S1 and S2; see Figure 6 [141,142].
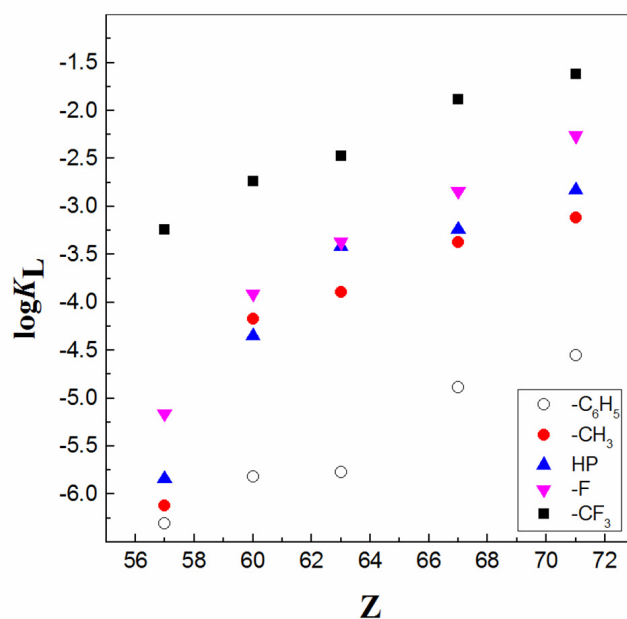
Figure 11. LogK_L of various 4-acylpyrazolones (diluent $CHCl_3$) vs. atomic number Z of La, Nd, Eu, Ho and Lu.

It is necessary to point out the peculiar behaviour of the principal extractant in use (HL) and its essential role in establishing synergism. This fact stands out clearly when different reagents from the family of pyrazolones are considered. The obtained values of the equilibrium constants decrease approximately in the following order: HPMFBP−S1 > HP−S1 > HPPMBP−S1 > HPMMBP−S1, as shown in Figure 12. Moreover, the comparison of the log$K_{L,S}$ values for Eu^{3+} with those of the other four studied 4f ions shows that log-log plots describing their behavior in five mixtures are nevertheless parallel to one another (Figure 12). Nonetheless, it is necessary to clarify here that $CHCl_3$ is the diluent used for the system HPMFBP−S1, whereas in the cases with monofunctional synergistic agents the diluent is $C6H6$. In other words, we cannot underestimate the exceptional benefits of calixarene molecules in any way.
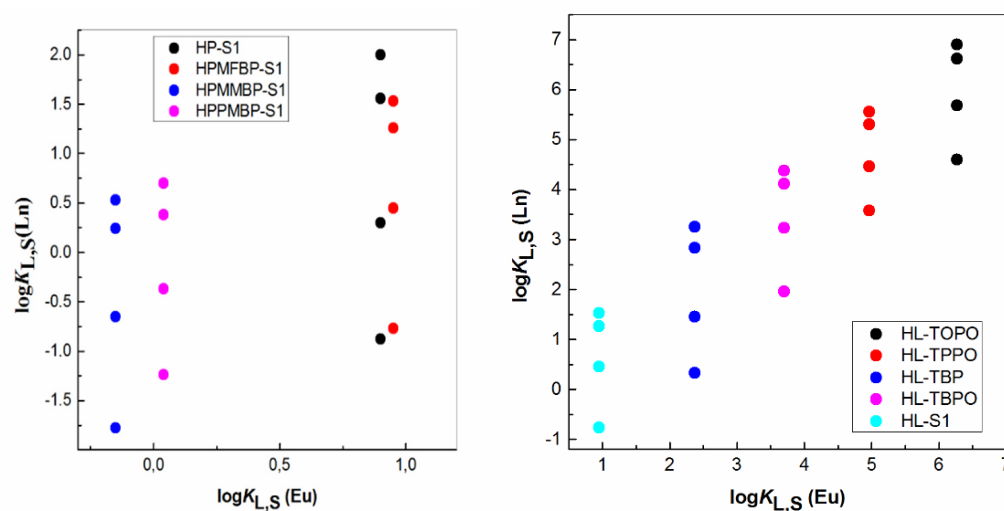
Figure 12. Comparison of log$K_{L,S}$ (La, Nd, Ho and Lu) vs. log$K_{L,S}$ (Eu) values obtained using several synergistic mixtures.

