INVESTIGATION ON THE DILUENT EFFECT ON SOLVENT EXTRACTION

PROCESSES OF TRIVALENT $f$-ELEMENTS BY

ACIDIC DI-ALKYL ORGANOPHOSPHORUS

EXTRACTANTS

By

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A dissertation submitted in partial fulfillment of
the requirements for the degree of

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To the Faculty of Washington State University:

The members of the Committee appointed to examine the dissertation of THIBAUT JEAN-MICHEL LUCIEN LÉCRIVAIN find it satisfactory and recommend that it be accepted.

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« Que tu es plein de bon sens, mon petit bonhomme ; un de ces jours je te ferai passer docteur en gai savoir »

Translation

« You have plenty of common sense my little guy, one of this days I will make you doctor of merry knowledge »

Francois Rabelais - Gargantua. chap. 13

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ACIDIC DI-ALKYL ORGANOPHOSPHORUS

EXTRACTANTS

Abstract

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Solvent extraction is the most common chemical technique used in hydrometallurgical separations and purification of transition metals and f-elements. Solvent extraction of metallic cations, such as the f-elements, needs the use of organic ligands (extractants) to coordinate the targeted cation, to make it soluble in an organic phase and then allow the phase transfer from the aqueous phase to the organic one. The family of acidic di-alkyl organophosphorus extractants are the extractants of choice for trivalent metals. Furthermore, the large catalogue of diluents available for experimentation is one of the delightful aspects of solvent extraction chemistry (and probably to other chemistry domains). There are so many to choose from, and each has its special applications where it outshines the rest.

This dissertation is focusing on the influence of the choice of the diluent on the solvent extraction process of selected trivalent f-elements (Nd$^{3+}$, Eu$^{3+}$, Tm$^{3+}$ and Am$^{3+}$) by HEH[EHP]. The results show that the diluent influences the efficiency of the extraction (characterized by the $K_{ex}$), but also the stoichiometry of the metal chelate. Spectrophotometry shows that the coordination of the metal
chelate is invariant from one diluent to another. The results of the extraction of Eu$^{3+}$ by HEH[EHP] are then compared to the diluent properties that are relevant for the solvation process (cavitation, dispersion and association). Finally, van’t Hoff analysis is applied to the extraction of Am$^{3+}$ and Nd$^{3+}$ by HDEHP in various diluents, revealing an entropy and enthalpy compensation effect.
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Dedication

This dissertation is dedicated to my wife Lindsey, my mother, and father for your support, kindness, and selflessness.
CHAPTER ONE
INTRODUCTION

1.1 Solvent Extraction

1.1.1 Generality

Solvent Extraction (SX) is one of the most common separation techniques, because of its simplicity, speed and wide scope. SX is a practice that has been performed for centuries to achieve many objectives.[1] It is the main process involved in perfume and dye extractions, but also the reprocessing of Rare Earth Elements for energy production and technology development,[2] the purification of plutonium for the making of atomic bombs,[3], the recycling of nuclear fuels,[4], and the separation and purification of strategic transition metal.[5]. This technique has also been shown by Rydberg to be extremely useful in the determination of metal-ligand stability constants.[6] Therefore, modern use has made this process an essential daily practice in many scientific laboratories. The main concept of solvent extraction is using the difference of solubility of an analyte (S) between two immiscible liquids to partition the solute between the two phases.

Figure 1-1. Schematic representation of solvent extraction, where a solute S is distributed between the upper (lighter) yellow phase and the lower (heavier) blue phase.
The distribution law, derived in 1898 by W. Nernst\textsuperscript{[7]}, relates the distribution of a solute between phase 1 and phase 2.

\[ S_{\text{phase } 1} \rightleftharpoons S_{\text{phase } 2} \quad (1.1) \]

The equilibrium constant for reaction (1.1), the Nernst distribution law, called the distribution constant (originally described in French: “coefficient de partage”), can be written as shown in equation (1.2).

\[ K_D = \frac{[S_{\text{phase } 2}]}{[S_{\text{phase } 1}]} \quad (1.2) \]

where the brackets denote the concentration of the solute. If \( K_D \) is greater than one, the solute will move from phase 1 to phase 2. Conversely, the solute will remain in phase 1 if the distribution constant is less than one.

The \( K_D \) is an interesting parameter for solvent extraction, it is applicable to describe the distribution of a molecular solute that can be stabilized in either phase by the action of solvation alone (Nernst law). The Nernst partitioning coefficient does not apply if the analyte needs a chemical reaction to be extracted. If a chemical reaction other than solvation is required, the primary parameter in solvent extraction is the distribution ratio \( D \), calculated by the ratio of the formal concentration of the analyte in the organic phase over the formal concentration of the same analyte in the aqueous phase.

\[ D = \frac{\sum[A]}{\sum[A]} \quad (1.3) \]
In 1976, Bale et al.[8] published a study on the equilibrium constants of partitioning of dibutyl phosphoric acid (HDBP). This molecule is an acidic organophosphorus extractant that can be present by itself in multiple species in each phase. In the organic phase it is present primarily as a dimer \((\text{HA})_2\), but also in smaller quantities as a monomer HA. In aqueous solution, it acts as a weak acid, and therefore is present as a protonated (HA) acid and its conjugate base \(A^-\). Therefore the only distribution constant for a HDBP describes the partitioning of the protonated monomer (a):

\[
K_D = \frac{[\text{HA}]}{[HA]} 
\tag{1.4}
\]

while the distribution ratio accounts for \((HA)_2, HA, \) and \(A^-\).

\[
D = \frac{\sum [\text{HA}]}{\sum [HA]} = \frac{[HA] + 2[(HA)_2]}{[HA] + [A^-]} \tag{1.5}
\]
The Nernst partitioning constants and the distribution ratio describing two different analytes can be significantly different depending on the experimental conditions. This difference can be exploited to separate two analytes. This process is called liquid-liquid separation (extraction) and is characterized by the separation factor (SF), which is defined by the equation (1.6)

\[ SF_{S1/S2} = \frac{K_{DS1}}{K_{DS2}} \]  

(1.6)

\[ SF_{S1/S2} = \frac{D_{S1}}{D_{S2}} \]  

(1.6)

It is also interesting to note that in more “practical” situations (such as in chemical engineering for characterizing separation schemes), solvent extraction can be characterized in percent extraction of a solute (also called the extraction factor):

\[ \%E = 100 \frac{D}{1 + D} \]  

(1.7)

1.1.2 Different Types of Solvent Extraction of Metal Cations

During the early years of the solvent extraction sciences, SX was mostly used by organic chemists for separating organic substances. Since in those extraction the solute often exists under the same molecular (or supramolecular) form, the system is often referred to as non-electrolyte reaction (NE), also called nonreactive extraction. Later it was discovered that many organic weak acids (or
bases) could complex a targeted ion in an aqueous phase, to form a complex soluble in an organic phase.

\[ S^{+/-} + A^{-/+} \rightleftharpoons SA \]  

(1.8)

where S represents the targeted ionic solute in the aqueous phase, A the organic ligand, SA the complex and the bar on the top of the complex specifies that the complex is solvated in the organic phase. This is an example of an *ion pairing extraction*. The reagent responsible for forming the extractable (solvable) complex is termed the *extractant*.

1.1.2.1 *Solvent Extraction by Solvating Agent*

Here the SX by Solvating Agent (SXSA) is in particular the one described as *extraction of metal complex as adducts* in *Solvent Extraction, Principle and Practice*. Solvent extraction by a solvating agent is the extraction process in which a neutral extractant is extracting a neutral species. If the neutral extractant is coordinatively unsaturated, it forms a \( \text{MA}_x(\text{H}_2\text{O})_k \) hydrated species. If the ligand A is not an extractant, this hydrated species does not partition into the organic phase. However, if the aqueous molecules are replaced by organic neutral molecules, the lipophilicity of the adduct will drastically increase (proportionally to the number of coordinated organic extractant) until saturation.

\[ M^{z+} + zA^- + b\overline{B} \rightleftharpoons \text{MA}_x\cdot \overline{bB} \]  

(1.9)
Figure 1-3. Solvating extractant extraction process, where M represent a metal cation, A represent an anion, B a solvating extractant

For this SX process to be optimal, the coordination number of the cation must be equal to \( n_z + x \), where \( n \) is equal to the denticity of A, \( z \) the number of A needed to neutralize M, and \( x \) the number of water molecules coordinating the \( M_{A_z} \) complex. In SXSA processes, several type of adducts can exist, for example, A can be either an inorganic anionic salt (ClO\(_4\)-, F\(-\), NO\(_3\)-, etc.), or an organic anionic neutralizer (DBP, COONa, etc), or even a metallic weak acid, (TcO\(_4\)-). It is also possible that \( B \) is the protonated neutral variant of A of the same molecule (self adducts).

Examples of metal ion SXSA:

Example 2: Cation extraction: extraction equilibrium of CsNO\(_3\) by calixarene extractant\[^{[11]}\]:

\[
\text{Cs}^+ + \text{NO}_3^- + \text{Clx} \rightleftharpoons \text{CsNO}_3 \cdot \text{Clx} \quad (1.10)
\]

Here the metal ion is cesium cation (Cs\(^+\)), neutralized by a nitrate anion (NO\(_3\)^-) and extracted by the solvating agent Calix[4]arene-bis(t-Octylbenzo-Crown-6) in 1,2-Dichloroethane (Clx)
Example 3: Anion extraction: extraction equilibrium of perrhenic acid by tri alkyl amine$^{[12]}$:

$$\text{ReO}_4^- + H^+ + \text{TiOA} \rightleftharpoons \text{HReO}_4 \cdot \text{TiOA} \quad (1.11)$$

Here the metal ion is the perrhenate anion (ReO$_4^-$), neutralized by a proton (H$^+$) and extracted by the solvating agent tri-isooctyl amine (TiOA).

1.1.2.2 Solvent Extraction by Ion Exchange

The method of SX by Ion eXchange process (SXIX) is in particular the method described as *extraction of coordinatively saturated metal chelate type complex* in Solvent Extraction, Principle and Practice.$^{[9]}$ This SX process uses organic/lipophilic weak Brönsted acids as extractants. The organic acid ligands are able to complex a metal ion through multiple binding sites of basic atoms (such as O, N, S) to form a metal chelate. This type of chelation provides, to the metal complex, an extra stability in the organic phase. In the extraction reaction, an equivalent number of hydrogen ions to the cationic charge are exchanged to the aqueous phase simultaneously with cation transfer to the organic phase to maintain electroneutrality in both phases:

$$M^{+z} + z\text{HA} \rightleftharpoons M\text{A}_z + z\text{H}^+ \quad (1.12)$$
In order to describe more precisely SEIX, it is not unusual to describe the extraction process through a stepwise reaction with the deprotonated anion A\(^-\) added until the coordination sphere of the metal being mostly (or completely) saturated with the extractant (water could be also present in the coordination sphere, depending on the denticity and the concentration of the extractant). When the number of extractants are sufficient for the metal chelate to become hydrophobic, the complex can partition between the phases.

![Diagram](image)

**Figure 1-5.** Solvent Extraction by ion exchange process, where M represent a metal cation, HA represent a weak acid organic extractant, and A its aqueous conjugate base

It is relevant to note that chelated multidentate acidic extractants can also create adducts with free ligand in the organic phase, creating self adduct system similar to the one described at the end of the SXSA paragraphs (section 1.1.2.1). Also, the same metal chelate can react with another metal chelate present in the organic phase if their concentrations are large enough, creating heavy organic polynuclear species.
Example 4: Extraction of Al(III) by TTA$^{[13]}$

Acetylacetone, representative of the class of extractants known as β-diketones, can coordinate in multiple ways to the metal atom. For the extraction by ion exchange, it must complex through a dissociated anionic enol form. In those condition (and those condition only can it act as a weak acid extractant).

$$\text{Al}^{3+} + 3\text{HTTA} \rightleftharpoons \text{Al(TTA)}_3 + 3\text{H}^+ \quad (1.13)$$

Here the metal extracted is trivalent aluminum ($\text{Al}^{3+}$) extracted by three anionic TTA$. It is important to note that for this extraction, the pH is a factor in determining the position of the equilibrium.

![Structure of the acetyl acetone derivative thenoyltrifluoroacetone (HTTA)](image)

**Figure** 1-6. Structure of the acetyl acetone derivative thenoyltrifluoroacetone (HTTA)

1.2 Calculation of Equilibrium Constants

The previous section presented chemical equilibria that describe the extraction of metals from an aqueous phase into an organic phase. However to fully understand solvent extraction processes, the identification of the species extracted and the determination of biphasic equilibrium constants are critical (and generally strongly correlated). The creation of models can provide a rational
understanding of the chemical principles of solvent extraction to determine those equilibrium constants.

Two of major methods of determination of critical stability constants are the *Ligand Number Method* and *Graphic Slope Analysis*, both usually referred to as *slope analysis*.

1.2.1 Ligand Number Method (LNM)

In 1941, Bjerrum developed the LNM method to identify the average composition of the metal species in the system\(^{[14]}\). This method considers the extraction of MA\(_n\) into the organic phase and assumes that the metal exists as one species, MA\(_n\), in the aqueous phase. Taking the derivative the logarithm of the distribution of the metal between each phase versus the logarithm of the formal concentration of extractant in the system the following equation (1.14) is obtained\(^{[15]}\):

\[
\frac{\partial \log D}{\partial \log [A]}|_{[M][H][X][S]} = m \cdot n_{org} - m \cdot n_{aq}
\]  \( (1.14) \)

Where \( m \cdot n_{org} \) and \( m \cdot n_{aq} \) are the metal:ligand ratio in the respective phases. The subscript indicates other parameters that are held constant. \([M], [H], [X], [S]\), refer respectively to the metal, hydrogen ion, background electrolyte, and diluent. While it is commonly assumed that the number of ligands per central atom is a whole number (indicating a fixed stoichiometry), in 1941 Bjerrum presented the concept of *average ligand number*, defined as the mean number of ligands per central atom\(^{[14]}\).

\[
\bar{n}_{org} = \frac{\sum n_{[MA_n]}}{[M]}
\]  \( (1.15) \)
It has been also be shown that the $n$ can be substituted by $\bar{n}$ in equation (1.16) so it can be redefined as\cite{9,15}:

$$
\left. \frac{\partial \log D}{\partial \log [A]} \right|_{[M][H][X][S]} = \bar{n}_{org} - \bar{n}_{aq}
$$

(1.16)

Similarly, equation (1.17) defines the average metal number per complex:

$$
\left. \frac{\partial \log D}{\partial \log [M]} \right|_{[A][H][X][S]} = \bar{m}_{org} - \bar{m}_{aq}
$$

(1.17)

and equation (1.18) defines the average number of hydrogen ions per metal complex:

$$
\left. \frac{\partial \log D}{\partial \log [H]} \right|_{[A][M][X][S]} = \bar{h}_{org} - \bar{h}_{aq}
$$

(1.18)

In the case of the extraction of a metal cation by a weak acid (e.g. Example 4: Extraction of Al(III) by TTA\cite{13}), equation (1.18) will give a negative result, indicating the number of protons needed to exchange to achieve a charge balance between the extracted metal and the weak acid to extract a neutral species\cite{15}.

1.2.2 Graphic Slope Analysis:

The graphic slope analysis (GSA) method is the most common analytical plot used to characterize a solvent extraction system. If used correctly it can give multiple types of critical information on an extraction system, such as the average ligand number and the coefficient of extraction.
For a rational application of the GSA, it is important to measure the distribution ratio of the analyte with one variable component with the concentration of all other components of the system being kept constant. By this method, the solvent extraction equation can be expressed into a polynomial of type:

\[ y = a_0 + \sum a_i x^i \]  

(1.19)

where \( y \) is a function of the distribution ratio of the analyte and \( x \) is a function of the variable for the graphic analysis.

**Example 5: Utilization of a GSA in a system humic and fulvic acids with Th(IV)\textsuperscript{[16]}**

In a study probing the interaction of humic and fulvic acids with Th(IV) using solvent extraction by HDEHP, Nash and Choppin characterized their system with GSA using a second order polynomial:

\[ \frac{D}{D_0} - 1 = a\beta_x(Z) + b^2\beta_y(Z)^2 \]  

(1.20)

with \( y \) being the ratio of \( D \) over \( D_0 \) minus 1, \( D_0 \) being the distribution ratio of thorium in absence of aqueous carboxylate, \( a \) and \( b \) fitting parameters, \( \beta_x \) and \( \beta_y \) respectively the researched stability constants for 1:1 binding site and a 1:2 binding site, and \( Z \) the total carboxylate binding sites.
However, when the expression can be expressed in a simple linear plot where $i=1$, 
$(y = a_0 + a_1 \cdot x)$ from the plot of $y$ vs. $x$ the intercept on the $x$ axis yields the $a_0$ parameter and the
slope yields the $a_1$ parameter. This treatment method can be referred as the \textit{limiting value method}.
However, in a more general case, this method also called \textit{linear slope graphic analysis}.\cite{1}

\textbf{Example 6: Simple linear slope graphic analysis: extraction of Cu(II) by TTA} \cite{9, 17}

In the Figure 1-7, Liljenzin \textit{et al.} used acetylacetonate to extract divalent copper from 1
mol.L$^{-1}$ perchlorate media as function of pH and free extractant. The following equilibrium
is the accepted solvent extraction mechanism which is based on the charge balance and the
coordination of Cu(II):

$$\text{Cu}^{2+} + 2 \text{HTTA} \rightleftharpoons \text{Cu(TTA)}_2 + 2 \text{H}^+$$ (1.21)

However, in the case an investigative study of this mechanism the previous equilibrium
need to be demonstrated. Here the oxidation state is unknown:

$$\text{Cu}^{n+} + n \text{HTTA} \rightleftharpoons \text{Cu(TTA)}_n + n \text{H}^+$$ (1.22)

To solve for this equilibrium, it is assumed that TTA cannot self-adduct (create an oligomer
composed exclusively of multiple molecules of TTA) based on the stereochemistry of
Cu(II), the coordinative atoms (O, O\textsubscript{2}), the number of acidic group (1) and the chelate ring
size (6, Cu-O-C=C-C=O::Cu). In \textbf{Figure 1-7} the logarithm of the distribution ratio of
copper ($D_{Cu}$) has been plotted versus the pH at equilibrium at constant [HTTA] (large plot)
and, in the insert plot, the logarithm of the free ligand at constant pH. In \textbf{Figure 1-7}, it can
be seen that log $D_{Cu}$ is a function of pH at constant F$[^{[HA]}$, while at constant $pH$ the log $D_{Cu}$
depends only on $F_{[HA]}$. Here the notation $F_{[HA]}$ is used, since free TTA is distributed between the organic phase and the aqueous phase. It is evident that the distribution curve approaches two asymptotes, one horizontal (zero slope) and one different from 0 (in the low $pH$ and the high $-\log [A]$ range). In the case of a linear slope analysis, the non-zero asymptote is the most relevant, because it gives crucial information on the stoichiometry of the extraction process.

**Figure 1-7.** Extraction of Cu(II) from 1 mol.L$^{-1}$ NaClO$_4$ into benzene as a function of pH (large figure) and of free acetylacetonate ion concentration (insert) at several formal concentrations of acetylacetone. *Figure from ref [17]*

Using equation (1.18), the asymptote at the low pH on the dependency (regardless of the $F_{[HA]}$), the number of protons exchanged for the extraction is determined to be 2, and using the equation (1.16) on the ligand dependence the number of chelating ligands is determined to also be 2. Using equilibrium (1.22) and those two parameters the equilibrium (1.21) can be determined.
Then using this equilibrium the following extraction equilibrium can be determined.

\[
K_{ex} = \frac{[Cu(TTA)_2][H^+]^2}{[Cu][HTTA]^2}
\]

(1.23)

Using equation (1.3) to simplify the equation (1.23) the following equation can be determined:

\[
K_{ex} = D_{Cu} \frac{[H^+]^2}{[HTTA]^2}
\]

(1.24)

1.3 Analytical Determination of Distribution Ratios.

In the previous section, the role of the distribution ratio of the analyte has been shown to be crucial for the determination of the coefficient of extraction \(K_{ex}\). Today a large number of methods of measuring distribution coefficients has been developed, and this number is more likely going to increase over time (based on the creativity of the solvent extraction community). In addition, even if there are multiple distribution ratio determination methods, there are some that are most commonly used.

1.3.1 Spectrophotometric Determinations

Spectrophotometric determination of distribution ratios is a commonly used method. Spectrophotometric determination of concentration (and thereby distribution ratios) has the main advantage of being readily accessible and generally accepted. Unfortunately, only a few analytes are capable of absorbing light in the UV-Vis region, with a large enough coefficient of extinction. For that reason a number of the spectrophotometric methods use a color forming reagent, such as
Azo dyes, using an azo link between two aromatic rings possessing an o-hydroxy group. The most commonly used dye is Arsenazo III, which offers a high sensitivity for the majority of transition metals and f-elements.

Figure 1-8. Picture of a solution of Arsenazo III in absence of metal (left) and the same solution in presence of Eu(NO)₃

Proper calibration methods allow for the creation of equation (1.25).

\[ I = I_0 + m[S]_{standard} \]  

where \( I_0 \) and \( m \) are calibration parameters determined in one specific medium. If the concentration of analyte is directly measurable, the distribution ratio can be determined using equation (1.26):

\[ D = \frac{[S]}{[S]} = \frac{(I - I_0)}{m} \times \frac{m}{(I - I_0)} \]  

The main disadvantage of equation (1.26) for the spectrophotometric determinations of D is that to obtain the organic calibration parameters, calibration standard, for the diluent used, must be
available and generally accepted. A common solution to this problem could be to strip the analyte from the organic phase to an aqueous phase (back extraction), and then to analyze it. This method only works if it is possible to establish a complete back extraction of the analyte, including possible dilution effects. If such standard and back extractions are too complicated, a simpler method is possible based on assuming mass balance. Providing that no third phase is created during the extraction process, the following equation is true:

$$[S]_{eq} = [S]_{initial} - [S]_{eq}$$  \hspace{1cm} (1.27)

where $[S]_{eq}$ and $[S]_{eq}$ are respectively the concentration of analyte in the organic and aqueous phase at equilibrium, and $[S]_{initial}$ the concentration of analyte in the aqueous phase before extraction. Equation (1.27) can be used to define the distribution ratio, $D$ as follows,

$$D = \frac{[S]_{initial} - [S]_{eq}}{[S]_{eq}}$$  \hspace{1cm} (1.28)

or, as written in terms of absorption intensity:

$$D = \frac{I_{initial} - I_{eq}}{I_{eq}}$$  \hspace{1cm} (1.29)

This expression is independent of any calibration as long as the intensity of the signal is above the limit of detection and below the saturation.
1.3.2 Flame, Inductively Coupled Plasma, Spectroscopy

These techniques are atomic spectroscopy, which means that the analyte is atomized by combustion with a flame or a plasma. Due to the atomization process (all molecular species are decomposed into atoms, and sometimes a change also in the oxidation state). Atomic spectrophotometry is particularly used for the determination of metal concentration. In principle, these techniques are extremely similar to the spectrophotometric determination for the determination of D, permitting the utilization of the equation (1.29) in most of the cases, although some research groups decide to calibrate their system for the analyte and to use equation (1.26).

1.3.3 Mass Spectrometry

Regardless of the ionization and mass measurement process, mass spectrometry (MS) is a relatively versatile analytical method. It has long been used to measure isotopes, decipher organic structures, and even determine microorganism identification. For SX of metal chelates, the most common utilization is the measure the mass of ions using coupled ICP-MS. The utilization of a high resolution MS adds the option to take into account the isotopic ratio of the cations studied. For example, silver possesses two naturally occurring isotopes with a difference of isotopic masses of 2 Da. If the resolution of the MS is not high enough, one of the isotope of silver could be easily confounded with another element. If the instrument is used to its best potential, ICP-MS enables simultaneous study of a large number of metal distribution ratios in a single experiment. The determination of D for MS is usually done using equation (1.29).
1.3.4 Radiometric Analysis

1.3.4.1 The Use of Radioactivity

The radiometric determination of a distribution ratio is most likely the most common method used by radiochemists around the world. This method uses the proportionality between the concentration of radioactive analyte (RA) and the radioactivity of the solution – equation (1.30).

\[
[RA] \propto \frac{R}{V} \tag{1.30}
\]

where \( R \) is the radioactivity in Bq of the analyte, and \( V \) the volume of solution. Knowing the equation (1.30), and analyzing equal volume samples of each phase, the following equation is true:

\[
D = \frac{[RA]}{[RA]} = \frac{\bar{R}}{\bar{R}} \tag{1.31}
\]

One challenge in the utilization of the radiometric method is the choice of the appropriate detection method. The easiest method is the detection of gamma rays (if gamma rays are emitted). With the assumption that the difference in the linear energy absorption of gamma ray is negligible between an organic phase and an aqueous phase, the following equation can be used:

\[
D = \frac{\bar{A}}{\bar{A}} \tag{1.32}
\]

where \( A \) is the measured signal of a gamma ray of a specific energy per aliquot of phase (in Bq/mL). The utilization of high-resolution gamma spectrometers allow the analysis of a large number of gamma emitter at the same time - Figure 1-9.
For the analyses of beta emitters, a direct measure of the $A$ is not always possible, due to the fast loss of energy of a beta particle. To simplify the measurement of beta activity, the analyte can be diluted into a scintillation liquid, converting the energy of the beta decay into light.

Unfortunately, this process does not work for all systems, such as when the radioactive analyte is solvated in aromatic and chlorinated diluents, where the signal is strongly quenched by the diluent. To counter this effect, equation (1.29) can be used to measure the distribution ratio.

1.3.4.2 Neutron Activation Analysis

Neutron Activation Analysis (NNA) is one of the most commonly used method by radiochemists. This is a nuclear process used for determining the concentrations of elements in a vast amount of materials. NAA allows discrete sampling of elements as it disregards the chemical form of a
sample, and focuses solely on its nucleus. The method is based on neutron activation and therefore requires a source of neutrons.

The main difficulty of NAA is access to a neutron reactor, and the useful neutron cross section of analyte.

1.4 Research Focus

1.4.1 The Acidic Organophosphorus Extractant HEH[EHP]

Solvent extraction has generally been the method of choice for the purification of metals, regardless of their utilization, from transition metals (such as copper\textsuperscript{[18]}, cobalt, nickel\textsuperscript{[19]}, etc), rare earth elements\textsuperscript{[2],[20]}, even hazardous metal such as actinides and other radioactive materials\textsuperscript{[21],[22]}.

As stated previously in section 1.1.1, solvent extractions / separations are based on the difference in solubility of chemical species dissolved in each phase of a biphasic (liquid-liquid) system. However, metal electrolytes (ions) are not soluble by themselves in a non-aqueous phase due to the poor solvating ability of the organic solvent for charged species. Therefore, they cannot be extracted without the help of lipophilic complexing agent called an extractant. IUPAC describes the extractant as the \textit{active component(s) primarily responsible for transfer of a solute from one phase to the other}\textsuperscript{[23]}.

Most modern extractants are amphiphilic molecules, due to their increased extraction efficiency\textsuperscript{[24]}. However extractants that can distribute between each phase are still frequently used.

The variety of extractants commercially available is extremely large, and a significant portion of them are used for the purification of metallic cations. The \textit{organophosphorus extractant} family is one of the major families of extractants used in research and at industrial scale.
Organophosphorus compounds, both acid and neutral, provide a versatile range of solvent extraction, either as a primary extractant or as a synergetic agent. In the 1950s, it was recognized that the radiolysis/hydrolysis products of tributyl phosphate (TBP) mono and dibutyl phosphoric acids were very effective extractant for the hexavalent uranium.\[25\]

![Structures of tributyl phosphate (a) dibutyl phosphoric acid (b) and monobutyl phosphoric acid (c)](image)

**Figure 1-10.** Structures of tributyl phosphate (a) dibutyl phosphoric acid (b) and monobutyl phosphoric acid (c)

\[
\text{(RO)}_3\text{PO} + n\text{H}^+ \xrightarrow{\text{radiolysis/hydrolysis}} (\text{RO})_{3-n}\text{PO(OH)}_n + n\text{R}^+ \tag{1.33}
\]

\[
\text{UO}_2^{2+} + 2(\text{RO})_2\text{PO(OH)} \rightleftharpoons \text{UO}_2((\text{O})\text{OP(OR)}_2)_2 + 2\text{H}^+ \tag{1.34}
\]

Acidic organophosphorus extractants extract metals by cation exchange (see section 1.1.2.2, page 7) of enough acidic hydrogen ions of the extractant(s) to allow the extraction of an electroneutral complex of the metal ion. Unlike the large majority of the other acidic extractants, which do not associate molecularly in non-polar media, acidic organophosphorus extractants have a strong tendency toward association into dimer in the non-polar organic phase. Also it is common for the metal extractant complex MA\(_2\) to get solvated by one or more additional extractant molecule HA
(degree of solvation), MA_2(HA)_y. The nomenclature of the acidic organophosphorus extractant can be extremely confusing between sources. Without attempting to favor any of them,

Table 1-1 is a non-exhaustive list of the most common acidic organophosphorus compounds.

<table>
<thead>
<tr>
<th>Name</th>
<th>Schematic representation</th>
<th>Linear representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>di-alkyl phosphoric acid</td>
<td><img src="image" alt="di-alkyl phosphoric acid" /></td>
<td>(RO)_2PO(OH)</td>
</tr>
<tr>
<td>Alkyl (alkyl) phosphonic acid</td>
<td><img src="image" alt="Alkyl (alkyl) phosphonic acid" /></td>
<td>(RO)(R)PO(OH)</td>
</tr>
<tr>
<td>di-alkyl phosphinic acid</td>
<td><img src="image" alt="di-alkyl phosphinic acid" /></td>
<td>(R)_2PO(OH)</td>
</tr>
<tr>
<td>Mono-alkyl phosphoric acid</td>
<td><img src="image" alt="Mono-alkyl phosphoric acid" /></td>
<td>(RO)PO(OH)_2</td>
</tr>
<tr>
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<td>(R)PO(OH)_2</td>
</tr>
</tbody>
</table>

Over the last 70 years these acidic organophosphorus extractants have been intensively studied, with different phosphorus groups, alkyl chains\(^{[26]}\) (symmetric and asymmetric), salting conditions, extracted cation, etc.\(^{[27],[28]}\) In the last 60 years, the TALSPEAK process ((Trivalent Actinide Lanthanide Separation by Phosphorus reagent Extraction from Aqueous Komplexes), developed in the 60’s at Oak Ridge National Laboratory\(^{[29]}\), has been heavily studied and improved with the objective of separating trivalent actinides from the trivalent lanthanides. This process is based on the partitioning of lanthanides and actinides between an di-alkyl phosphoric acid, HDEHP (bis-2-ethyl(hexyl) phosphoric acid - Figure 1-11a) solution and an aqueous phase containing a
polyaminopolycarboxylate complexant. The latter reagent is principally responsible for holding back the trivalent actinides, allowing the selective transfer of the lanthanides into the organic phase.\textsuperscript{30}-\textsuperscript{33} In the last decade, an advanced TALSPEAK process has been suggested, proposing to replace HDEHP with a less acidic but structurally analogous extractant alkyl(alkyl)phosphonic acid HEH[EHP] (2-ethyl(hexyl)phosphoric acid mono-2-ethyl(hexyl) ester - \textbf{Figure 1-11b})\textsuperscript{34}. Different arguments on the use of HEH[EHP] vs. HDEHP have been made, focusing on the \textit{green chemistry} aspect of the use of less acidic extractant.\textsuperscript{35}

\begin{figure}[h]
\centering
\includegraphics[width=0.6\textwidth]{figure11.png}
\caption{Chemical structure of (a) Bis-2-ethyl(hexyl) phosphoric acid (HDEHP) and (b) 2-Ethyl(hexyl)phosphoric acid mono-2-ethyl(hexyl) ester. pKa values from ref \textsuperscript{35}}
\end{figure}

The use of HEH[EHP] in SX system allow for work in less acidic conditions allowing the use of other buffer and aqueous complexants and increasing the predictability of SX processes. While a reasonable amount of information on the \textit{aqueous chemistry} exists of SX using HEH[EHP], very little is known about the organic phase. This is mostly due to a number of options of user friendly
analytical methods and techniques able to probe molecular interactions in this phase. Furthermore, even less information is available on the role of the diluent in the SX process using HEH[EHP].

The generally accepted equilibrium of SX of metal cation by HEH[EHP] is described as follows:

\[ M^{n+} + n(HA)_2 \rightleftharpoons M(AHA)_n + nH^+ \]  \hspace{1cm} (1.35)

with the following extraction equilibrium constant

\[ K_{ex} = \frac{[M(AHA)_n][H^+]^n}{[M^{n+}][(HA)_2]^n} \]  \hspace{1cm} (1.36)

Using equation (1.3), equation (1.36) can be simplified to:

\[ K_{ex} = D \left( \frac{[H^+]}{[(HA)_2]} \right)^n \]  \hspace{1cm} (1.37)

**Figure 1-12.** Accepted schematic diagram of equilibria in extraction of cation (M) by HEH[EHP] (HA) based on literature equilibria
Following this mechanism, and accepting that HEH[EHP] complexes with metal cation as described in the literature\textsuperscript{[9],[34],[2]} - Figure 1-13 – the metal chelate is formed through two basic atoms O\(^-\) and \(\ddot{O}\_)\(\ddot{O}\_), with a ring size of 7 atoms, metal excluded (M-O=P=O--H-O=P=O--M).

\[ \text{Figure 1-13. Accepted structure of the metal chelate formed between a metal cation of charge } n \text{ and } n \text{ dimers ref [9]- appendix D} \]

However, it should be emphasized, that it has been demonstrated that for similar mono acidic organophosphorus extractant (such has di-butyl phosphate and di-octyl phosphate, etc), the \( K_{ex} \), the average ligand number (also called degree of polymerization, degree of solvation, average stoichiometry, etc), and the degree of dimerization of the free extractant are sensitive to various experimental parameters\textsuperscript{[27],[28],[36]}:

- Organic diluent,
- pH of the aqueous solution,
- Ionic strength of the aqueous solution,
- Background electrolyte used,
- Extractant used,
- Cation extracted,
- Etc.
In the past, it has been hypothesized that the main reason for the deviation from the ideal behavior (Figure 1-13) lies in the particular state of solvation of these extractants (are they completely solvated, dimerized, polymerized, complexed, etc.).\textsuperscript{[10]}

For the purpose of the presented work, the focus is going to be extended to the effect of the organic diluent on the solvent extraction process of trivalent $f$-elements by HEH[EHP] and HDEHP.

1.4.2 The Diluent effect

The alchemist’s research for a “Menstruum universal” (universal solvent) indicates the importance given to the diluent and the process of solubility in a larger scheme, with the development of the popular “Similia Similibus Solvuntur” (similar solubilizes similars). Diluents are liquids, under the conditions of this application, in which other substance can be solvated (hydrated if the diluent is water). In the case of SX, the diluent refers exclusively the non-aqueous phase (organic or ionic liquid).

As stated in section 1.4.2, the SX process can be strongly impacted by the diluent itself. Regarding understanding of the SX processes, the development of our knowledge on the diluent effect reflects, to some extent, to development of the solvent extraction chemistry itself.

A large variety of liquids (condensed fluids) can be used in solvent extraction. They are usually divided, in the context of SX, into different classes\textsuperscript{[37]}:

- **Class 1:** Liquids capable of forming three-dimensional networks of strong hydrogen bonds.
  
  Eg. Water, poly and amino alcohol, hydroxyl-acids etc.
• **Class 2:** Liquids with both active hydrogen atoms and donor atoms (oxygen, nitrogen, and fluorine) but that cannot create a three dimensional network. They are generally called protic and protogenic substances.

  Eg. Primary alcohols, carboxylic acids, primary and secondary amines, nitro compound with α-positioned hydrogen atoms, condensed ammonia etc.

• **Class 3:** Liquids containing donor atoms without hydrogen donor atoms. They are generally called dipolar aprotic substance.

  Eg. Ether, ketone, aldehydes, esters, ternary amines, nitro compounds without α-hydrogen, phosphoryl group containing solvent etc.

• **Class 4:** Liquids composed of molecules containing active hydrogen atoms, but no donor atoms.

  e.g. Chloroform, dichloromethane, etc.

• **Class 5:** Liquids with no hydrogen-bond forming capability and no donor atoms. This class can be also subdivided into two sub category

  o **Class 5.1:** Aliphatic liquids. They are in general open chains (linear or branched) hydrocarbons, but can also possess one or multiple non-aromatic cycles.

    e.g. Ethenes, paraffins, etc.

  o **Class 5.2:** Aromatic liquids: they are in general liquid that verify the Hückel’s rule of aromaticity.

    e.g. Class 5’s benzene derivatives
In solvent extraction, only classes 3 to 5 are used as diluent, since they are generally insoluble in aqueous media. The classes 4 and 5 do not solvate any salt without the help of extractants, however it has been shown that class 3 can also act as an extractant by itself, without the need of additional extractants.