It may be worthwhile to compare the selectivity of 4f ions, applying various 4-arylpyrazolones in combination with one synergistic agent, i.e., calix[4]arene (S1), for example, in the molecular diluent CHCl$_3$. The impact of para-substitution with –F, 4-aroyl-3-methyl-1-phenyl-pyrazol-5-one, on the selectivity of the lighter lanthanoid pair Nd/La can be easily detected, as illustrated in Figure 13. At the same time, the calculated SFs for middle and heavier 4f representatives obtained with the 4-fluorophenyl terminal group are approximately identical compared with other substituents in the para-position of the 4-acylpyrazolones. The jump, however, is more than drastic, based on the pillars of the graph, when moving from Nd/La to Eu/Nd as the investigated pair.
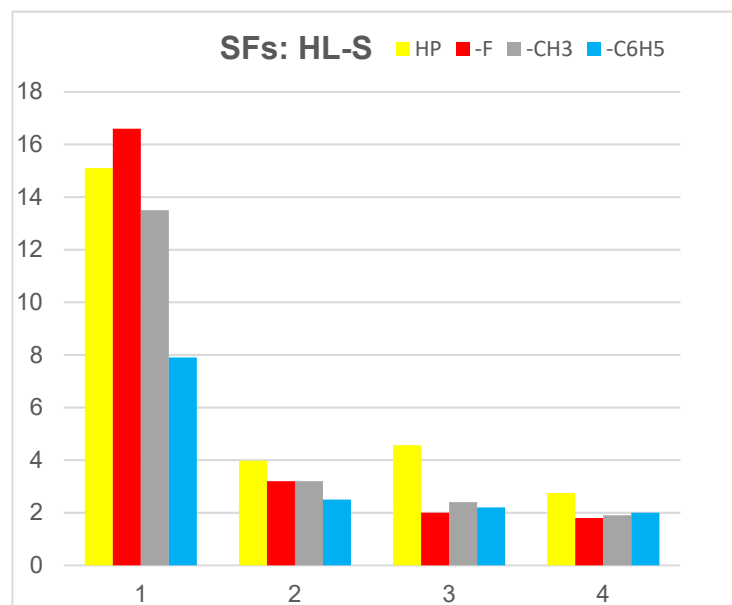
Figure 13. Comparison of the SFs calculated for synergistic mixtures of HL−S1, applying a different chelating agent, HL, in CHCl$_3$: 1-Nd/La; 2-Eu/Nd; 3-Ho/Eu and 4-Lu/Ho.

In addition, with regard to the factors affecting the stability of the synergistic adduct, the following generalizations can be made [147]. (i) In general, with organophosphorus compounds as the neutral ligands, the order of synergistic enhancement is that of increasing base strength. Of course, with considerable restrictions as to steric factors, the stability increases with increased donor properties of the molecule. (ii) Though the composition of the adduct remains unaffected, a change in the diluent employed frequently affects the synergistic enhancement. In some extreme cases, the diluent may have an effect on the established synergism greater than the initial synergistic effect. (iii) Sometimes, there is a small but finite decrease in the synergistic enhancement with a decreasing ionic radius of the metal, as shown in Figure 14. The phenomenon can be attributed, at least partially, to the lower energy needed to accommodate the neutral ligand with the increased ionic radius of the central metal atom. (iv) As a whole, stronger chelating agents, which form strong metal complexes, have a lower tendency to facilitate the binding of the neutral ligand to the metal than weaker chelating agents. On the other hand, Irving wrote, "Can we generalize and say that the stronger the complex, the smaller the tendency to form an adduct . . . and the smaller the synergistic effect in solvent extraction?".
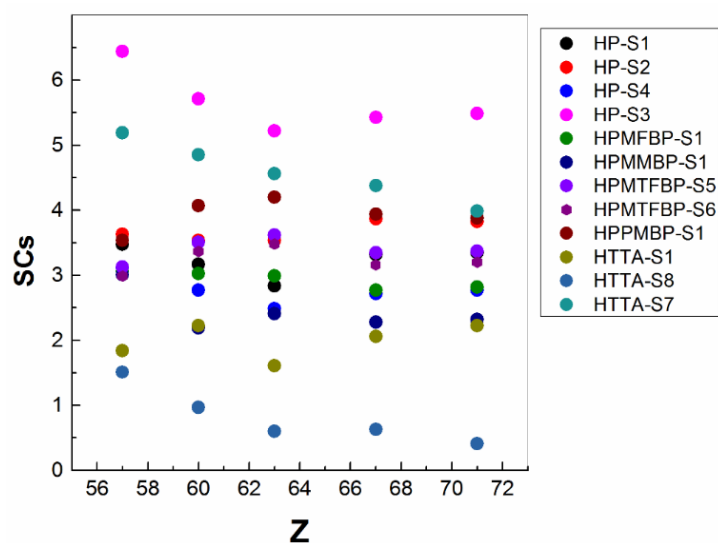
Figure 14. SCs vs. Z for several solvent mixtures.