Other varieties of classification of diluents has been described in the literature, but the previously described have been found the most relevant to this work. Some other ones are commonly used and cited below, and will be used later in this work. The Reichardt 2003 solvent classification scheme\cite{38} (Table 1-2) is mostly based on the structure of the diluent.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>i  Non-polar</td>
<td>Hexane, tetra chloromethane, cyclohexane</td>
</tr>
<tr>
<td>ii low polarity</td>
<td>Toluene, chloroform</td>
</tr>
<tr>
<td>iii Aprotic dipolar</td>
<td>Acetone, ketones, octanal</td>
</tr>
<tr>
<td>iv Protic and protogenic</td>
<td>Ethanol, octanol, nitro-alkals</td>
</tr>
<tr>
<td>v  Basic</td>
<td>Pyridine, polyaminoethane</td>
</tr>
<tr>
<td>vi Acidic</td>
<td>3-methylphenol, butanoic acid</td>
</tr>
</tbody>
</table>

The classification of Kolthoff\cite{39} and Reichardt\cite{38} is according to the polarity (described by the physical bulk properties of the diluent as media, the dielectric constant $\varepsilon$ and the dipole moment $\mu$) but also the hydrogen bond donation ability $E_r^N$ (Table 1-3).
### Table 1-3. Kolthoff and Reichardt solvent classification scheme

<table>
<thead>
<tr>
<th>Designation</th>
<th>$\varepsilon$</th>
<th>$\mu$</th>
<th>$E_{t}^{N}$</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>i Apolar aprotic</td>
<td>&lt;15</td>
<td>&lt;8.3</td>
<td>0.0-0.3</td>
<td>$n$-octane, bromo-octane, etc.</td>
</tr>
<tr>
<td>ii Weakly polar aprotic</td>
<td>&lt;15</td>
<td>&lt;9.3</td>
<td>0.0-0.3</td>
<td>Ethers, esters, etc.</td>
</tr>
<tr>
<td>iii Dipolar aprotic</td>
<td>&gt;15</td>
<td>8.3</td>
<td>0.3-0.5</td>
<td>Ketone, nitro, sulfoxide, etc.</td>
</tr>
<tr>
<td>iv protic</td>
<td></td>
<td></td>
<td>0.5-1.0</td>
<td>Water, alcohol, acids, etc.</td>
</tr>
</tbody>
</table>

The last one, the Chastrette classification\cite{40}, stresses the hydrogen bonding and electron pair donation abilities, polarity and the self-association.

### Table 1-4. Chastrette solvent classification scheme

<table>
<thead>
<tr>
<th>Solvent class</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>i Apolar, aprotic</td>
<td>$n$-octane, carbone tetra halide</td>
</tr>
<tr>
<td>ii Apolar, aprotic, electron pair donors</td>
<td>Amines, ether</td>
</tr>
<tr>
<td>iii Slightly polar, aprotic, aromatic</td>
<td>Halogeno-benzenes</td>
</tr>
<tr>
<td>iv Apolar, aprotic, aromatic</td>
<td>Benzene, substituted aromatic hydrocarbon</td>
</tr>
<tr>
<td>v Aprotic dipolar</td>
<td>Nitromethane, acetone, ketone</td>
</tr>
<tr>
<td>vi Highly polar aprotic</td>
<td>Dimethyl sulfoxide, nitrobenzene</td>
</tr>
<tr>
<td>vii Highly polar, polarizable aprotic</td>
<td>Hexamethyl phosphoamine, sulfolane</td>
</tr>
<tr>
<td>viii Hydrogen bonding</td>
<td>Alcohol, phenol.</td>
</tr>
<tr>
<td>ix Highly associated hydrogen bonding</td>
<td>Water, ethylene glycol</td>
</tr>
<tr>
<td>x miscellaneous</td>
<td>Chloroform, aniline,</td>
</tr>
</tbody>
</table>
1.4.2.1 Basic diluent properties: the intermolecular forces

The existence of these diluents as liquids at room temperature is the result of cohesive forces between molecules. The lowest cohesive force for a diluent (diluent class 5.1 and 5.2) is the London dispersion (also called dispersive force). The motions of the electrons in the atoms of the molecule induce a transient electric dipole in a neighboring molecule, which in turn strengthens the temporary dipole in the first molecule. This mutual interaction produces an attractive cohesive force. The class 5.1 and class 5.2 diluents are hold together in a condensed phase by such forces.

Polar liquids (characterized by the presence of at least one permanent dipole moment) can spontaneously “arrange” in a head to tail configuration, driven by a dipole-dipole interaction (the localized positive charge of one dipole orients toward the negative charge of the neighboring molecule). This association results in a larger attraction force than the London dispersion. The energy associated with this force is proportional to the product of the dipole moment of the molecule and inversely proportional to the sixth power of the mean distance between them.
Finally, some liquids that are used in solvent extraction interact through intermolecular hydrogen bond. Such molecules have a hydrogen atom attached to a very electronegative atom (F, O, N). Those atoms are able to attract an hydrogen atom from a neighboring molecule, forming an rigid hydrogen bridge. This is the strongest bond existing in the liquid state.

The three forces described above collectively as the cohesive force. They are the forces that keep the molecules of liquid together and are ultimately responsible for a large majority of chemical properties of liquids.

One method commonly used to characterize the cohesive nature of a liquid is by measuring the heat of vaporization of the liquid, $\Delta_v H$. Using $\Delta_v H$ in the equation (1.38) the parameter $\delta^2$ can be calculated. This parameter is called the cohesive energy density.\(^{[41]}\)

$$\delta^2 = \frac{\Delta_v H - RT}{V} \quad (1.38)$$

where $R$ is the gas constant, $T$ is the absolute temperature, $V$ the molar volume. This parameter (Hildebrand or Hildebrand-Scott parameter) is called the cohesive energy density\(^{[41]}\), and can also
be found in the literature as $\Delta U/V$ instead of $\delta^2$, enacing the mechanical side of the process ($\Delta U$ being the work needed to create an empty space in the fluid).

1.4.3 Indication of Diluent Effect in Solvent Extraction

1.4.3.1 Water extraction

As described in section 1.1.1 solvent extraction described the process of selective partitioning of solute between two phases. All liquids have some measurable degree of mutual miscibility – “Ideal” solvent extraction behavior is best represented by systems that exhibit limited miscibility of aqueous/organic phases. Globally, it is largely accepted that each organic diluent does not solubilize the same amount of water, as described in Table 1-5. The log P factor is a parameter used in biochemistry to describe the partition constant of a solvent as an analyte (solute, $s$ in equation (1.39)), at infinite dilution between $1$-octanol and water.$^{[42]}$

$$P = \lim_{[s]_{tot} \to 0} D = \frac{[s]}{[s]}$$ (1.39)

<table>
<thead>
<tr>
<th>Diluent</th>
<th>In water$^{[43]}$</th>
<th>Water in$^{[43]}$</th>
<th>log P</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-octane</td>
<td>$1.04 \cdot 10^{-9}$</td>
<td>$6.02 \cdot 10^{-4}$</td>
<td>5.18</td>
</tr>
<tr>
<td>$n$-dodecane</td>
<td>$3.9 \cdot 10^{-12}$</td>
<td>$6.1 \cdot 10^{-6}$</td>
<td>6.8</td>
</tr>
<tr>
<td>benzene</td>
<td>$4.13 \cdot 10^{-4}$</td>
<td>$2.75 \cdot 10^{-3}$</td>
<td>2.13</td>
</tr>
<tr>
<td>toluene</td>
<td>$1.01 \cdot 10^{-4}$</td>
<td>$1.71 \cdot 10^{-3}$</td>
<td>2.69</td>
</tr>
<tr>
<td>$n$-butanol</td>
<td>$2.6 \cdot 10^{-2}$</td>
<td>$5.15 \cdot 10^{-1}$</td>
<td>0.75</td>
</tr>
<tr>
<td>$n$-octanol</td>
<td>$4.4 \cdot 10^{-5}$</td>
<td>$2.75 \cdot 10^{-1}$</td>
<td>3.15</td>
</tr>
<tr>
<td>Methyl-$i$-butyl ketone (MIBK)</td>
<td>$3.10 \cdot 10^{-3}$</td>
<td>$9.72 \cdot 10^{-2}$</td>
<td>1.31</td>
</tr>
<tr>
<td>chloroform</td>
<td>$1.24 \cdot 10^{-3}$</td>
<td>$6.1 \cdot 10^{-3}$</td>
<td>1.94</td>
</tr>
</tbody>
</table>
As a primitive analysis, it can be seen that the diluents “extract” more water following this order: alcoholic > MIBK > chloroform > aromatic > aliphatic-hydrocarbons. Comparing $n$-octane to $n$-dodecan it is apparent that increasing the length of the chain of the diluent decreases the solubility of water (similar observation can be made between $n$-butanol and $n$-octanol), and by functionalizing benzene with a methyl group (toluene) decrease the solubility of water.

There are other criteria that impact the choice of a diluent, beside its influence on the chemistry itself (shift of equilibria, change in stoichiometry, kinetics, etc.), and its miscibility with water. The physical properties are also a major concern (especially for large-scale utilization of SX); properties to be considered (depending on the projected application include properties like density, viscosity, volatility, flash point, resistance to degradation by contact with aqueous acid/base/redox active species or radiolysis. Further criteria for choice are also the cost, toxicity, chemical reaction hazard, etc.

**Example 7: practical examples of the importance of the choice of the diluent for SX based on physical properties**

**Density:** fluorobenzene is a diluent with a density that can be equal to aqueous solution (density of fluorobenzene$^{[42]}$ : 1.02 kg·L$^{-1}$, density of 0.5 mol.L$^{-1}$ nitrate ionic strength$^{[44]}$ : 1.03 kg·L$^{-1}$). This relatively close density makes the stable top/bottom positioning of the phases impossible (or at least more complicated) - **Figure 1-16**.

**Viscosity:** Tri-$n$-butyl phosphate can be used as a diluent, however is relatively high viscosity make the phase engagement (increasing of the surface by mechanically creating an emulsion) more difficult. This difficulty is one of the reasons why TBP is dissolved in kerosene for the PUREX process$^{[21]}$. 
Interfacial tension: in the system heptane/water in high concentration of sodium bis(2-ethylhexylsulfosuccinate) the interfacial tension can become significantly low\cite{45}. Because of that, after phase engagement, the two phases remain in intimate contact, in an emulsion system. In this system the disengaging of the phases requires extensive/extreme centrifugation to separate the phases.

![Figure 1-16. Schematic representation of observed water/diluent positioning for fluorobenzene used as a diluent (this work)](image)

1.4.3.2 Diluent effect on extraction of metal chelate

Several examples of the effect of the diluent on SX of metal chelate follow.

In the Example 6 page 13, the solvent extraction process of copper by TTA has been studied using slope analysis. Knowing the extraction equilibrium expression (1.23), $K_{ex}$ can be calculated. Sekine and Dyrssen\cite{46} and Allard et al.\cite{47} conducted the same study on the distribution constants of acetylacetones and various metal-acetylacetonate with different diluents.
**Table 1-6.** Partitioning ($K_d$) and extraction equilibrium ($K_{ex}$) constants involving HTTA, from 1 mol·L⁻¹ (Na-H)ClO₄ into various diluents.

<table>
<thead>
<tr>
<th>Diluent</th>
<th>log $K_d$ (TTA)</th>
<th>log $K_{ex}$ Zn(TTA)₂[^46]</th>
<th>log $K_{ex}$ Cu(TTA)₂[^46]</th>
<th>log $K_{ex}$ Np(TTA)₄[^47]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-hexane</td>
<td>-0.022</td>
<td>-1.57</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.013</td>
<td>-1.16</td>
<td>-0.04</td>
<td>0.8</td>
</tr>
<tr>
<td>Carbontetrachloride</td>
<td>0.52</td>
<td>-0.39</td>
<td>0.85</td>
<td>2.7</td>
</tr>
<tr>
<td>$1,3,5$-trimethylbenzene</td>
<td>0.44</td>
<td>-</td>
<td>0.43</td>
<td>-</td>
</tr>
<tr>
<td>Xylenes</td>
<td>0.57</td>
<td>-0.47</td>
<td>0.8</td>
<td>-</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.66</td>
<td>-0.37</td>
<td>0.85</td>
<td>-</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.77</td>
<td>-0.21</td>
<td>1.04</td>
<td>3.3</td>
</tr>
<tr>
<td>Dibutylether</td>
<td>-</td>
<td>-1.05</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MIKB</td>
<td>0.77</td>
<td>-0.15</td>
<td>0.61</td>
<td>-</td>
</tr>
<tr>
<td>Chloroform</td>
<td>1.38</td>
<td>0.83</td>
<td>2.54</td>
<td>-</td>
</tr>
<tr>
<td>Benzonitrile</td>
<td>-</td>
<td>0.21</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

| log $K_d$ vs. log $K_{ex}$ $R^2$ | - | 0.974 | 0.882 | 0.990 |

---

**Figure 1-17.** Graphic plot between the distribution ratio of the TTA and the coefficient of extraction of the metal chelate from
Table 1-6 and Figure 1-17 shows that if the distribution of the extractant TTA between an organic phase and an aqueous is strongly dependent of the diluent, the distribution of the metal chelate is strongly dependent as well. From this data it appears that the more soluble the extractant is in the diluent, more soluble the M(TTA)$_n$ chelate is in the same diluent. Also, it appears that the higher the ligand number, the higher the diluent effect will be. As a primitive analysis, we can observe that the mutual miscibility of the extractant and the diluent translates in general to more energetically efficient cation extraction. In this example, the diluent controls the efficiency of the extraction and the distribution of the extractant in the following this order:

chloroform > aromatic > MIBK > branched aromatic > carbon tetrachloride > non aromatic ring > aliphatic hydrocarbon

While it seem obvious that an increased $K_d$ would lead to a large $K_{ex}$ this is not always the case, as demonstrated by the acidic organophosphorus extractant family as discussed below.

In the 60’s Dyrsen et al.[48]–[50] intensively studied thermodynamic data of HDBP (in particular the distribution of HDBP, free and in a metal chelate). Some of there data have been corrected by Kolarik in his reviews on acidic organophosphorus extractants.[27],[28]

The results of extractions shown in Table 1-7 and plotted in Figure 1-18 shows the relation between $K_d$ and $K_{ex}$ for HDBP. These results seem to indicate that less the extractant is soluble in
the diluent more the extractant is efficient to extract a metal. Also the diluent effect on the efficiency of the extraction follows this order:

normal aliphatic hydrocarbon > tetrachloromethane > branched aromatic (e.g., toluene) > chloroform > di-i-propyl ether > MIBK.

Table 1-7. Thermodynamic data involving HDBP, distribution \(^{[49]} K_d\) and extraction data of metal chelate\(^{[27]}\), \(K_{ex}\) from 0.1 mol·L\(^{-1}\) (Na-H)NO\(_3\) into various diluents. Bold: aqueous 1.0 mol·L\(^{-1}\) (Na-H)NO\(_3\). Parenthesis: distribution form another source.\(^{[28]}\) r: corrected value

<table>
<thead>
<tr>
<th>diluent</th>
<th>log (K_d) (HDBP)</th>
<th>log (K_{ex})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>-2.34 (-2.31)</td>
<td>4</td>
</tr>
<tr>
<td>di-i-propyl ether</td>
<td>0.52</td>
<td>0.66</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.24</td>
<td>1.03</td>
</tr>
<tr>
<td>Tetra chloromethane</td>
<td>-1.44</td>
<td>2.95</td>
</tr>
<tr>
<td>MIBK</td>
<td>1.36</td>
<td>-0.75</td>
</tr>
<tr>
<td>Toluene</td>
<td>-0.59</td>
<td>1.25</td>
</tr>
</tbody>
</table>

log \(K_d\) vs. log \(K_{ex}\) \(R^2\) - 0.990 (0.960) 0.993
In 1967 Kolarik published a study on the diluent effect on the extraction of Eu(III) and Tb(III) by di-octyl-phosphoric acid (HDOP) - Figure 1-19a.\textsuperscript{[36]} This extractant (and this study) is particularly interesting for the work described here since the alkyl chain of HDOP, HDEHP and HEH[EHP] contain the same number of carbon atoms in the alkyl chain (8), and because of this feature the $K_d$ can be approximated to be the same.\textsuperscript{[28]} Furthermore, the $K_d$ is sufficiently large to support the approximation that the extractant is essentially immiscible in water, especially since the $K_d$ is larger for aqueous salted solution that for pure water (all reported $K_d$ for HDOP give between 99.8 and 100% HDOP in the organic phase).\textsuperscript{[28]} This study introduced for the first time a change in the
average number of ligands in the extracted metal chelate as a function of the diluent used - Figure 1-19cb.

<table>
<thead>
<tr>
<th>diluent</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>log $K_{ex}$</td>
<td>$\bar{n}$</td>
<td>log $K_{ex}$</td>
<td>$\bar{n}$</td>
</tr>
<tr>
<td>Eu</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n$-heptane</td>
<td>2.98</td>
<td>2.5</td>
<td>3.88</td>
<td>2.5</td>
</tr>
<tr>
<td>$i$-octane</td>
<td>2.81</td>
<td>2.5</td>
<td>3.75</td>
<td>2.5</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>2.55</td>
<td>2.5</td>
<td>3.46</td>
<td>2.5</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.25</td>
<td>3</td>
<td>1.25</td>
<td>3</td>
</tr>
<tr>
<td>Tetrachloro methane</td>
<td>-</td>
<td>3</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Bromoform</td>
<td>-</td>
<td>3</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Di-butyl-ether</td>
<td>2.14</td>
<td>3</td>
<td>3.1</td>
<td>3</td>
</tr>
<tr>
<td>MIBK</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.13</td>
<td>3</td>
<td>2.11</td>
<td>3</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.2</td>
<td>3</td>
<td>2.39</td>
<td>3</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>1.2</td>
<td>3</td>
<td>2.25</td>
<td>3</td>
</tr>
<tr>
<td>nitrobenzene</td>
<td>0.89</td>
<td>2.5</td>
<td>1.9</td>
<td>2.5</td>
</tr>
</tbody>
</table>
The change in the average ligand number indicates that the chelate ring is can vary from 8 (M-O-P=O--H-O-P=O--M), to 4 (M--O=P-O-M). However, if this chelate ring changes as a function of the diluent used, no dependence has been demonstrated between $\bar{n}$ and $K_{ex}$.\textsuperscript{27,36}

All of these results indicate that the diluent used in a SX process has a direct impact on the behavior of the extractant, as a free ligand and as a chelating agent, but also on the coordination and stereochemistry itself.
1.5 Research scope

The impact of the diluent on SX processes has been cited in literature since its creation. A large amount of literature exists on the impact of the diluent on the phase transfer, from a thermodynamic point of view, kinetic, colloidal, thermal, coordination, etc.

The goal of this work is to improve the understanding the fundamental chemistry of the green extractant HEH[EHP], in the context of solvent extraction of trivalent \( f \)-elements (Ln-Am). The \( f \)-elements have been chosen due to their similar chemical behavior (same oxidation number, small change in the ionic radii), which would help to understand the mechanism by reducing the possible variation from one metal to another.

First, an advanced method for calculation of the \( K_{ex} \) will be developed, integrating the concept of average ligand number in the form of a \( MA_3(HA)_n \) metal chelate, instead of a the classic fixed ligand number in the form of \( M(AHA)_3 \). This method is going to be completed by spectroscopy on the metal chelate (UV-Vis and Luminescence) to prove the conservation of the octahedral environment (regardless of the diluent used).

Based on the methodology developed for the calculation of the \( K_{ex} \), a comparison between the extraction of different \( f \)-elements is going to be described. This will give information on the mechanism driving the SX process. To do so, a large number of diluents were used, with the objective of plotting Linear Free Energy Diagram (LFED). Also particular attention was paid to the impact of \( 1 \)-octanol as a co-diluent (phase modifier), a mixed diluent system (cyclohexane:benzene), the extraction of water by HEH[EHP] in the different diluents, and to a phosphine oxide as extractant in different diluents.
Finally, complementary thermometric characterization of the diluent effect has been investigated to characterize the diluent effect with entropic and enthalpic data.
1.6 References


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CHAPTER TWO
METHODS

1.1. Materials

All aqueous solutions were prepared using reagent grade materials and 18 MΩ distilled de-ionized water. Most organic diluents were obtained Alfa/Aesar and Sigma-Aldrich Corp with a purity >98%. Some organic diluents were kindly provided from other professors at WSU. Select organic diluents were purified by contacting with a potassium permanganate solution, separated, and then a fractional distillation was performed. The extractant, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) was obtained from eNovation Chemical and Yick/Vic with low purity. Sigma-Aldrich provided Di-(2-ethylhexyl)phosphoric acid (HDEHP) with low purity. A third phase formation procedure was used to purify the HEH[EHP] to >99% and copper salt precipitation method was used to purify the HDEHP to >99%[1] - see below. The purity of the cleaned extractants was verified by phosphorus NMR spectroscopy and colorimetric titration.

Metal nitrate solutions were prepared by conversion from the solid oxide (purchased from Arris International Co. with a purity of 99.999%) to the soluble nitrate by evaporating the dissolved oxide down and re-dissolving in HNO₃ multiple times. When needed the metal concentrations were standardized using the complexometric colorimetric titration with the indicator dye Arsenazo III. The concentration of H⁺ was determined by colorimetric titration with standardized NaOH using phenolphthalein as a colorimetric indicator. The concentration of HO⁻ was determined by colorimetric titration using KHP as primary standard and phenolphthalein as a colorimetric indicator. The NO₃⁻ concentration was determined using ion-exchange chromatography (Dowex 50x beads, acidic form). The metals studied were Nd, Eu, Tm and Am.
The organic solutions were prepared gravimetrically daily when needed. The aqueous solution were prepared at the desired pH and ionic strength prior to utilization and stored under refrigeration when not in use. HEH[EHP] and HDEHP were stored in the dark so as to prevent degradation.

Radiotracer $^{147}$Nd, $^{152/154}$Eu, $^{170}$Tm were produced in-house by neutron activation with the 1.0 MW TRIGA reactor at the WSU NSC, see method below. Radiotracer $^{241}$Am was kindly provided by Pacific Northwest National Laboratory.

### 1.2. Purification methods

Most of commercially available acidic organophosphorus extractants typically contain multiple phosphorus-bearing impurities. Though it has been demonstrated that those impurities do not suppress the efficiency of most extraction system at a large scale, they still must be removed for fundamental research matters. The most common impurities present in the di-alkyl phosphoric acid and the alkyl alkyl phosphonic acid, are the di-alkyl phosphonate, alky akyl phosphinate, Mono-alkyl phosphoric acid, Mono-alkyl phosphonic acid.$^{[2]}$

![Common impurity found in di alkyl phosphoric acid (mostly A, and C) and alkyl alkyl phosphonic acid (mostly B, C and D). A: di-alkyl phosphonate, B: alkyl alkyl phosphinate, C: Mono-alkyl phosphoric acid, Mono-alkyl phosphonic acid.$^{[2]}$](image)

Figure 2-1. Common impurity found in di alkyl phosphoric acid (mostly A, and C) and alkyl alkyl phosphonic acid (mostly B, C and D). A: di-alkyl phosphonate, B: alkyl alkyl phosphinate, C: Mono-alkyl phosphoric acid, Mono-alkyl phosphonic acid.$^{[2]}$
2.1.1 Purification of HDEHP

The steps recommended by Partridge et al\textsuperscript{[1]} for the purification of organophosphorus acid extractant by copper salt precipitation are as follows:

1. A solution 25\% mass of copper(II) sulfate in water (250 mL) is contacted in a round bottom flask with a solution of 30 g of HDEHP in diethyl ether.

2. Slowly 8 g of a saturated solution of NaOH is added dropwise (with the use of a syringe pump), to prevent the precipitation of copper oxide. After NaOH addition is complete, the solution is allowed to stir overnight. As the NaOH is added to the dissolved CuSO\textsubscript{4}, it immediately forms Cu(OH)\textsubscript{2}; the Cu(OH)\textsubscript{2} then reacts with the HDEHP to form the Cu/HDEHP.

3. The organic phase is then separated using a separation funnel, placed into an Erlenmeyer flask, and gently heated to reduce the volume by 75-90\%. Then the solution is cooled down into an ice bucket (or stored overnight under refrigeration).

4. The Cu/HDEHP complex is then precipitated from the ether by addition of cold acetone. This is done by increasing the stirring rate of the solution and adding enough acetone until the (light blue) solid stops forming.

5. The precipitate is vacuum filtered and washed with acetone. The precipitate is then transferred into a round bottom flask and contacted with an excess of a 3 mol·L\textsuperscript{−1} HCl solution.

6. The mixture will have separated into two phases when the HDEHP protonation step is complete. The top layer will be a clear oily layer which consists of the desired HDEHP, and the bottom layer will be a green CuCl\textsubscript{2} solution. The solution is transferred in a separatory funnel and a couple of milliliters of ether is added to solvate the HDEHP.
7. The HCl layer is removed and then the organic phase is washed with DI water multiple times.

8. The organic phase is dried with Na$_2$SO$_4$(s), and distilled from the extractant to remove the residual ether to produce a high purity HDEHP.

2.1.2 Purification of HEH[EHP]

The steps recommended by Zhengshui et al.\textsuperscript{[3]} for the purification of an organophosphorus acid extractant by the middle phase micro emulsion method are as follows:

1. A solution of approximately 20\% (by volume) impure extractant solution (HEH[EHP]) in the acidic form in hexane is placed in a separatory funnel. A equivalent volume of an aqueous solution of 1 mol·L$^{-1}$ NaOH/0.15 mol·L$^{-1}$ Na$_2$SO$_4$ is added to the separatory funnel. The funnel is shaken vigorously / vented multiple times and then allowed to rest overnight. A three-fluid phase system is formed.

2. The middle phase is isolated, placed into a separatory funnel, contacted multiple times with fresh 6 mol.L$^{-1}$ HCl solution to convert the extractant to the acidic form. The organic phase (predominantly extractant) is then washed with DI water multiple times.

3. The organic phase is dried with Na$_2$SO$_4$(s), and the excess hexane is distilled from the extractant leaving the purified HEH[EHP] as a nearly colorless, viscous liquid

2.1.3 Purity control

Pure acidic organophosphorus extractants are liquids, slightly viscous, retains slight yellow colors, and has a slight sweet scent. The exact purity is determined by colorimetric titration and $^{31}$P-NMR. A pure acidic organophosphorus compound $^{31}$P-NMR spectrum should have one, sharp peak, in the Figure 2-2, no impurities were detected in purified HEH[EHP].
1.3. Neutron Activation

Activation by neutron capture of Ln(NO$_3$)$_3$ was used to create radiotracers with the 1.0 MW NSC TRIGA$^1$ reactor. The Lns are available as Ln(III) oxides with a 99.999% purity. First, the oxides were converted into nitrate by dissolving less than 100 mg of the oxide into 2 mL of 10 mol·L$^{-1}$ of HNO$_3$ and 90% evaporated multiple times to ensure a complete conversion into the nitrate form. The nitrate solution was then evaporated down to 90% volume and diluted in 2 mL of DI water multiple times. The final solution was dissolved in 0.5 mL of HNO$_3$ pH=2.

---

$^1$ TRIGA: Training, Research, Isotopes, General Atomic
Each sample preparation step was done at low heat with a stir plate and IR heat lamp set up, and under argon to prevent the solution to dry, boil, parasite reactions with the air.

A 0.5 mL aliquot of the Ln(NO$_3$)$_3$ is transferred to a new clean 1.5 mL (2/5 dram) polyethylene vial for irradiation. Then the vial is sealed to prevent any leak during the time in the reactor.

A sample is activated by being placed into a homogenous neutron flux for a specific amount of time to reach the activity desired. The solute is irradiated by a neutron flux, and the resulting specific activity $A$ (Bq) is determined by the following:

$$A = n \cdot \phi_T (1 - e^{-\lambda t_{irr}})(e^{-\lambda t_{cool}})(\sigma + r \cdot \varepsilon_{eth})$$  \hspace{1cm} (2.1)

**Activation facility controlled parameters:** $\Phi_T$ the thermal flux in neutron·cm$^{-2}$·s$^{-1}$, $t_{irr}$ and $t_{cool}$ respectively the irradiation time and cooling time in s, and $\varepsilon_{eth}$ the epithermal fraction.

**NSC WSU Reactor flux** (from calibration): $\Phi_T = 1.05 \cdot 10^{13}$ n·cm$^{-2}$·s$^{-1}$, $\varepsilon_{eth} = 2.5 \%$

**Analyte properties parameters:** $n$ is the number of atoms of lanthanide (taking into account natural abundance), $\lambda$ is the decay constant of the activated isotope in s$^{-1}$, $\sigma$ the cross section of the targeted lanthanide in barn (10$^{-24}$ cm$^2$), and $r$ the integral of the resonance of the lanthanides.

For the production of $^{170}$Nd, 90 mg of Nd$^{3+}$ has been irradiated for 4 hours, and let cool for 7 days before utilization (Activity Immediately After Irradiation: 9.62 MBq). For the production of $^{170}$Tm, 39 mg of Tm$^{3+}$ has been irradiated for 15 min, and let cool down for 24 h before utilization (Activity Immediately After Irradiation: 13.7 MBq)
1.4. Solvent Extraction Method

2.1.4 Gamma emitters

The distribution ratios for extraction can be calculated by measuring the amount of radioactivity of both aqueous and organic phases; hence the distribution ratio is defined by the ratio of specific radioactivity.

\[ D = \frac{\bar{A}}{A} \]  \hspace{1cm} (2.2)

The following method is used:

1. In a 2 mL disposable glass vial, 495 µL of acidic solution without any metal (\( \mu = 0.1 \) mol.L\(^{-1} \)) and 500 µL of an organic phase containing the extractant.
2. Five µL of radiotracer solution is pipetted into each vial.
3. The vials are then prepared for shaking. They are capped and parafilm is then used to seal the vial. For double containment, the vials have been placed in a plastic bag and tied shut.
4. Mix for approximately 30 min on a vortex mixer and centrifuge for approximately 15 min at 7 000 RPM.
5. The bag and the cap are removed and put into radioactive material disposal.
6. Two hundred µL of the top organic phase is sampled and put into gamma counting tube.
7. Another 200 µL of the top organic phase is removed and disposed of in a radioactive organic waste vial.
8. Two hundred µL of the interface (the rest of the organic phase and whatever amount of
the aqueous phase is accidentally pulled up) is removed and dispose in a radioactive
organic waste vial.

9. Two hundred µL of the aqueous phase is sampled and put into another gamma counting
tube.

10. The last 200 µL of the aqueous phase is removed, disposed in a radioactive aqueous
waste vial and the vial put into radioactive material disposal.

11. The gamma tubes then are capped and transported to the gamma counter.

The Gamma counter is a Packard Model 5003 Cobra II Auto Gamma Counter; this instrument has
an energy window between 15 – 2000 keV. Americium-241 is counted between 60-80 keV,
Neodymium-147 is counted between 85-120 keV, and Europium-152/154 is counted between 15-
70 keV.
2.1.5 Beta emitters

The distributions ratios for extraction can be calculated by measuring the amount of radioactivity in the aqueous phases before and after extraction; hence the distribution ratio is defined by the ratio of the specific activity before and after extraction minus one.

\[
D = \frac{A_{\text{initial}} - A_{\text{final}}}{A_{\text{final}}} = \frac{A_{\text{initial}}}{A_{\text{final}}} - 1
\]  

(2.3)

The following method is used:

1. Two hundred µL of a stock solution of the aqueous phase at a desired pH and ionic strength containing the radiotracer (\(\mu = 0.1 \text{ mol} \cdot \text{L}^{-1}\)) is sampled and put into scintillation counting tube, with 4 mL of scintillation fluid.

2. In a 2 mL disposable glass vial, 500 µL of acidic solution from the stock solution and 500 µL of an organic phase containing the extractant.

3. The vials are then prepared for shaking. They are capped, parafilm is then used to seal the vial. For double containment, the vials have been into a plastic bag and tied shut.

4. Mix for approximately 30 min on a vortex mixer and centrifuge for approximately 15 min at 7 000 RPM.

5. The bag and the cap are removed and put into radioactive material disposal.

6. Six hundred µL of the organic phase & interface (the totality of the organic phase and whatever amount of the aqueous phase is accidentally pulled up) is removed and dispose in a radioactive organic waste vial.

7. Two hundred µL of the aqueous phase is sampled and put into scintillation counting tube with 4 mL of scintillation liquid.
8. The last 200 µL of the aqueous phase is removed, disposed in a radioactive aqueous waste vial and the vial put into radioactive material disposal.

9. The counting tubes then are capped and transported to the scintillation counter for analysis.

The liquid scintillation counter is a Beckman LS 6500 Auto Counter, used on the complete energy range.

Figure 2-4. Liquid scintillation counter, Beckman LS 6500 Auto Counter

1.5. Spectroscopic Methods

2.1.6 Absorbance Measurement

Absorbance spectrophotometry was used to observe the potential spectral changes and to monitor the coordination mode of neodymium-HEH[EHP] metal chelate in the organic phase. The
coordination mode was monitored by observing the hypersensitive transitions $^4I_{9/2} \rightarrow ^4G_{5/2}, ^4G_{7/2}$, between 550 nm and 620 nm.\textsuperscript{[4]} The characteristic spectra of an octahedral Nd$^{3+}$ should result in six bands.\textsuperscript{[5]-[7]} Absorbance measurements were done using a double beam high-resolution spectrophotometer Cary 5000 UV-Vis-NIR with a Cary Dual Cell Peltier temperature control accessory.

The sample solutions were prepared by extracting Nd$^{3+}$ from a 50 mmol·L$^{-1}$ Nd(NO$_3$)$_3$ pH = 3 HNO$_3$ solution, using the method previously described. The 50 mmol·L$^{-1}$ Nd(NO$_3$)$_3$ solution were standardized using HDTPA / AAIII standardization method developed in the Nash group. The samples were measured in a screw top 1 cm 6Q micro cuvette. The Varian scan application 3.00 provided by Cary was used for data output, and each measurement was background and baseline corrected.

The spectra were analyzed and deconvoluted using the OriginPro 2018 software using the Gaussian function for six peaks deconvolution:

$$I_\lambda = I_0 + \sum_{i=1}^{6} \frac{A}{\pi w^2} e^{-\frac{4 \ln 2 (\lambda - \lambda_{max})^2}{w^2}}$$

where $I_0$ is the baseline, $\lambda_{max}$ the wavelength at maximum intensity for the band $i$, $A$ the area of the peak, and $w$ the full width at half maximum. The concentration of metal chelate in the organic phase was determined using the isotopic dilution method. After a volume of organic phase was removed for the absorbance analysis, an equivalent volume of the aqueous phase was also removed and a spike of $^{147}$Nd radiotracer was added to the biphasic system. Then the classic solvent
extraction method was applied to determine $D$ and the following equation was solved to determine the metal chelate concentration $[Nd]$

\[
D = \frac{[Nd]}{[Nd]} = \frac{50 - [Nd]}{[Nd]} \quad (2.5)
\]

2.1.7 Luminescence Measurement

To monitor the coordination mode of europium-HEH[EHP] metal chelate in the organic phase, luminescence spectrophotometry was used to search for potential spectral changes. Many lanthanide ions exhibit luminescence, emitting radiation from an excited electronic state. The light that is emitted as sharp lines characteristic of f-f transitions of a Ln$^{3+}$ ion. The coordination mode was monitored by observing the transitions $^5D_0 \rightarrow ^7F_J$ luminescence transitions between 550 nm and 630 nm$^{[4]}$ (using an excitation monochromatic light beam at 393 nm). The characteristic spectra of an octahedral Eu$^{3+}$ should be studied probing the $^5D_0 \rightarrow ^7F_0, ^7F_1, ^7F_2$ transitions$^{[8]}$ - Table 2-1.

**Table 2-1. Feature of $^5D_0 \rightarrow ^7F_J$ luminescent transitions for Eu$^{3+}$.$^{[8]}$**

<table>
<thead>
<tr>
<th>transition</th>
<th>Regions (nm)</th>
<th>Intensities</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^5D_0 \rightarrow ^7F_0$</td>
<td>570-585</td>
<td>Very weak</td>
<td>Only observed in C$<em>n$, C$</em>{nv}$ and C$_s$ symmetry. Absent in high symmetry – “forbidden”</td>
</tr>
<tr>
<td>$^5D_0 \rightarrow ^7F_1$</td>
<td>585-600</td>
<td>Strong</td>
<td>Intensity largely dependent of environment</td>
</tr>
<tr>
<td>$^5D_0 \rightarrow ^7F_2$</td>
<td>605-615</td>
<td>Very strong</td>
<td>Hypersensitive transition; intensity very strongly dependent on environment. Absent if ion on inversion center – “forbidden”</td>
</tr>
</tbody>
</table>
Luminescence measurements were done using high-resolution spectrofluorometer, Horiba Scientific FluoroMax-4 equipped with temperature control accessory.

The sample solutions were prepared by extracting Eu$^{3+}$ from a 1 mmol·L$^{-1}$ Eu(NO$_3$)$_3$ pH = 2 HNO$_3$ solution using the method previously described. The samples were measured in a 1 cm 6Q micro cuvette, using the 1 cm path for the excitation, and the 0.4 mm path for the luminescence beam – Figure 2-5. The FluorEssence V3.5 software provided by Horiba was used for data output.

![Figure 2-5. Schematic of the utilization of the cuvette for Eu$^{3+}$ luminescence](image)

The concentration of metal chelate in the organic phase was determined using the isotopic dilution method. After a volume of organic phases was removed for the absorbance analysis, an equal volume of the aqueous phase was removed and a spike of $^{152/154}$Eu radiotracer was added to the biphasic system. Then the classic solvent extraction method was applied to determine $D$ and the following equation is solved to determine the metal chelate concentration $\langle \text{Eu} \rangle$

$$D = \frac{[\text{Eu}]}{[\text{Eu}]} = 1 - \frac{[\text{Eu}]}{[\text{Eu}]}$$ (2.6)
1.6. References


CHAPTER THREE

DETERMINATION OF STABILITY CONSTANTS OF SOLVENT EXTRACTION OF f-ELEMENTS BY HEH[EHP] IN VARIOUS DILUENTS

3.1 Preface

The purpose of this chapter is to characterize the impact of the organic diluent used in solvent extraction of some selected trivalent f-elements (Nd$^{3+}$, Eu$^{3+}$, Tm$^{3+}$, Am$^{3+}$) by the acidic (cation exchanging) organophosphorus extractant 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester – HEH[EHP]. The analytical method consists of using a Graphic Slope Analysis (GSA) and the Ligand Number Method (LNM) using different diluents in similar aqueous conditions. The graphic plot of each GSA and LNM has been analyzed but are not included in this dissertation, only the final result of each individual set of experiments. The results of the GSA and LNM on the Eu$^{3+}$ extraction have been done in cooperation of multiple Nash group members over multiple years of combined effort.