8. Combination of 4-Acyl-5-Isoxazolones and Organophosphorus Ligands

A survey of the data is presented in Table 7.

Additionally, an examination of the relevance of "inclined-W" plots has been performed in some research cases as well, showing that the obtained linearity is somewhat maintained within the four segments, as shown in Figure 15.
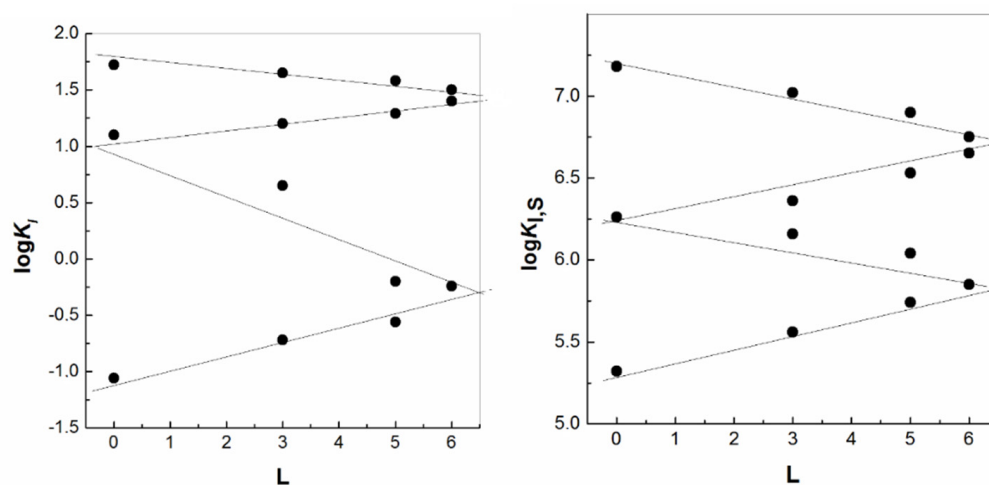

Figure 15. Variation of $\log K_I$($K_{I,S}$) values with total angular momentum, L, of the rare earth ions. The straight lines are drawn for visual impacts only.