In Chapter 3, the coefficient of extraction and $\bar{n}$ for the extraction of Nd$^{3+}$, Eu$^{3+}$, Tm$^{3+}$, and Am$^{3+}$ by HEH[EHP] have been determined for an extensive list of different diluents. The aqueous media contained only the background electrolyte (H-Na)NO$_3$. Overall when compared side by side in the same diluent, the coefficient of extractions were organized as expected, Tm$^{3+}$ > Eu$^{3+}$ > Nd$^{3+}$ > Am$^{3+}$ (regardless of the diluent used). Linear free energy diagrams were also obtained between metal ions, suggesting that as expected the metal-extractant bonding interactions are predominantly electrostatically driven under these conditions. The primary diluent effect study suggests that the aromatic diluents have a lower efficiency of extraction that the aromatics ones, but exhibit higher overall M:L stoichiometry in the extracted complex.
The diluent effect for the extraction of Eu$^{3+}$ by HEH[EHP] has been accepted for publication in Solvent Extraction and Ion Exchange, Rydberg Special Editions. However, the data has been expended since submitted. A special acknowledgment is needed for the co-authors of this publication, for the joint effort and the development of the analytical method, especially Doctor Kimberlin and Doctor Dodd.
3.2 Introduction

Liquid cation exchanger extractants accomplish cation transfer via the exchange (between two phases at the interface) of an appropriate number of ions of the same sign as the extracted species to maintain electroneutrality. This exchange mechanism requires that there is an exchangeable ion in the organic phase. For an acidic extractant, the most common cation exchanged is the hydrogen ion, as the following equilibrium suggests\(^1\):

\[
M^{n+} + (m + n)(HA) \rightleftharpoons MA_n \cdot HA_m + nH^+ \quad (3.1)
\]

Because the HO(O=)P< group is polar, for most of the phosphorus cation exchangers and in the majority of organic solvents, the free HA extractants tend to form hydrogen bonded dimers in the bulk organic phase (dimer form \((HA)_2\))\(^2\,^3\)

\[
M^{n+} + \frac{m + n}{2}(HA)_2 \rightleftharpoons MA_n \cdot HA_m + nH^+ \quad (3.2)
\]

Though the dominance of the organic phase extractant dimer is widely expected, information concerning dimerization equilibrium constants is comparatively limited and subject to substantial uncertainty\(^3\).

Determination of the extraction equilibrium constant is critical for improved understanding of an extraction system. While solvent extraction methods have been used extensively to study aqueous phase equilibria, organic phase equilibria (though integral to the solvent extraction process) have been the subject of far fewer detailed studies. In particular, the effect of the “inert” diluent on metal ion extraction has been touched upon by a small number of authors\(^2\,^4\,^14\) As a starting
assumption, the diluent is usually considered as inert, since it does not appear in the extraction equilibrium expression. However, the impact of the diluent has already been demonstrated on multiple occasions for various systems. Mason et al.\textsuperscript{[5][11][12][15][16]} investigated the influence of the diluent on numerous organophosphorus extractants through Graphic Slope Analysis (GSA) and observed that the “inert” diluent had a significant effect on the efficiency of the extraction. They also observed, using Ligand Number Method (LNM), that some diluents appeared to decrease the number of extractant molecules in the final extracted metal complex. The diluent did not seem to affect the apparent amount of $\text{H}^+$ exchanged for the metal when cation exchanging extractants were used, as a slope of three was observed.\textsuperscript{[5][11][12][16]}

The effect of the diluent on extractant behavior in solvent extraction of trivalent lanthanides by HEH[EHP] and similar families of extractants has not been extensively investigated in the literature due to the limited number of appropriate analytical techniques that are well adapted to understand the chemistry of the organic phase. The GSA combined with the LNM have been used to analyze the impact of the diluent on the solvated metal chelate, through its distribution and stoichiometry. Those two method are then supported by spectroscopic inspection of the cations and the free ligand.

3.3 Experimental

3.3.1 Method: Combined Graphic Slope Analysis and Ligand Number Method

The extraction of trivalent $f$-elements from dilute nitric media by acidic organophosphorus extractants is generally considered to occur via the following equilibrium (3.1):

$$\text{M}^{3+} + 3(\text{HA})_2 \rightleftharpoons \text{M(AHA)}_3 + 3\text{H}^+$$ (3.1)
This equilibrium requires that three hydrogen ions are exchanged (to the aqueous phase) from three extractant dimers to satisfy the requirement of charge balance; the coordination of three dimers (the dominant form of the extractant in typical diluents) in principle represents a nearly octahedral arrangement of O-donor atoms around the metal center. In this hypothetical complex, the cation should be surrounded by three eight-membered chelate rings (M-O-P=O:--H-O-P=O:--M).

However, to be true, the equilibrium (3.1) should predict the slope for a GSA. With this fixed equilibrium, the GSA of the extraction of a trivalent metal should have shown to be inversely third power dependent upon the concentration of hydrogen ion in the aqueous phase (charge balance), but also third power dependent upon the concentration of the extractant.

In the late 60’s, extensive studies of lanthanide extraction by di-alkyl phosphoric acids showed that, under some circumstances (in general, using different diluents), the apparent integrated ligand number in the metal chelate could be 2.5, with a proposed dominant complex of \( \text{MA}_3(\text{HA})_2 \).

\[
\text{MA}_3(\text{HA})_2 \rightleftharpoons \text{MA}_3(\text{HA})_2 + 3\text{H}^+ \tag{3.3}
\]

\[
K_{ex} = \frac{[\text{MA}_3(\text{HA})_2]}{[\text{M}^{3+}]} \cdot \frac{[\text{H}^+]^3}{[(\text{HA})_2]^{2.5}} \quad \tag{3.4}
\]

In the past, most of the equilibria have been characterized in a binary way, where the stoichiometry was either \( \text{MA}_3(\text{HA})_2 \) or \( \text{MA}_3(\text{HA})_3 \) for trivalent \( f \)-elements. The difference in those stoichiometries found by LNM have been attributed to “activity effects”, used as a correction factor
to fit the experimental slopes to the theoretical defined stoichiometries. However, considering the Bjerrum’s concept of *average ligand number* defined as the mean number of ligands per central atom\(^{[17]}\), the system could allow the extraction to yield different stoichiometries of metal chelate for a given metal center. In this kind of system, it is possible to imagine a solution where MA\(_3\)(HA)\(_2\) and MA\(_3\)(HA)\(_3\) coexist in the same solution. Considering an average ligand number, the following equation should be used.

\[
\text{M}^{3+} + \frac{3 + n}{2} \text{(HA)}_2 \rightleftharpoons \text{MA}_3\text{(HA)}_n + 3\text{H}^+ \quad (3.5)
\]

\[
K_{\text{ex}}^* = \frac{[\text{MA}_3\text{(HA)}_n]}{[\text{M}^{3+}]} \cdot \frac{[\text{H}^+]^3}{[\text{(HA)}_2]^{3+n}} = D \cdot \frac{[\text{H}^+]^3}{[\text{(HA)}_2]^{3+n}} \quad (3.6)
\]

Then with a linearization and reorganization of the equation (3.6) the following equation can be obtained:

\[
\log D = \log K_{\text{ex}}^* + \frac{3 + n}{2} \cdot \log([\text{HA}_2^{2-}]) - 3 \cdot \log[\text{H}^+] \quad (3.7)
\]

with the average ligand number obtained as follows (for dimeric extractant).

\[
\bar{n} = \frac{3 + n}{2} \quad (3.8)
\]

It has been shown in the past that if the concentration of metal chelate in the organic phase is high enough, poly-nuclear metal complexes can be created in the form M\(_n\)A\(_{3n}\)(HA)\(_p\), which
considerably complicate the system and might limit the applicability of simple GSA\textsuperscript{[18]}.

By maintaining the concentration of metal at very low concentrations (e.g., by utilizing radioanalytical methods) such poly-nuclear species should be avoided. By studying the distribution ratio of the tracer extraction, while varying the acid concentrations, a slope of 3 is always seen. This is only true in acidic conditions to prevent hydrolysis of the metal. However, by carefully studying the distribution ratio of the extraction while varying the extractant concentration, the slope can reveal a subtle constant deviation from the ideal stoichiometries.

An article recently submitted for publication by the Nash group presents an intensive study of the diluent effect on extraction of Eu(III) by HEH[EHP] from nitric acid media. This study shows, the main advantages of using the average ligand number obtained by the LNM method in a GSA to calculate the $K_{ex}$. This study also shows that the ligand number, and \textit{ipso facto} the $K_{ex}$, are both strongly dependent of the diluent used for the SX. This combined analytical method will be used to characterize the diluent effect of this dissertation.

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{example.png}
  \caption{Graphic slope analysis of sample plots for: left xylene, right n-octane. Unweighted fit of log $D$ vs. log [H\textsuperscript{+}] and log [(HA)\textsubscript{2}]. Metal $^{152/154}$Eu tracer extracted from nitric media (Na-H)NO\textsubscript{3} $\mu = 0.1$ mol\cdot L\textsuperscript{-1}.}
\end{figure}
The GSA and the LNM of the distribution data have been done on OriginPro 2018 to determine the slopes, using an unweighted linear fit \( y = a \cdot x + b \). Since the dimerization constants of HEH[EHP] in each diluent are unknown (especially since the dimerization constant in a biphasic system is dependent on the background electrolyte, the pH, the water dissolved in the organic phase, the distribution of the extractant between each phase etc.)\(^{[3]}\), the choice has been made to use the following equation (3.9) to calculate the \( \log K^*_\text{ex} \). This method is similar to the methods used by Mason et al.\(^{[5],[15]}\)

\[
\log K^*_\text{ex} = \log D + \log \frac{F_{\text{HNO}_3} \bar{n}^3}{F_{\text{HA}}} \quad (3.9)
\]

where \( K^*_\text{ex} \) represents the equilibrium constant using an average ligand number \( \bar{n} \), the formal concentration of nitric acid \( F_{\text{HNO}_3} \) and the formal concentration of extractant \( F_{\text{HA}} \).

During the experiments, slope analysis using \( n \)-octane and \( n \)-dodecane as diluent has been performed with and without pre-contact of the phases before injection of the europium radiotracer, with the objective to observe a potential change in extraction behavior. The \( \log K^*_\text{ex} \) obtained were identical within errors, regardless of the pre-contact action. The impact of the pre-contact has not been studied for the other diluents, which may behave differently.
3.3.2 Results

3.3.2.1 Europium Extraction Result and Proof of Concept

The extractions were done at room temperature, 25°C ± 1°C, with an ionic strength of 0.1 mol·L⁻¹ (H-Na)NO₃. Since the europium radiotracers used, ¹⁵²/¹⁵⁴Eu, were both gamma emitters, the method used were the solvent extraction method for gamma emitters. Some examples of results of the LNM are shown in the Figure 3-2. Those results emphasize the impact that a diluent has on the average ligand number, represented by the slope.

![Figure 3-2. LNM and GSA plot for the extraction of Eu³⁺ by HEH[EHP] from (H-Na)NO₃ media μ = 0.1 mol·L⁻¹ and room temperature. The logarithm of the distribution of europium between the organic and aqueous phase, versus the logarithm of the formal concentration of extractant. Unweighted fit. Top left in iso-octane, top right in benzene, bottom left in methyl iso butyl ketone, and bottom right in chloroform.](image)

---

**Figure 3-2.** LNM and GSA plot for the extraction of Eu³⁺ by HEH[EHP] from (H-Na)NO₃ media μ = 0.1 mol·L⁻¹ and room temperature. The logarithm of the distribution of europium between the organic and aqueous phase, versus the logarithm of the formal concentration of extractant. Unweighted fit. Top left in iso-octane, top right in benzene, bottom left in methyl iso butyl ketone, and bottom right in chloroform.
Table 3-1 shows the average ligand numbers obtained by the LNM method and the \( K_{ex}^* \) obtained with the equation (3.9), organized according to their \( K_{ex}^* \). Generally, the complexes closer to EuA\(_3\)(HA)\(_2\) are aliphatic hydrocarbons, and EuA\(_3\)(HA)\(_3\) are aromatic hydrocarbons, and the complex EuA\(_3\)(HA)\(_4\) observed in MIBK. The addition of less than 3 molecules of HEH[EHP] to the EuA\(_3\) can be attributed to the stepwise equation.

\[
K_{ex}^* = \frac{1}{K_2^{\bar{n}/2}} \cdot \frac{1}{K_d^{\bar{n}}} \cdot \frac{1}{K_a^3} \cdot \beta \cdot K_D \cdot \beta_{Agg} \quad (3.10)
\]

where \( K_2 \) is the dimerization constant, \( K_d \) the distribution constant of the monomeric extractant, \( K_a \) the acidic association constant, \( \beta \) the association constant between one metal and three extractants molecules, \( K_D \) the distribution constant of the MA\(_3\) complex, and \( \beta_{agg} \) the association constant of additional extractant HA.

The table also shows the log \( K_{ex} \) defined with the classic calculation method as comparison. This calculation assumes that the chelate ring is always composed of two dimerized ligands.

\[
\log K_{ex} = \log D + \log \left( \frac{[H]}{[(HA)_2]} \right)^3 \quad (3.11)
\]

A comparison of the log \( K_{ex} \) (calculated by using defining a 1:6 ligand stoichiometry) and the log \( K_{ex}^* \) (calculated by using the stoichiometry determined by the LNM), and specifically the errors attributed those constants, show that the result for log \( K_{ex} \) are less internally consistent due to the larger standard deviation on the data for the same set GSA.
As a primitive analysis of the diluent effect, the highest extraction efficiencies and lowest average ligand numbers are observed with the “inert” diluent. In this case, inert refers to the tendency of the diluent to not enter into any type of association with the solute (the only interactions are the London dispersive forces), especially with the extractant. The molecule of HEH[EHP] is able to form hydrogen bonding either through the hydroxyl or the phosphoryl group. The aromatic type diluents are characterized by the higher suppressing activity toward the extractions and higher average ligand number.
Table 3-1. Equilibria constants of extraction of Eu$^{3+}$ by HEH[EHP] for 0.1 mol·L$^{-1}$ (Na-H)NO$_3$ at 25°C ± 1°C. log $K_{ex}$ represent the equilibria constant considering only the complex Eu(AHA)$_3$, log $K_a$ consider the average ligand number $n$. Complex* refer to the largest portion of complex considering the average ligand number. Type of diluent: i = inert, D = donor, A = acceptor. (a) the efficiency of the extraction seem to be one order of magnitude lower than expected, (b) the efficiency of the extraction seem to be a couple of order of magnitudes lower than expected.
Acceptor diluents, such as chloroform, form very stable molecular complexes with HEH[EHP] due to the high basicity of the phosphoryl group. For the same reason alcoholic diluents would also suppress the extraction.\textsuperscript{[19]}

Other equilibria that involve diluent effect will be discussed in the next chapter.

3.3.2.2 Thulium Extraction Results

Extractions were done at room temperature, 25°C ± 1°C, with an ionic strength of 0.1 mol·L\textsuperscript{-1} (H-Na)NO\textsubscript{3}. Since the thulium radiotracer used (\textsuperscript{170}Tm) is a beta emitter, the method used for quantitation was the solvent extraction method for beta emitters. Some examples of results of the LNM are shown in the Figure 3-3. These results emphasize the impact that the diluent has on the average ligand number, represented by the slope.

The Table 3-2 shows the average ligand numbers obtained by the LNM method and the log $K_{ex}^*$ obtained with the equation (3.9), organized according to their log $K_{ex}^*$. Generally, the average stoichiometries of the Tm complexes seem to be lower than the ones obtained with Eu in the previous section. This could imply that the $\beta_{agg}$ is dependent on the cation extracted.

$$\text{LnA}_3 + n(\text{HA})_2 + m\text{HA} \rightleftharpoons \text{LnA}_3(\text{HA})_{\frac{n}{2}+m} \tag{3.12}$$

Since this equilibrium seems to be exclusively driven by a Lewis Acid/base adduct formation, it may indicate that the denticity of the ligand around the metal is at the origin of the difference between Tm and Eu.
Figure 3-3. LNM and GSA plot for the extraction of Tm$^{3+}$ by HEH[EHP] from (H-Na)NO$_3$ media at 0.1 mol·L$^{-1}$ and room temperature. The logarithm of the distribution of thulium between the organic and aqueous phase, versus the logarithm of the formal concentration of extractant. Unweighted fit. Top left in toluene, top right in chloroform, bottom left in iso-octane, and bottom right in nitrobenzene.

A first analysis of the diluent effect on the log $K_{ex}^{*}$ for Tm shows similar observations to those made with Eu. The inert diluents generally have an higher log $K_{ex}^{*}$. The aromatic type diluents are characterized by the higher suppressing activity toward the extractions, and chloroform seems to suppress extraction the most.
<table>
<thead>
<tr>
<th>Compound</th>
<th>pH</th>
<th>[HA] Range</th>
<th>log $K_{ex}$</th>
<th>log $K_{e}^*$</th>
<th>$\bar{n}$</th>
<th>Complex*</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>iso-octane</td>
<td>1.20</td>
<td>0.01 - 0.05</td>
<td>2.19 ± 0.10</td>
<td>1.87 ± 0.08</td>
<td>2.81 ± 0.13</td>
<td>TmA$_3$(HA)$_3$</td>
<td>i</td>
</tr>
<tr>
<td>n-decane-</td>
<td>1.20</td>
<td>0.01 - 0.12</td>
<td>1.95 ± 0.14</td>
<td>1.48 ± 0.05</td>
<td>2.65 ± 0.07</td>
<td>TmA$_3$(HA)$_2$</td>
<td>i</td>
</tr>
<tr>
<td>n-heptane</td>
<td>1.20</td>
<td>0.01 - 0.09</td>
<td>1.74 ± 0.10</td>
<td>1.47 ± 0.08</td>
<td>2.82 ± 0.13</td>
<td>TmA$_3$(HA)$_3$</td>
<td>i</td>
</tr>
<tr>
<td>n-octane</td>
<td>1.20</td>
<td>0.01 - 0.09</td>
<td>1.85 ± 0.12</td>
<td>1.45 ± 0.07</td>
<td>2.74 ± 0.09</td>
<td>TmA$_3$(HA)$_2$</td>
<td>i</td>
</tr>
<tr>
<td>Decalin</td>
<td>1.20</td>
<td>0.02 - 0.09</td>
<td>1.67 ± 0.12</td>
<td>1.24 ± 0.06</td>
<td>2.68 ± 0.10</td>
<td>TmA$_3$(HA)$_2$</td>
<td>i</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>1.20</td>
<td>0.01 - 0.06</td>
<td>1.76 ± 0.14</td>
<td>1.00 ± 0.02</td>
<td>2.57 ± 0.03</td>
<td>TmA$_3$(HA)$_2$</td>
<td>i</td>
</tr>
<tr>
<td>bromo ethane</td>
<td>1.20</td>
<td>0.02 - 0.17</td>
<td>0.89 ± 0.60</td>
<td>0.87 ± 0.06</td>
<td>3.10 ± 0.09</td>
<td>TmA$_3$(HA)$_3$</td>
<td>i</td>
</tr>
<tr>
<td>Tetralin</td>
<td>1.20</td>
<td>0.05 - 0.21</td>
<td>0.88 ± 0.13</td>
<td>0.46 ± 0.22</td>
<td>2.59 ± 0.20</td>
<td>TmA$_3$(HA)$_2$</td>
<td>$\pi$-D</td>
</tr>
<tr>
<td>1,3-diisopropylnaphthalene</td>
<td>1.20</td>
<td>0.01 - 0.10</td>
<td>1.13 ± 0.27</td>
<td>0.23 ± 0.06</td>
<td>2.36 ± 0.08</td>
<td>TmA$_3$(HA)$_2$</td>
<td>$\pi$-D</td>
</tr>
<tr>
<td>n-dodecane</td>
<td>1.20</td>
<td>0.01 - 0.05</td>
<td>2.26 ± 0.23</td>
<td>-0.02 ± 0.08</td>
<td>2.42 ± 0.13</td>
<td>TmA$_3$(HA)$_2$</td>
<td>i</td>
</tr>
<tr>
<td>methyl isobutyl ketone</td>
<td>2.00</td>
<td>0.04 - 0.12</td>
<td>0.00 ± 0.07</td>
<td>-0.04 ± 0.07</td>
<td>2.97 ± 0.22</td>
<td>TmA$_3$(HA)$_3$</td>
<td>n-D</td>
</tr>
<tr>
<td>tetrachloroethylene</td>
<td>1.20</td>
<td>0.02 - 0.09</td>
<td>0.54 ± 0.35</td>
<td>-0.23 ± 0.11</td>
<td>2.32 ± 0.08</td>
<td>TmA$_3$(HA)$_2$</td>
<td>i</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>1.20</td>
<td>0.09 - 0.16</td>
<td>0.08 ± 0.35</td>
<td>-0.36 ± 0.02</td>
<td>2.69 ± 0.16</td>
<td>TmA$_3$(HA)$_2$</td>
<td>i</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>1.20</td>
<td>0.06 - 0.21</td>
<td>-0.42 ± 0.24</td>
<td>-0.71 ± 0.05</td>
<td>2.80 ± 0.14</td>
<td>TmA$_3$(HA)$_3$</td>
<td>$\pi$-D</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>1.20</td>
<td>0.01 - 0.12</td>
<td>0.64 ± 0.27</td>
<td>-0.78 ± 0.03</td>
<td>2.05 ± 0.04</td>
<td>TmA$_3$(HA)</td>
<td>n-D</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.20</td>
<td>0.06 - 0.11</td>
<td>-0.57 ± 0.32</td>
<td>-0.81 ± 0.03</td>
<td>2.91 ± 0.20</td>
<td>TmA$_3$(HA)$_3$</td>
<td>$\pi$-D</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>1.20</td>
<td>0.09 - 0.17</td>
<td>-0.45 ± 0.25</td>
<td>-0.84 ± 0.02</td>
<td>2.70 ± 0.10</td>
<td>TmA$_3$(HA)$_2$</td>
<td>$\pi$-D</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.20</td>
<td>0.06 - 0.13</td>
<td>-0.67 ± 0.05</td>
<td>-0.95 ± 0.05</td>
<td>2.74 ± 0.14</td>
<td>TmA$_3$(HA)$_2$</td>
<td>$\pi$-D</td>
</tr>
<tr>
<td>o-dichlorobenzene (a)</td>
<td>1.20</td>
<td>0.02 - 0.10</td>
<td>-0.03 ± 0.21</td>
<td>-1.10 ± 0.03</td>
<td>2.21 ± 0.08</td>
<td>TmA$_3$(HA)$_1$</td>
<td>$\pi$-D</td>
</tr>
<tr>
<td>Chloroform</td>
<td>1.20</td>
<td>0.16 - 0.36</td>
<td>-1.80 ± 0.07</td>
<td>-5.99 ± 0.03</td>
<td>3.46 ± 0.11</td>
<td>TmA$_3$(HA)$_4$</td>
<td>A</td>
</tr>
</tbody>
</table>

Table 3-2: Equilibria constants of extraction of Tm$^{3+}$ by HEHEHP at 0.1 mol L$^{-1}$ (Na$_2$H$_2$O$_2$ at 25°C ± 1°C. log $K_{e}$ represent the equilibria constant considering the complex TmA$_3$(HA)$_3$. log $K_{e}^*$, consider the average ligand number. $\bar{n}$ represent the largest portion of complex considering the average ligand number. Type of diluent: i = inert, D = donor, A = acceptor. (a) the efficiency of the extraction seem to the one order of magnitude lower than expected.
3.3.2.3 *Neodymium and Americium Extraction Results*

In this set of experiment, radiotracers of Am and Nd have been used in the same extraction. Therefore, the condition of the extractions of both metals have been identical, and will be easier to compare. The extractions were done at room temperature, 25°C ± 1°C, with an ionic strength of 0.1 mol·L⁻¹ (H-Na)NO₃. Since the radiotracers used ²⁴¹Am and ¹⁴⁶Nd, were both gamma emitters, the method used was the solvent extraction method for gamma emitters. Some examples of results of the LNM are shown in the **Figure 3-4**. Those results emphasize the impact that a diluent have on the average ligand number, represented by the slope.

The analysis of the diluent effect on the log $K_{ex}^*$ shows similar trends to those made with Eu, and Nd. The inert diluents seem to have an higher log $K_{ex}^*$. The aromatic type diluents are characterized by the higher suppressing activity toward the extractions despite higher stoichiometry (in principle, a more hydrophobic outer shell) in the extracted complex.
Figure 3-4. LNM and GSA plot for the extraction of Nd\(^{3+}\) (blank) and Am\(^{3+}\) (solid) by HEH[EHP] from (H-Na)NO\(_3\) media at 0.1 mol·L\(^{-1}\) and room temperature. The logarithm of the distribution of tracers between the organic and aqueous phase, versus the logarithm of the formal concentration of extractant. Unweighted fit. Top left in n-octane, top right in benzene, bottom left in MIBK, and bottom right in chloroform.
<table>
<thead>
<tr>
<th>Complex</th>
<th>pH</th>
<th>[HA] Range</th>
<th>$\log K_{ax}$</th>
<th>$\log K^*_c$</th>
<th>$\bar{n}$</th>
<th>Complex</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>isooctane</td>
<td>2.29</td>
<td>0.01-0.05</td>
<td>-2.05 ± 0.15</td>
<td>-2.18 ± 0.15</td>
<td>2.92 ± 0.29</td>
<td>NdA$_3$(HA)$_3$</td>
<td>i</td>
</tr>
<tr>
<td>n-octane</td>
<td>1.70</td>
<td>0.06-0.12</td>
<td>-2.24 ± 0.08</td>
<td>-2.70 ± 0.05</td>
<td>2.56 ± 0.27</td>
<td>NdA$_3$(HA)$_2$</td>
<td>i</td>
</tr>
<tr>
<td>n-decane</td>
<td>2.29</td>
<td>0.04-0.15</td>
<td>-2.47 ± 0.16</td>
<td>-3.22 ± 0.03</td>
<td>2.29 ± 0.09</td>
<td>NdA$_3$(HA)$_2$</td>
<td>i</td>
</tr>
<tr>
<td>1,1,2,2-tetrachloroethane</td>
<td>2.29</td>
<td>0.19-0.45</td>
<td>-3.89 ± 0.07</td>
<td>-3.65 ± 0.04</td>
<td>3.45 ± 0.14</td>
<td>NdA$_3$(HA)$_4$</td>
<td>i</td>
</tr>
<tr>
<td>1,3-diisopropylbenzene</td>
<td>2.29</td>
<td>0.09-0.24</td>
<td>-3.37 ± 0.13</td>
<td>-3.68 ± 0.11</td>
<td>2.63 ± 0.36</td>
<td>NdA$_3$(HA)$_2$</td>
<td>π-D</td>
</tr>
<tr>
<td>2,3-dichlorobenzotrifluoride</td>
<td>2.29</td>
<td>0.11-0.26</td>
<td>-3.77 ± 0.07</td>
<td>-3.75 ± 0.06</td>
<td>3.00 ± 0.25</td>
<td>NdA$_3$(HA)$_3$</td>
<td>π-D</td>
</tr>
<tr>
<td>tetrachloroethylene</td>
<td>2.29</td>
<td>0.07-0.20</td>
<td>-3.43 ± 0.06</td>
<td>-3.77 ± 0.01</td>
<td>2.65 ± 0.04</td>
<td>NdA$_3$(HA)$_2$</td>
<td>i</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>2.29</td>
<td>0.04-0.21</td>
<td>-3.18 ± 0.27</td>
<td>-4.11 ± 0.09</td>
<td>2.03 ± 0.19</td>
<td>NdA$_3$(HA)$_3$</td>
<td>i</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>2.29</td>
<td>0.12-0.28</td>
<td>-4.16 ± 0.07</td>
<td>-4.31 ± 0.06</td>
<td>2.80 ± 0.23</td>
<td>NdA$_3$(HA)$_3$</td>
<td>n-D</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>2.29</td>
<td>0.16-0.36</td>
<td>-3.54 ± 1.62</td>
<td>-4.45 ± 0.02</td>
<td>2.74 ± 0.15</td>
<td>NdA$_3$(HA)$_2$</td>
<td>i</td>
</tr>
<tr>
<td>Xylene</td>
<td>2.29</td>
<td>0.22-0.33</td>
<td>-4.56 ± 0.02</td>
<td>-4.49 ± 0.02</td>
<td>3.13 ± 0.15</td>
<td>NdA$_3$(HA)$_3$</td>
<td>π-D</td>
</tr>
<tr>
<td>Methyl isobutyl ketone</td>
<td>2.29</td>
<td>0.20-0.42</td>
<td>-4.53 ± 0.03</td>
<td>-4.51 ± 0.03</td>
<td>3.05 ± 0.16</td>
<td>NdA$_3$(HA)$_3$</td>
<td>n-D</td>
</tr>
<tr>
<td>1,3,5-trimethylbenzene</td>
<td>2.29</td>
<td>0.19-0.33</td>
<td>-4.41 ± 0.05</td>
<td>-4.64 ± 0.03</td>
<td>2.60 ± 0.17</td>
<td>NdA$_3$(HA)$_2$</td>
<td>π-D</td>
</tr>
<tr>
<td>n-dodecane</td>
<td>2.29</td>
<td>0.06-0.16</td>
<td>-4.25 ± 0.08</td>
<td>-4.74 ± 0.03</td>
<td>2.50 ± 0.09</td>
<td>NdA$_3$(HA)$_2$</td>
<td>i</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.70</td>
<td>0.20-0.39</td>
<td>-4.64 ± 0.13</td>
<td>-4.74 ± 0.08</td>
<td>2.90 ± 0.09</td>
<td>NdA$_3$(HA)$_3$</td>
<td>π-D</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>2.29</td>
<td>0.12-0.20</td>
<td>-4.64 ± 0.05</td>
<td>-4.93 ± 0.04</td>
<td>2.65 ± 0.23</td>
<td>NdA$_3$(HA)$_2$</td>
<td>π-D</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>2.29</td>
<td>0.11-0.15</td>
<td>-3.73 ± 2.09</td>
<td>-5.31 ± 0.02</td>
<td>2.29 ± 0.19</td>
<td>NdA$_3$(HA)$_2$</td>
<td>π-D</td>
</tr>
<tr>
<td>Chloroform</td>
<td>2.29</td>
<td>0.15-0.37</td>
<td>-5.90 ± 0.02</td>
<td>-5.81 ± 0.01</td>
<td>3.14 ± 0.03</td>
<td>NdA$_3$(HA)$_3$</td>
<td>A</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.29</td>
<td>0.20-0.40</td>
<td>-6.60 ± 0.04</td>
<td>-6.42 ± 0.03</td>
<td>3.34 ± 0.11</td>
<td>NdA$_3$(HA)$_4$</td>
<td>π-D</td>
</tr>
<tr>
<td>Complex</td>
<td>pH</td>
<td>[HA] Range</td>
<td>(\log K_{ex})</td>
<td>(\log K'_{ex})</td>
<td>(\bar{n})</td>
<td>Complex Type</td>
<td></td>
</tr>
<tr>
<td>-----------------------------</td>
<td>------</td>
<td>------------</td>
<td>------------------</td>
<td>-----------------</td>
<td>-------------</td>
<td>--------------</td>
<td></td>
</tr>
<tr>
<td>iso-octane</td>
<td>2.29</td>
<td>0.01 - 0.05</td>
<td>-2.30 ± 0.12</td>
<td>-2.49 ± 0.11</td>
<td>2.88 ± 0.22</td>
<td>NdA₃(HA)₃ i</td>
<td></td>
</tr>
<tr>
<td>n-octane</td>
<td>1.70</td>
<td>0.06 - 0.12</td>
<td>-2.01 ± 0.06</td>
<td>-2.91 ± 0.03</td>
<td>2.62 ± 0.18</td>
<td>NdA₃(HA)₂ i</td>
<td></td>
</tr>
<tr>
<td>n-decane</td>
<td>2.29</td>
<td>0.04 - 0.15</td>
<td>-2.71 ± 0.10</td>
<td>-3.21 ± 0.01</td>
<td>2.53 ± 0.03</td>
<td>NdA₃(HA)₂ i</td>
<td></td>
</tr>
<tr>
<td>1,1,2,2-tetrachloroethane</td>
<td>2.29</td>
<td>0.19 - 0.45</td>
<td>-3.89 ± 0.07</td>
<td>-3.65 ± 0.04</td>
<td>3.45 ± 0.14</td>
<td>NdA₃(HA)₄ i</td>
<td></td>
</tr>
<tr>
<td>tetrachloroethylene</td>
<td>2.29</td>
<td>0.07 - 0.20</td>
<td>-3.68 ± 0.03</td>
<td>-3.66 ± 0.02</td>
<td>3.03 ± 0.11</td>
<td>NdA₃(HA)₃ i</td>
<td></td>
</tr>
<tr>
<td>1,3-diisopropylbenzene</td>
<td>2.29</td>
<td>0.09 - 0.24</td>
<td>-3.65 ± 0.08</td>
<td>-3.84 ± 0.07</td>
<td>2.78 ± 0.22</td>
<td>NdA₃(HA)₃ (\pi)-D</td>
<td></td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>2.29</td>
<td>0.04 - 0.21</td>
<td>-3.29 ± 0.18</td>
<td>-3.90 ± 0.05</td>
<td>2.36 ± 0.11</td>
<td>NdA₃(HA)₂ i</td>
<td></td>
</tr>
<tr>
<td>2,3-dichlorobenzotrifluoride</td>
<td>2.29</td>
<td>0.11 - 0.26</td>
<td>-4.08 ± 0.08</td>
<td>-4.07 ± 0.07</td>
<td>2.98 ± 0.26</td>
<td>NdA₃(HA)₃ (\pi)-D</td>
<td></td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>2.29</td>
<td>0.12 - 0.28</td>
<td>-4.16 ± 0.07</td>
<td>-4.31 ± 0.06</td>
<td>2.80 ± 0.23</td>
<td>NdA₃(HA)₃ n-D</td>
<td></td>
</tr>
<tr>
<td>methyl isobutyl ketone</td>
<td>2.29</td>
<td>0.20 - 0.42</td>
<td>-4.53 ± 0.03</td>
<td>-4.51 ± 0.03</td>
<td>3.05 ± 0.16</td>
<td>NdA₃(HA)₃ n-D</td>
<td></td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>2.29</td>
<td>0.16 - 0.36</td>
<td>-3.82 ± 1.64</td>
<td>-4.68 ± 0.03</td>
<td>2.81 ± 0.16</td>
<td>NdA₃(HA)₃ i</td>
<td></td>
</tr>
<tr>
<td>Xylene</td>
<td>2.29</td>
<td>0.22 - 0.33</td>
<td>-4.83 ± 0.02</td>
<td>-4.74 ± 0.01</td>
<td>3.16 ± 0.12</td>
<td>NdA₃(HA)₃ (\pi)-D</td>
<td></td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>2.29</td>
<td>0.12 - 0.20</td>
<td>-4.94 ± 0.08</td>
<td>-4.85 ± 0.08</td>
<td>3.11 ± 0.48</td>
<td>NdA₃(HA)₃ (\pi)-D</td>
<td></td>
</tr>
<tr>
<td>1,3,5-trimethylbenzene</td>
<td>2.29</td>
<td>0.19 - 0.33</td>
<td>-4.68 ± 0.04</td>
<td>-4.89 ± 0.03</td>
<td>2.64 ± 0.17</td>
<td>NdA₃(HA)₂ (\pi)-D</td>
<td></td>
</tr>
<tr>
<td>o-dichlorobenzene</td>
<td>2.29</td>
<td>0.11 - 0.26</td>
<td>-4.75 ± 0.08</td>
<td>-4.91 ± 0.08</td>
<td>2.79 ± 0.31</td>
<td>NdA₃(HA)₃ (\pi)-D</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>2.29</td>
<td>0.20 - 0.39</td>
<td>-4.90 ± 0.13</td>
<td>-5.03 ± 0.10</td>
<td>2.85 ± 0.09</td>
<td>NdA₃(HA)₃ (\pi)-D</td>
<td></td>
</tr>
<tr>
<td>n-dodecane</td>
<td>2.29</td>
<td>0.06 - 0.16</td>
<td>-4.53 ± 0.10</td>
<td>-5.12 ± 0.02</td>
<td>2.40 ± 0.06</td>
<td>NdA₃(HA)₂ i</td>
<td></td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>2.29</td>
<td>0.11 - 0.17</td>
<td>-4.04 ± 2.02</td>
<td>-5.46 ± 0.01</td>
<td>2.43 ± 0.10</td>
<td>NdA₃(HA)₂ (\pi)-D</td>
<td></td>
</tr>
<tr>
<td>Chloroform</td>
<td>2.29</td>
<td>0.15 - 0.37</td>
<td>-6.17 ± 0.01</td>
<td>-6.13 ± 0.01</td>
<td>3.07 ± 0.02</td>
<td>NdA₃(HA)₃ A</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>2.29</td>
<td>0.20 - 0.40</td>
<td>-6.86 ± 0.04</td>
<td>-6.72 ± 0.03</td>
<td>3.25 ± 0.18</td>
<td>NdA₃(HA)₄ (\pi)-D</td>
<td></td>
</tr>
</tbody>
</table>

Table 34. Equilibria constants of extraction of Am by HEHEHP for 0.1 mol L⁻¹ Na-HNO₃ at 25°C ± 1°C. \(K_a\) represent the equilibrium constant considering only the complex Am(HA)₃. \(K'_{ex}\) consider the average ligand number. \(\bar{n}\). Complex* refer to the largest portion of complex considering the average ligand number. Type of solvent: i = inert, D = donor, A = acceptor.
3.3.2.4 Spectroscopic Data

3.3.2.4.1 Europium Luminescence

A large fraction of the lanthanides cations exhibit luminescence, emitting radiation from an excited electronic state; the emitted light shows a relatively good resolution (sharp lines) characteristic of an f-f transition. The process occurs as summarized in Figure 3-5.