Furthermore, it may be interesting to mention that some linearization is possible if one uses the J quantum number instead of the L for the trivalent lanthanoids [148]. The variation of J with the atomic number of f-electrons for the trivalent lanthanoids is shown in Figure 16.
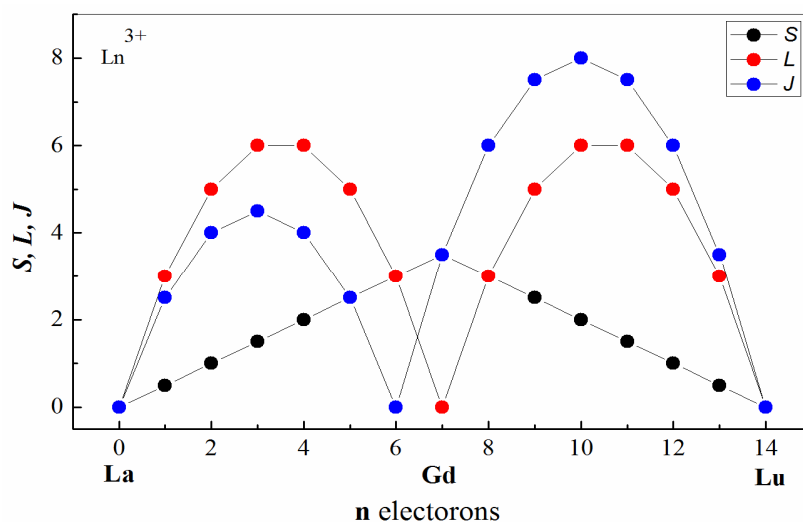
Figure 16. Variation of the *J* quantum number for the trivalent lanthanoids with the number of f-electrons in the series.

Table 7. Recommended data (noted as "P") for the synergistic system of 4-acyl-5-isoxazolone and organophosphorus ligands.

Cation	*I* (mol dm^{-3})	Diluents	Equilibrium	log*K*	Refs.
	0.2 NaNO$_3$	C$_6$H$_6$	LnL$_3$·2TBP L: 4-acyl-3-phenyl-5-isoxazolones		[149]
Pr			4-acetyl	3.34 [P]	
Eu				3.93	
Yb				3.25	
Pr			4-benzoyl	6.01	
Eu				6.40	
Yb				5.56	
Pr			4-(4-toluoyl)-	5.41	
Eu				6.15	
Yb				5.14	
Pr			4-(4-fluorobenzoyl)-	5.89	
Eu				6.27	
Yb				5.40	
Pr			4-(4-nitrobenzoyl)-	5.93	
Eu				6.38	
Yb				5.55	
La	0.01 NaClO$_4$	xylene	ML$_3$ L: 3-phenyl-4-benzoyl-5-isoxazolone	-0.78 ± 0.02	[150]
Eu				0.26 ± 0.05	
Lu				0.48 ± 0.01	
La			ML$_3$·2TBP	7.13 ± 0.02	[150]
Eu				8.47 ± 0.02	
Lu				8.53 ± 0.02	

Table 7. *Cont.*

Cation	I (mol dm^{-3})	Diluents	Equilibrium	log$K$	Refs.
La	0.1 NaClO$_4$	CHCl$_3$	LnL$_3$ L: HPBI	-1.33 ± 0.05	[98]
Nd				-0.54 ± 0.05	
Eu				0.06 ± 0.05	
Ho				0.36 ± 0.05	
Lu				0.70 ± 0.05	
La^c	0.1 MES	CHCl$_3$	LnL$_3$; L: HPBI	-1.34 ± 0.1	[60]
Eu				0.85 ± 0.11	
Lu				0.73 ± 0.10	
La	0.1 MES	[C$_1$C$_4$im$^+$][Tf$_2$N$^-$]	LnL$_4^-$; L: HPBI	3.60 ± 0.02	[60]
Eu				5.12 ± 0.03	
Lu				5.07 ± 0.03	
La	0.1 NaClO$_4$	CHCl$_3$	LnL$_3\cdot$2S; S: S1, (Figure 6)	6.7 ± 0.05	[98]
Nd				7.98 ± 0.05	
Eu				8.60 ± 0.05	
Ho				8.96 ± 0.05	
Lu				9.46 ± 0.05	
La	0.1NaClO$_4$	C$_6$H$_6$	LnL$_3\cdot$S; L: HPBI; S: S7, (Figure 6)	5.32 ± 0.05	[151]
Ce				5.56 ± 0.05	
Pr				5.74 ± 0.05	
Nd				5.85 ± 0.05	
Sm				6.04 ± 0.05	
Eu				6.16 ± 0.05	
Gd				6.26 ± 0.05	
Tb				6.36 ± 0.05	
Dy				6.53 ± 0.05	
Ho				6.65 ± 0.05	
Er				6.75 ± 0.05	
Tm				6.90 ± 0.05	
Yb				7.02 ± 0.05	
Lu				7.18 ± 0.05	
La	0.1 NaClO$_4$	CHCl$_3$		3.18 ± 0.05	
Nd				3.87 ± 0.05	
Eu				4.54 ± 0.05	
Ho				5.02 ± 0.05	
Lu				5.45 ± 0.05	
La	0.1 NaCl	C$_2$H$_4$Cl$_2$		-1.25 ± 0.05	
Nd				-0.46 ± 0.05	
Eu				0.16 ± 0.05	
Ho				0.82 ± 0.05	