![Figure 3-5. Luminescence in lanthanide complexes](image)

The luminescence mechanism of a lanthanide metal chelate is as follows: a quantum of energy from an excitation beam promotes an electron into an excited state. This electron drops back to the lowest state of the excited singlet, from where it can return either to the ground state directly through a ligand fluorescence process or follow a non-radiative path to a triplet state of ligand. From this triplet state, it may either return to the ground state (phosphorescence) or undergo non-radiative intersystem crossing to the nearby excited state of the metal cation. It can then return to the ground state either by non-radiative emission or by metal ion fluorescence. Certain
lanthanide(III) cations have excited states lying at lower energy than the triplet states of the typical ligands and exhibit a strong luminescence, most markedly for europium(III), emitting a red-purple light during luminescence - **Figure 3-6.** The main emissions responsible are the $^5D_0 \rightarrow ^7F_n (n=4-0)$ with the transitions to $^7F_0$, $^7F_1$, and $^7F_2$ the most useful. The $^5D_0 \rightarrow ^7F_0$ and $^5D_0 \rightarrow ^7F_1$ (magnetic dipole transitions) and $^5D_0 \rightarrow ^7F_2$ (hypersensitive electric dipole transition) are the transitions that are the most affected by the local symmetry around the metal center.

![Figure 3-6](image1.jpg)

**Figure 3-6.** Europium luminescence under 245 nm excitation beam, left: europium(III) nitrate hexahydrate crystals, right: europium(III) oxide powder.

Study of the intensity and splitting pattern of certain transitions in the luminescence spectra of compound of Eu$^{3+}$ can give a useful information about the environment of the metal. The rules are summarized in the **Table 3-5.**
Table 3-5. Feature of the $^5D_0 \rightarrow ^7D_n$ luminescence transition for Eu$^{3+}$

<table>
<thead>
<tr>
<th>Transition</th>
<th>Wavelength (nm)</th>
<th>Relative intensity</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^5D_0 \rightarrow ^7F_0$</td>
<td>570–585</td>
<td>vw to s</td>
<td>Only observed in $C_n$, $C_{nv}$ and $C_s$ symmetry</td>
</tr>
<tr>
<td>$^5D_0 \rightarrow ^7F_1$</td>
<td>585–600</td>
<td>s</td>
<td>Intensity largely independent of environment</td>
</tr>
<tr>
<td>$^5D_0 \rightarrow ^7F_2$</td>
<td>610–630</td>
<td>s to vs</td>
<td>Hypersensitive transition; intensity very strongly dependent on environment</td>
</tr>
</tbody>
</table>

An example of europium(III) emission spectrum of the Eu-HEH[EHP] metal chelate is shown in Figure 3-7. In this figure the use of the first derivative is shown to emphasize the detection of the $^5D_0 \rightarrow ^7F_0$ transition (in green).

**Figure 3-7.** Red: example of a luminescence from an Eu-HEH[EHP] metal chelate in $n$-octane, excitation wavelength 393 nm, approx of 0.5 mmol·L$^{-1}$ of metal chelate extracted by 0.1 mol·L$^{-1}$ HEH[EHP], light red: first derivative of the luminescence spectra used to detect the $^5D_0 \rightarrow ^7F_{(0,2)}$ transitions.
The europium(III) phosphorescence spectra of the Eu-HA complexes are shown in Figure 3-8. The fact that the intensity of the $^5D_0 \rightarrow ^7F_2$ transition is higher than $^5D_0 \rightarrow ^7F_1$ is an indication that the symmetry around the metal center is low and deviation arises from an inversion center.[23] The fact that $^5D_0$ and $^7F_0$ levels are non-degenerate, since both the emitting and end states are non-degenerate, its number of components indicates the number of metal ion sites.[24] The splitting of the $^5D_0 \rightarrow ^7F_0$ indicates that the europium ion occupies two or more non-equivalent sites.[23]

Figure 3-8. Luminescence from an Eu-HEH[EHP] metal chelate in TCE (black), n-octane (red), toluene (blue), MIBK (green), chloroform (purple). Excitation wavelength 393 nm, approx 0.5 mmol·L$^{-1}$ of metal chelate extracted by 0.1 mol·L$^{-1}$ HEH[EHP], $^5D_0 \rightarrow ^7F_{0,2}$ transitions.
3.3.2.4.2 Neodymium Absorption

In contrast to the 3d transition metals, the 4f-4f transition in the electronic spectra of lanthanide spectra of lanthanide metal chelate is rarely used for analytical purposes. It also must be specified that the octahedral ion has very low extinction coefficients, due to the relatively high symmetry of the environment (relative to the aquo ion).\textsuperscript{[21]}

Some transitions are “hypersensitive” to any change in the environment, especially due to a change in the symmetry and the strength in the ligand field. Any change in the environment may induce a shift in the absorption band, as well as a band splitting and intensity variation.\textsuperscript{[21]} For the Nd\textsuperscript{3+} the most marked transition is the \( ^4I_{9/2} \rightarrow ^4G_{5/2}, ^4G_{7/2} \). The splitting of the \( ^4I_{9/2} \rightarrow ^4G_{5/2}, ^4G_{7/2} \) transition into six bands when Nd(III) is complexed in an octahedral environment has been reported.\textsuperscript{[25],[26]}

An example of Neodymium(III) spectrum of the Nd-HEH[EHP] metal chelate is shown in Figure 3-9. In this figure, the use of the first derivative the 6 peaks are visible to empathize the detection of the \( ^4I_{9/2} \rightarrow ^4G_{5/2}, ^4G_{7/2} \) transition.
On the basis of small-angle neutron scattering (SANS) investigations, Jensen et al.\textsuperscript{[27]} and Grimes et al.\textsuperscript{[18],[28]} proposed the formation of the dimeric species Ln\textsubscript{2}A\textsubscript{6} when the [HA]/[Ln\textsubscript{org}] molar ratio is around 10, using the following mechanism:

\[ 2\text{Ln}^{3+} + 3(\text{HA})_{2} \rightleftharpoons \text{Ln}_{2}A_{6} + 6\text{H}^{+} \quad (3.13) \]
Figure 3-10. Visible absorption of Nd-HEH[EHP] metal chelate in $n$-octane organic phase at different metal loading condition, mononuclear metal chelate in red, 3rd phase in black

A Nd saturated HEH[EHP] solution was created to obtain a spectrum of a third phase. To do so, an $n$-octane solution of 100 mmol·L⁻¹ HEH[EHP] was contacted with saturated aqueous Nd(NO₃)₃ solution for 30 min, centrifuged, and the aqueous phase changed with a fresh saturated aqueous Nd(NO₃)₃. The process was repeated 3 times. Visual observation of a gel-like layer at the interface between the aqueous and the organic phases verified the formation of a third phase. The Figure 3-10 displays the difference of spectrum between a mononuclear complex of Nd-HEH[EHP] and the third phase composed mostly of polymeric NdₐAₐ(HA)ₘ specie.
Figure 3-11. Neodymium-HEH[EHP] metal chelate visible molar absorptivity in different diluent: Toluene (black), \( n \)-octane (red), MIBK (blue), TCE (green), chloroform (purple). Other information in the Table 3-6.

In this study the metal loadings were kept as low as possible (represented by elevated \([HA]/[Ln]_{\text{org}}\) molar ratio). Since Grimes et al started to observe a measurable amount of the dimeric specie with a \([HA]/[Ln]_{\text{org}}\) ratio of 7.7 for a Gd-HDEHP metal chelate in \( p \)-xylene, and almost non measurable amount of dimeric species with a \([HA]/[Ln]_{\text{org}}\) ratio of 20.1, it has been hypothesized in this work that if the \([HA]/[Nd]_{\text{org}}\) is kept above 20, the species should be exclusively mono metallic.\[^{18},^{28}\] The information on the metal loading are given in Table 3-6.
### Table 3-6. Organic phase Nd(III) metal loading information

<table>
<thead>
<tr>
<th>Diluent</th>
<th>[Nd]$_{org}$ (mmol·L$^{-1}$)</th>
<th>[HA]/[Nd]$_{org}$</th>
<th>$\varepsilon_{574}/\varepsilon_{566}$</th>
<th>$\varepsilon_{580}/\varepsilon_{566}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCE</td>
<td>10.8</td>
<td>46.0</td>
<td>0.227</td>
<td>0.70</td>
</tr>
<tr>
<td>Toluene</td>
<td>7.9</td>
<td>64.6</td>
<td>0.217</td>
<td>0.65</td>
</tr>
<tr>
<td>n-octane</td>
<td>17.8</td>
<td>28.0</td>
<td>0.225</td>
<td>0.67</td>
</tr>
<tr>
<td>MIBK</td>
<td>10.4</td>
<td>48.2</td>
<td>0.383</td>
<td>0.84</td>
</tr>
<tr>
<td>chloroform</td>
<td>4.07</td>
<td>122.7</td>
<td>0.215</td>
<td>0.65</td>
</tr>
</tbody>
</table>

**Figure 3-11** displays the molar absorptivity of the organic Nd(III)-HEH[EHP] metal chelate in different diluents. All of the spectra indicate that the six bands in the hypersensitive region are consistent with the distorted octahedral structure.$^{[27][25]}$ Lumetta *et al.* proposed to use the $\varepsilon_{580}/\varepsilon_{566}$ intensity ratio to characterize the consistency in the metal center environment.$^{[25]}$ The consistency of the $\varepsilon_{580}/\varepsilon_{566}$ and $\varepsilon_{574}/\varepsilon_{566}$ ratio in all diluents beside MIBK indicate that a pseudo-octahedron of six oxygen atoms around the Nd(III) center persists across all diluents. On the other hand, the MIBK spectrum seems to be an obvious outlier in the resolution of peaks in the spectra (higher $\varepsilon_{574}/\varepsilon_{566}$ ratio). This probably indicates that MIBK participates as a ligand, forming a mixed ligand system, with a lower symmetry system through the carbonyl group of the MIBK group:

$$
\text{Nd}^{3+} + \frac{3+n}{2}(\text{HA}) + (3-n)S \rightleftharpoons \text{NdA}_3(\text{HA})_nS_{(3-n)} + 3\text{H}^+ \quad (3.14)
$$

where S is representing a molecule of MIBK. However since the spectrum obtained in MIBK is significantly different from the 3$^{rd}$ phase spectra from **Figure 3-10**, it is safe to assume that the species formed in MIBK are not polymeric.
3.4 Discussion

3.4.1 Spectroscopies of the Metal Chelates

The spectrophotometric spectra of Ln-HEH[EHP] metal chelates in each families of diluents were taken to assess potential variation on the Ln-O bonding mode in the first coordination sphere of the metal centers. The europium first coordination sphere was probed using luminescence and the neodymium bonding environment was probed using visible absorption.

For the europium metal chelates, the spectra were identical, suggesting that the diluents do not directly influence the primary coordination sphere of the metal center. This also suggests that the europium metal center stays in an octahedral mode, with six oxygen atoms coordinated in the primary coordination sphere regardless of the diluent used. However, these spectra do not eliminate the possibility of changes in the extractant dependency/stoichiometry further from the metal center, for example, in the “outer” coordination sphere. Which means that those spectra might not be able to differentiate the 4 atoms chelate ring from the 8 atoms chelate ring – Figure 3-12.

![Figure 3-12. Possible chelate rings around the metal center, left 4 atoms chelate ring, right 8 atoms chelate ring](image-url)
From the europium luminescence, it seems that both binding modes are virtually equivalent. One of the most interesting insights gained from the luminescence of europium is given by the splitting of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition into 3 peaks. This splitting may indicate that the europium ion occupies three non-equivalent sites.\[23\] Assuming all binding methods are inequivalent, there are three possible symmetry environments in the first coordination sphere, the *facial*, $\Delta$-meridional and $\Lambda$-meridional orientations\[29\][30] – Figure 3-13

![Diagram showing facial, Delta, and Lambda meridional orientations](image)

*Figure 3-13.* Octahedral isomers, left: facial isomer, center: left-handed $\Delta$-meridional isomers, right: right-handed $\Lambda$-meridional isomer. In blue the ionic binding of $\text{Eu}^{3+}--\text{O}=\text{P}$, in red the ion-dipole interaction $\text{Eu}^{3+}--\text{O}=\text{P}$, in black dash the chelate rings.

For the neodymium metal chelates, the molar absorptivity spectra were identical for all diluents, beside MIBK, suggesting that these diluents do not directly influence the primary coordination sphere of the metal center. However, all spectra showed an octahedral coordination suggesting that the neodymium metal center stays in an octahedral mode regardless of the diluent, with six oxygen atoms coordinated in the primary coordination sphere. The main difference between MIBK and the other diluents resides in the resolution between each band. A loss in the resolution may suggest a reduction in the symmetry around the metal center. This could be explained by the suppression
of the ion-dipole interaction between the Nd metal center and the phosphoryl group (\(\text{Nd}--\text{O}=\text{P(OH)(OR)(R)}\)) - Figure 3-14.

![Figure 3-14](image)

**Figure 3-14.** Possible coordination modes around the neodymium metal center, left 3 atoms chelate ring, center 7 atoms chelate ring, right no ring with a molecule of MIBK coordinated in the first coordination sphere.

3.4.2 Free Energy of Extraction

Owing to the lack of other stable oxidation states of the lanthanides and americium, the complexation behavior of the 4\(f\) and 5\(f\) series of elements can be compared. It is often instructive to establish a relationship between assemblies of thermodynamic data through a comparison of the Gibbs energy that describes the overall reaction. Such “Linear Free Energy Relationships” have been employed with useful results in several correlations of \(f\)-elements data. Each plot has been fit using an unweighted linear fit.

The deviation from the expected equilibria for chloroform and tetralin for Eu\(^{3+}\) extraction by HEH[EHP] was already pointed in a published study. The linear Gibbs energy relationship between the data reported by Kolarik on di-octyl phosphoric acid extraction into various diluent
and the equivalent results is represented in the Figure 3-16. The HDOP results overlap with this study on the eleven diluents common to the two studies (the aqueous media differ somewhat (0.1 mol·L⁻¹ vs. 1.0 mol·L⁻¹ nitrate media)). The linear correlation is acceptable for the more common diluents, deviating most significantly for chloroform and nitrobenzene. The linear Gibbs energy plots shows also that HEH[EHP] seems to be around a 30% stronger extractant than DOP.

Figure 3-15. Chemical structure of di-octyl phosphoric acid

Figure 3-16. Linear Gibbs energy plots of Eu³⁺ extraction equilibrium data. Correlation between the Gibbs energy of extraction of Eu³⁺ by di-octyl phosphoric acid (HDOP) and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) in various diluents. Red: inert diluents (aliphatic hydrocarbon), green : aromatic diluents, purple: n-donors.
Figure 3-17 represents the linear Gibbs energy plot between the log $K_{ex}^*$ of Eu$^{3+}$ and Tm$^{3+}$. The linear correlation is acceptable for the more common diluents, deviating most significantly for chloroform and tetralin (removed from the plot). Furthermore in Figure 3-17, the data indicate a statistical 8% stronger bonding with HEH[EHP] for the Tm$^{3+}$ relative to the Eu$^{3+}$. Figure 3-18 is a linear Gibbs energy plot of Eu$^{3+}$ and Tb$^{3+}$ extraction equilibrium data from Kolarik’s tabulated data.[6] Figure 3-19 represents the linear Gibbs energy plot between the log $K_{ex}^*$ of Nd$^+$ and Am$^{3+}$. 

![Figure 3-17. Linear Gibbs energy plot of Eu$^{3+}$ and Tm$^{3+}$ extraction by HEH[EHP] from nitrate media (H-Na)HNO$_3$ $\mu = 0.1$ mol·L$^{-1}$ at $T = 25^\circ$C – data from Table 3-1 and Table 3-2 Red: inert diluents (aliphatic hydrocarbon), green: aromatic diluents, purple: n-donors](image-url)
Figure 3-18. Linear Gibbs energy plot of Eu\(^{3+}\) and Tb\(^{3+}\) extraction by HDOP from nitrate media (H-Na)NO\(_3\) \(\mu = 1.0\) mol·L\(^{-1}\) at \(T = 25^\circ\text{C}\), data from Kolarik - Table 1, ref: [6]. Red: inert diluents (aliphatic hydrocarbon), green: aromatic diluents, purple: n-donors, orange: acceptor.

Figure 3-19. Linear Gibbs energy plot of Nd\(^{3+}\) and Am\(^{3+}\) extraction by HEH[EHP] from nitrate media (H-Na)HNO\(_3\) \(\mu = 0.1\) mol·L\(^{-1}\) at \(T = 25^\circ\text{C}\) – data from Table 3-3 and Table 3-4. Red: inert diluents (aliphatic hydrocarbon), green: aromatic diluents, purple: n-donors, orange: acceptor.
Evidence for the strongly ionic character of the bonding is found from **Figure 3-16** to **Figure 3-19**. The experimental values fit for hard cations behavior, in accordance with the known chemistry of the \( f \)-elements.\[^{21}\] In the **Figure 3-19**, the data indicate a statistical 8% stronger bonding with HEH[EHP] for the Am\(^{3+} \) relative to the Nd\(^{3+} \). Since the ionic radii are equivalents, a covalent component can be suggested for Am-HEH[EHP] bonding. This behavior is noteworthy since the oxygen of the phosphoryl group is considered a hard Lewis acid. These linear plots are consistent with the hypothesis that the trivalent lanthanides and actinide bonding to acidic organophosphorus extractant can be described satisfactorily by an electrostatic model and thus that the extraction might be driven by this electrostatic model, according to Choppin.\[^{31}\][^32]\] However, even for these results, careful inspection of the data provides evidence of a difference in the extraction behavior as a function of the nature of the diluents used. This will be further discussed in the next chapter.
3.5 Conclusion

The effect of the organic diluent on the extraction of selected trivalent $f$-element by HEH[EHP] has been characterized in a large list of organic diluents with various functional groups, dielectric constant, polarizability, shape, and size. It appears that the number of extractant molecules in the complex changes, while the coordination mode (probed by spectrophotometry) and the number of protons exchanged for the Eu$^{3+}$ remains constant at three.