Table 7. *Cont.*

Cation	I (mol dm^{-3})	Diluents	Equilibrium	log$K$	Refs.
Lu				1.24 ± 0.05	
La	0.1 NaCl	CCl$_4$		0.82 ± 0.05	
Nd				1.26 ± 0.05	
Eu				1.77 ± 0.05	
Ho				2.23 ± 0.05	
Lu				2.63 ± 0.05	

Additional notes in Supplementary Material.

It can be seen in Figure 16 that the breaks now occur at Nd, Eu and Dy, as the *J*-values are not symmetric around Gd(III), whereas the *L*-values are. Hence, the plot gives rise to an unsymmetrical inclined W. The next step is to present here a few of the plots constructed to depict the dependence of *K* on *J* quantum numbers (Figure 17).
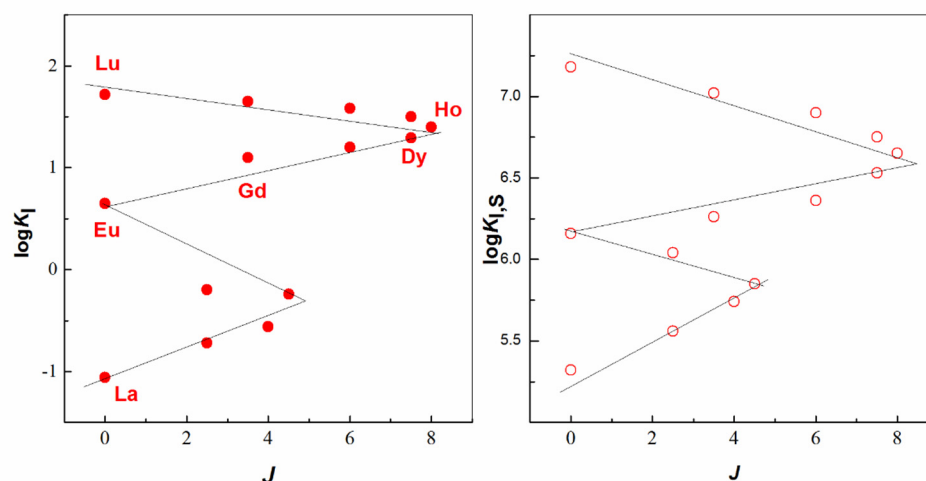

Figure 17. Variation of logK_I($K_{I,S}$) values with the quantum number, *J*, of the rare earth ions. The straight lines are drawn for visual impacts only.

It is important to point out that the application of the ionic liquid as an extracting phase greatly enhanced the solvent extraction performance of HPBI ligand for lanthanoid ions compared with that in the chloroform system [60]. Only one study has been reported in which the experimental average ligand numbers exceeded the value of three at a low ligand concentration, but definitive answers regarding their stabilities must await further investigations. The composition of the extracted species was determined to consist of anionic tetrakis entities Ln(PBI)$_4{}^-$ for light, middle and heavy lanthanoid ions in an ionic environment. Nevertheless, typical neutral chelate lanthanoid complexes of the type Ln(PBI)$_3$ were detected when the conventional molecular diluent chloroform was applied as an organic phase [59,98,151].

Among the eight molecules represented in Figure 6, 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) [98,123–125,151]. Note that to enhance the effectiveness of the solvent extraction process, a simple change in the organic molecular diluent can be applied (HTTA-S1 and HTTA-S7). The calculated SCs for system HPBI-S7 including CCl$_4$ were two orders of magnitude higher than the cases in which CHCl$_3$ and C$_2$H$_4$Cl$_2$ were used [151]. For a given 4f metal, the values of log$K_{L,S}$ increase in the following order: CHCl$_3$ < C$_2$H$_4$Cl$_2$ < C$_6$H$_6$ < CCl$_4$ [151]. It can be concluded that, on the whole, an increase in the diluent's

solvating ability hinders the extraction process. Furthermore, the separation values of Lu/Eu pairs produced by the system HP(HTTA)-S1 are very similar. In other words, the selectivity of these two elements remains almost constant (around seven) when using HPBI-S1(S7) or HTTA-S7, as well as combinations HP(S1, S3, S4). The outcome of this direct effect is that the various para-substituents (-F, -CH$_3$, -CF$_3$, -C$_6$H$_5$) of the 4-acylpyrazolone molecule do not influence the selectivity of Lu/Eu to a great extent in combination with the synergistic agent S1 or S5 and S6. The calculated values were between 4.7 and 3.7. Extraction ability and selectivity are a pair of contradictory elements, i.e., a good extraction efficiency is usually not accompanied by marked selectivity. The synergistic lanthanoid extraction observed with S1 increased in the following order of chelating ligands: HTTA < HP < HPBI. However, at the same time, the SFs decreased [22]. Therefore, the separation becomes poorer as the extractability increases, and the selectivity decreases with increase in the extractant's acidity, i.e., its pK_a value [17,59].

9. Combination of Organic Acid and Organophosphorus Ligands

Table 8 presents a survey of the literature on rare earth solvent extraction applying combinations of organic acid and organophosphorus ligands.

Table 8. Recommended data for the synergistic system of organic acid and organophosphorus ligands.

Cation	I (mol dm^{-3})	Diluents	Equilibrium	log$K$	Refs.
Pr	0.1 NaCl/acetate medium	heptane	LnL$_3$ L: 8-hydroxyquinoline	-11.52 ± 0.14	[152]
Nd			LnL$_3$	-11.54 ± 0.14	
Ln	1 NaNO$_3$	xylene	M = La, Nd, Eu: M(BMPP)$_3$·3HBTMPP where bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272, HBTMPP) M(BTMPP)$_2$(NO$_3$)2(TRPO); M = Y, Ho, Tm, Lu: M(BTMPP)$_3$(HBTMPP)(TRPO) where trialkylphosphine oxide (Cyanex 923, TRPO)		[153]
La			M(BMPP)$_3$·3HBTMPP	-6.73 ± 0.04	
Nd				-5.50 ± 0.03	
Eu				-4.05 ± 0.02	
Ho				-2.5 ± 0.02	
Tm				-1.71 ± 0.02	
Lu				-1.27 ± 0.02	
Y				-2.24 ± 0.02	
La			M(BTMPP)$_2$(NO$_3$)2(TRPO)	-0.75 ± 0.03	
Nd				0.11 ± 0.02	
Eu				0.55 ± 0.03	
Ho			M(BTMPP)$_3$(HBTMPP)(TRPO)	-1.74 ± 0.03	
Tm				-0.97 ± 0.03	
Lu				-0.36 ± 0.04	
Y				-1.93 ± 0.02	

Table 8. *Cont.*

Cation	I (mol dm^{-3})	Diluents	Equilibrium	log$K$	Refs.
La		1,2-dichloro-ethane	LnL$_3$·S L: picrolonic acid S: tetraphenylmethylene-diphosphine dioxide	9.21 ± 0.04	[154]
Ce				9.83 ± 0.05	
Pr				10.04 ± 0.05	
Nd				10.06 ± 0.05	
Sm				10.34 ± 0.05	
Eu				10.29 ± 0.05	
Gd				10.06 ± 0.05	
Tb				10.14 ± 0.05	
Dy				10.02 ± 0.05	
Ho				9.91 ± 0.05	
Er				9.73 ± 0.05	
Tm				9.64 ± 0.05	
Yb				9.51 ± 0.05	
Lu				9.31 ± 0.04	
La			LnL$_3$·2S; L: picrolonic acid S: tetraphenylmethylene-diphosphine dioxide	12.80 ± 0.06	
Ce				12.98 ± 0.06	
Pr				12.92 ± 0.06	
Nd				12.81 ± 0.06	
Sm				12.95 ± 0.06	
Eu				12.85 ± 0.06	
Gd				12.46 ± 0.06	
Tb				12.59 ± 0.06	
Dy				12.45 ± 0.06	
Ho				12.20 ± 0.06	
Er				12.06 ± 0.06	
Tm				11.91 ± 0.06	
Yb				11.72 ± 0.06	
Lu				11.48 ± 0.06	
La			LnL$_3$·2S S: 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis-(dimethylphosphinoylmethoxy)calix[4]arene	6.7 ± 0.05	
Nd				7.98 ± 0.05	
Eu				8.60 ± 0.05	
Ho				8.96 ± 0.05	
Lu				9.46 ± 0.05	

Additional notes in Supplementary Material.

10. Conclusions

This study, although presenting an enormous compilation of cited research cases and investigations, is certainly not comprehensive. However, on the basis of this "snapshot", the reader should be able to appreciate the overall scale and diversity of mixed-solvent systems for the 4f metals in the periodic table and some of the thought-provoking research considerations underlying their solvent extraction and separation processes in the last decades. The expected results will have a decisive impact on the prediction and optimization of liquid-liquid extraction systems of interest to rare earths industry and chemistry in order to improve the current "state-of-the-art" technologies. Solvent metal extraction has become the reference technique for the reprocessing of spent nuclear fuels at industrial scale as well. It appears that very small modifications of the chemical structure of the ligand (the chelating or synergistic agent) or the pre-organizing platform, as well as simple changes in a diluent, could impact the overall extraction mechanism or separation efficiency, and this is likely in pure molecular solvent systems. Beyond question, ionic liquids belong to the most investigated group of solvent systems in the last two decades, not only in the study of the solvent extraction and separation chemistry of metal species. However, the challenges related to both 4f extraction and separation are not easy to overcome in these organic media. Further proof of this is represented by the lack of published equilibrium constants. With the present study, the reader can obtain a fresh and first-hand view of the subject in hindsight. There is no useful guidance available pertaining to the question of which system is best for the solvent extraction of f ions. Therefore, new research strategies involving novel classes of interesting ligands (both intra- and intermolecular), non-fluorinated ILs, water-free systems, multiple organic phases, and so on, might provide better designs and more efficient synergistic mixtures in the near future. Nevertheless, the equilibrium constants represent one perfect parameter that can be used when estimating or predicting the results in this field of chemistry. We anticipate that this article will contribute to the further development of solvent extraction research incorporating 4f elements; clearly, there is still room for further investigations in this field.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/separations9110371/s1, Figure S1: Structural representation of 2-trifluoroacetyl-cyclopentanone (1), -cyclohexanone (2) and –cycloheptanone (3); Figure S2: Structural formula of 1-butyl-3-methylimidazolium-bis(trifluoromethanesulfonyl)imide, [C1C4im+][Tf2N−]; Figure S3: Structural formula of 4-acylbis(pyrazolones); Figure S4: Proposed structure of the extracted lanthanoid complexes; Figure S5: 4-Aroyl derivatives of 1-phenyl-3-methyl-5-pyrazolone studied; Figure S6: Structural representation of ligands; Figure S7: Structural representation of ligands; Figure S8: The equilibrium constants K1 and K2 for the Ln(III) extraction with HPMBP and compound I in toluene: the ionic strength was maintained at 0.1 mol dm^{-3} with (Na, H)Cl. Figure S9: Structural representation of ligands; Figure S10: Possible compositions of the mixed complexes with TBP; Figure S11: Structural representation of ligands; Table S1: Thermodynamic parameters of the synergistic extraction with the mixture of HEHHAP and Cyanex272.[Cyanex272] = [HEHHAP] = 0.015 mol dm^{-3}, [YbCl3] = [LuCl3] = 0.002 mol dm^{-3}, pH = 2, [Cl−] = 0.3 mol dm^{-3}. References [155–183] are cited in the Supplementary Material.

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