The log $K_{ex}$ value generally decreases as the diluent gains the ability to enter into hydrogen bonding with the extractant or the extracted metal complex, in accord with the following trend described by Kolarik and Andrew et al[6][19]:

inert diluents > $n$-donor > $\pi$-donor > Acceptor.

There are many aspects of solvent extraction chemistry that were not taken into account in this work. For example, the dimerization of the extractant likely changes with the diluent ($K_2$). The interfacial behavior, $pK_a$, and the amount of water solubilized and nitrate in the organic phase are all diluent-dependent and will affect the extraction and dimerization equilibria. More studies to determine these and other organic phase parameters in a large variety of diluents would greatly assist in determining the exact origins of the diluent effect.
3.6 References


(16) Peppard, D. F.; Mason, G.; Lewey, S. Di N-Octyl Phosphinic Acid as a Selective Extractant for Metallic Cations, Selected M(III) and M(VI) Tracer Studies; 1965; Vol. 27.


CHAPTER FOUR

CHARACTERIZATION OF THE DILUENT EFFECT ON SOLVENT EXTRACTION OF Eu(III) BY HEH[EHP] AS FUNCTION OF FUNDAMENTAL CHEMICAL PROPERTIES OF THE DILUENTS

4.1 Introduction

There are many aspects of solution chemistry, and the effect of solvation in solution is one of the most fascinating. Since the solvent (diluent) is fundamental to solution chemistry, it is necessary to be familiar with their properties in order to understand their role and how they can be used to increase our degree of control on a system. In addition, solvent extraction has been referred to as the "ultimate solution chemistry experiment" due to its complexity, in general due to the cohabitation of two condensed phases in the same system.

In the previous chapter an extensive list of diluents were used to demonstrate the general impact of a diluent on the solvent extraction behavior of f-elements by an acidic organophosphorus extractant. In this chapter, special attention will be given, first, to the theory of the diluent effect, then a more detailed analysis will be done on the data from Chapter 3, tying it to information from the literature. The main objective of this chapter is to attempt to integrate all of the collected information to achieve a deeper understanding of the impact of the diluent on the solvent extraction processes, specifically focusing on an acidic organophosphorus extractant.

2 Personal quote from prof Ken Nash
4.2 Theory of Thermodynamics of the Solvation Process

The first aspect, and probably the most important one, that must be considered on the choice of a diluent is its ability to dissolve a solute through a solvation process. In order to study the solvation process, it is critical to first agree on a definition of this process. In 1984 Ben-Naim and Marcus defined the solvation process as\cite{1}:

"The process in which a particle of the solute is transferred at a given temperature and pressure from a fixed position in the ideal gas phase into a fixed position in the liquid phase in which it is solvated"

This definition is particularly interesting, as it emphasizes the phenomenology and the thermodynamic aspects of the process. This definition implies that a change must occurs in the diluent (creation of a “cavity”) for the particle to take place in within it, such as the rearrangement of the diluent molecules and if needed the other solute molecules.\cite{2}

Gibbs energy of solvation of a diluent particle in its own liquid (e.g., one molecule of ethanol is condensed in an ethanol media) is defined as\cite{3}\cite{4}:

$$\Delta_d G^\circ = -RT \cdot \ln \frac{pM}{RTd}$$  \hspace{1cm} (4.1)

where $p$ is the saturation vapor pressure, $M$ is the molar mass, $d$ the density, $R$ the ideal gas constant, and $T$ the absolute temperature. Solubility is often defined as the mole fraction of a solute $x_s$ at a given temperature, at the saturation point\cite{5}:

$$\Delta_{solution} G^\circ = -RT \cdot \ln x_s$$  \hspace{1cm} (4.2)
The $\Delta_{solution}G^\circ$ is interpreted as the difference between the Gibbs energy of solvation of the solute in the solvent and any Gibbs energy related to diluent-diluent interaction that is lost during the solvation process. It is necessary to furnish work against the cohesive force of the diluent, as the first stage of the solvation process is the creation of a cavity to accommodate the solute itself. **Figure 4-1** demonstrates a schematic representation of the cavitation process. Simply, the creation of an empty volume in the liquid is needed to provide space for the solute in the liquid. The total volume fraction of the solute takes into account any change in the volume to the system:

$$
\phi_s = \frac{1}{1 + \frac{V_d(1 - x_s)}{V_s}}
$$

(4.3)

where $V_d$ and $V_s$ are the molar volume of the diluent and the solute respectively, and $x_s$ being the mole fraction of the solute. In dilute solution, this parameter can be approximated to:

$$
\phi_s = [S] v_s
$$

(4.4)

where $[S]$ is the concentration of the solute S in mol·L$^{-1}$ and $v_s$ is the partial molar volume of the solute in the solution in L·mol$^{-1}$. The solvation of a solute molecule in a diluent affects the diluent-diluent interaction in addition to the solute-diluent interaction that takes place. Knowing that, it seem obvious that the forces that reside in the diluent itself, and *ipso facto* the properties of the diluents, are going to have a major role into the diluent effect.
Conceptually it is possible to decompose the solvation process into multiple steps:\(^5\):

1. First a cavity is formed, breaking down the cohesive forces of the diluent.
2. Then, dispersive forces are “switched on”, allowing any solute particle to be dispersed (regardless of the polarity, polarizability of the particle considered).
3. Then interactive forces a “switched on” to provide the interactive contributions (interaction of polar and polarizable molecule, electron and hydrogen donor and acceptor actions).

4.2.1 Cavitation

Each of these steps are interesting to consider, even if it is an approximation to separate them into distinct contributions, as it helps to articulate a better understanding of the overall process. When the cohesive forces of the diluent are low (weak diluent-diluent interaction), the Hildebrand’s solubility parameter concept provides a very useful equation with the Gibbs energy of cavitation:\(^6\):

\[
\Delta_{cav} G = A_{cav} V_s \delta_d^2
\]  

(4.5)

where \(A_{cav}\) is a proportionality coefficient, \(V_s\) is the molar volume of the solute, and \(\delta_d^2\) the cohesive energy density of the solvent. Thus, in a series of diluents for the same solute, the positive contribution of cavity formation to the free Gibbs energy of solvation increases with the square of the Hildebrand solubility parameter.

![Figure 4-1. Schematic representation of a cavitation process needed for the solvation process of a solute in a non-interacting diluent](image)
4.2.2 Dispersion

The contribution of the diluent to the dispersion of a large particle is negative (attractive force) and proportional to the surface area of the interacting molecules or to the number \( N \) of segment present and depends on their chemical nature. For classic molecule a segment may be a \(-\text{CH}_2-\), a \(-\text{CH}_3\), or a \(-\text{CH}=(\text{aromatic})\) or equivalents for oxygen, nitrogen, phosphorus atoms in a molecule.

\[
\Delta_{\text{disp}}G = \sum A_{isd} \cdot N_{id} \cdot N_{is} = A_\pi \cdot \pi
\]

where \( A_{isd} \) is the negative interaction Gibbs energy of the pair of segment \( i \), and the sum extend over all the different kind of segments. \( A_\pi \) being a proportionality coefficient, and \( \pi \) the polarizability of the diluent.

4.2.3 Interactive forces

There may be additional, specific, interactions between the solute and the diluent. Hydrogen bonding arise in protic diluents (e.g., water, alcohols) with very basic atoms with lone pair of electrons as hydrogen acceptor. Also, donor-acceptor bond adducts can be formed if the diluent presents a very basic and or acidic atom.

\[
\Delta_{\text{inter}}G = A_\alpha \cdot \alpha + A_\beta \cdot \beta
\]

with \( A_\alpha \) and \( A_\beta \) being proportionality coefficients, \( \alpha \) being hydrogen bond donation (acidity), and \( \beta \) for hydrogen bond acceptance (basicity).
Then the Gibbs energy could be summarized as:

$$\Delta_{solvation}G = \Delta_{cav}G + \Delta_{disp}G + \Delta_{inter}G$$  \hspace{1cm} (4.8)

4.3 Metrics and Objectives

In the past, few attempts have been made to try to relate the diluent effect to the properties of the diluent, with arguably the most successful being the study of Marcus in 1989.\textsuperscript{[7]} Generally, when the diluent effect (or more often called solvent effect in the literature) is carefully investigated, the phenomena studied may be chemical equilibria $K$, reaction rates $k$, and electromagnetic spectra. The classic methodology is to set up a scale based on one phenomenon (in general the logarithm of $K$ or $k$) plotted against a scale, with the ultimate objective to yield a mathematically significant correlation, usually a straight line. The slope of the line may then be interpreted as a “measure” of the susceptibility of the molecule or the reaction to changes in the particular solvent property on which the scale is based.

This modus operandi is often termed linear free energy relationship (LFER), since it seems to work better when the scales are based on the logarithm of $K$ (or $k$) which are related to the Gibbs energy of reaction:

$$\Delta_{reaction}G = -RT\ln K$$  \hspace{1cm} (4.9)
where $\Delta_{reaction}G$ is the Gibbs free energy of reaction, $R$ the ideal gas constant ($R = 8.314462 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), $T$ the temperature ($T = 25^\circ \text{C} = 298.15^\circ \text{K}$) and $K$ the equilibrium constant of the reaction. In the context of this chapter, the following equations are applied:

$$\Delta_{extraction}G^* = -RT \ln K_{ex}^*$$  \hspace{1cm} (4.11)

where $\Delta_{extraction}G^*$ is the Gibbs energy of extraction associated with the constant of extraction $K_{ex}^*$. Since diluent effect studies of a cation have been done in the same condition, regardless of the diluent used, it is possible the consider this equation to follow more precisely the diluent effect:\[8\]:

$$\Delta\Delta_{extraction}G^* = -RT \ln \frac{K_{ex}^*}{K_{ex}^0} = \Delta_{extraction}G^* - \Delta_{extraction}G^0$$  \hspace{1cm} (4.10)

where $\Delta\Delta_{extraction}G^*$ is the variation of the Gibbs energy of extraction from a reference and $\Delta_{extraction}G^0$ is an arbitrary Gibbs energy of extraction used as reference. For the remainder of this document, carbon tetrachloride (CCl$_4$) has been chosen to be the diluent of reference, due to its absence of polarity, symmetry, hardness (relative to the Marcus’s softness factor\[9\]) and rigidity.\[10\] This variation of the Gibbs energy is similar to the those used by Marcus\[7\] and Shmidt et al.\[8\]\[11\]. In their publication, Shmidt et al. related this variation in the $\Delta\Delta_{extraction}G^*$ to an empirical parameter they created based on observation, the parameter BP (from Влияние Растворителя, Solvent Influence in English). This parameter was obtained for the distribution of ZnCl$_2$ with tri-$n$-octyl-amine with different diluents.\[11\] It was the first important step into the development of a systematic quantitative approach in the study of diluent effects in solvent extraction, even though this parameter applied to a very limited number of systems\[11\].
Following Shmidt, a very large number of empirical parameters have been derived by chemists, with the objective to correlate the diluent properties (characterized by their scales) in the equilibria and rate. In all cases it appears that the effect of a given diluent seems to the sum of many properties, similar to the theory of solvation described by Marcus (section 4.2). Knowing that, it is safe to assume that

$$
\Delta \Delta_{\text{extraction}} G^* = \Delta \Delta_{\text{solvation}} G = \Delta \Delta_{\text{cav}} G + \Delta \Delta_{\text{disp}} G + \Delta \Delta_{\text{inter}} G
$$  \hspace{1cm} (4.11)

The statistical study made by Buncel et al. suggested that the $\Delta \Delta_{\text{cav}} G$ and $\Delta \Delta_{\text{disp}} G$ should be studied together and the $\Delta \Delta_{\text{inter}} G$ should be divided into two components, the acidic interactions and basic interactions.\[12\] According to the literature, the cavitation and dispersion mechanisms can be classified in the non-specific interaction diluent effect (also called general interaction).\[13\] In the non-specific interaction (NSI), each diluent is treated as a dielectric continuum. According to Marcus\[14\] and Stairs \[15\], it is reasonable to study NSI due to the cavitation and dispersion processes in the same time. According to literature, specific interaction (SI) can be described in term of donor-acceptor interactions. Drago described the SI as interactions involving orbitals by using electrostatic and covalence parameters.\[16\] However, more recent studies described SI in terms of acid-base hydrogen-bonding interactions.\[17\][18][19]

In the rest of this chapter, the equilibrium constant data from Chapter 3 are going to be investigated as a function of each of the components of the $\Delta \Delta_{\text{solvation}} G$, with the objective of understand how each parameter influences the solvation process. Non-Specific Interaction: Cavitation and Dispersion
4.3.1 Hildebrand Solubility Parameters

In Chapter 1 the solubility parameter has been described as the cohesive force that keeps molecules together. This solubility parameter is usually described by:

\[ \delta^2 = \frac{\Delta_{vap} H^\circ - RT}{V_m} \]  

(4.12)

where \( \delta^2 \) is the cohesive energy density, and \( \delta \), the Hildebrand solubility parameter, \( V_m \), the molar volume of the considered molecule, and \( \Delta_{vap} H^\circ \) the molar heat of vaporization. The molar volume information have been taken from the CRC Handbook\textsuperscript{[20]} and the molar heat of vaporization taken from the NIST Standard Reference Database Number 69\textsuperscript{[21]}. This equation is considered as true for a regular solution\textsuperscript{3} that shows ideal entropy effects in mixing solute and solvent and no interactions occur beside the cohesive forces between the solute and the solvent. For this equation to be true, it should not have any change of state in association or in orientation, which makes this an unlikely parameter to accurately characterize diluents that can coordinate to the metal chelate (i.e., n-donors) or diluents that can associate with the free extractants (i.e., n-donors, \( \pi \)-donors, and acceptors).

Figure 4-2 represents the correlation between the \( \Delta \Delta_{\text{extraction}} G^\ast \) of europium by HEH[EHP] (results of the extractions from the Chapter 3, Table 3.1) and the \( \delta^2 \). Multiple interesting features can be observed from this correlation. First, it seems that the higher the cohesive energy of a diluent, higher the energy of solvation of the europium metal chelate, with a slope of 63 ± 10 cm\(^3\)·mol\(^{-1}\) (\( R^2 = 0.68 \), nitrobenzene excluded). It appears that the inert diluents and the \( \pi \)-donor diluents form two independent groups, with a large variation within the inert diluents, in

---

\textsuperscript{3} Regular solutions exhibit heat changes when mixed, ideal solutions exhibit a heat of mixing of 0.
the range of $\delta^2 = 197 - 365 \text{ J} \cdot \text{cm}^3$ and a cluster of $\pi$-donors, in the range of $\delta^2 = 320 - 422 \text{ J} \cdot \text{cm}^3$ (1,3-diisopropylbenzene excluded). There are too few data to develop any correlation among the $n$-donors group or the acceptor group. A look at the inert diluents shows that the alkanes (red squares) seem to be a different behavioral group from the halogenated diluents (open red squares), and the variation in the inter alkanes seem increase with the molecular weight of the diluent. This could be explained by the rigidity of the diluent; the larger the diluent molecule, higher the degree of freedom.

![Figure 4-2. Correlation between the variation of the Gibbs energy of europium extraction in different diluents by HEH[EHP] (results from the extraction from the Chapter 3, Table 3.1, results relative to carbon tetrachloride) and the cohesive energy density calculated from equation (4.12)
This type of behavior suggests that the equilibria that are influenced by this parameter are equilibria that do not involve any association constant between the solutes (HA, (HA)$_2$, MA$_3$(HA)$_n$) and the diluent.

$$\text{HA} \rightarrow \text{HA}$$ \hspace{1cm} (4.13)

$$\text{(HA)}_2 \rightarrow 2 \text{HA}$$ \hspace{1cm} (4.14)

$$\text{MA}_3(\text{HA})_n \rightarrow \text{MA}_3(\text{HA})_n$$ \hspace{1cm} (4.15)

This behavior has been observed and heavily characterized and nicely correlated for β-Diketone extractants, for the equilibria (4.13) and (4.15).\textsuperscript{[22][23][24]} The scattering observed in their system could be attributed to potential diluent-solute interactions:\textsuperscript{[25]}

$$\text{HA} + \bar{S} \rightarrow \text{HA} \cdot \bar{S}$$ \hspace{1cm} (4.16)

4.3.2 Polarity Parameters

4.3.2.1 Polarity

The polarity of a diluent is commonly described using a macroscopic scale (corresponding to the polar properties of the bulk solvent) as a function of the relative permittivity of a medium composed exclusively of this molecule, and on a molecular scale by the electrical dipole and the dipole moment. Characterizing the diluent using macroscopic scales to describe the polarity, means that the diluent is treated as a continuum and it can well be replaced by an electric field.\textsuperscript{[26]}

111
The macroscopic scales do not take into account the interaction of the solutes with the solvent molecules that are necessary for the creation of the solvation shell around a solute. For that purpose, the molecular scales are more useful. The Debye function (also called “dielectric function”[13]) is the most common equation used to described polarity at a molecular scale: \[ f(\varepsilon_r) = \frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{\rho \cdot N_a}{3 \cdot M \cdot \varepsilon_0} \left( \frac{\pi}{3} + \frac{\mu^2}{3 \cdot k \cdot T} \right) \] (4.17)

where \( \varepsilon_r \) is the relative permittivity, \( \rho \) is the density, \( N_a \) is Avogadro’s number, \( M \) the molar mass, \( \varepsilon_0 \) is the permittivity in vacuum, \( \pi \) is the polarizability, \( \mu \) is the dipole moment, \( k \) is the Boltzmann constant, and \( T \) the temperature.

The Figure 4-3 is the correlation between the variation of the Gibbs energy of europium extraction in different diluents (relative to carbon tetrachloride) and the polarity of the diluent calculated from the Debye function using equation (4.17). The low polarity diluents \( f(\varepsilon_r) < 0.3 \) are composed exclusively of the inert diluents, and the Gibbs energy of extraction generally increases with the polarity of the diluent. At polarity \( f(\varepsilon_r) > 0.3 \), the relative Gibbs energy maintains a constant average within ± sigma of zero (or maybe -2 kJ/mol).
Figure 4-3. Correlation between the variation of the Gibbs energy of europium extraction in different diluents by HEH[EHP] (results from the extraction from the Chapter 3, Table 3.1, results relative to carbon tetrachloride) and the polarity of the diluent calculated from the Debye equation calculated using equation (4.17).

However, even if 1,3-diisopropylbenzene shows a low polarity for a π electron donating diluent, it is also showing an unusual low Gibbs free energy of extraction. On the other hand 1,3-diisopropylbenzene but also benzene, toluene, and xylenes fits perfectly with the rest of the $f(\varepsilon_r) < 0.3$ region, with a dependency of $132 \pm 25 \text{ kJ} \cdot \text{mol}^{-1}$ ($R^2 = 0.707$) – Figure 4-4.
4.3.2.2 Polarizability

It is important to specify that dipolar bonds in a molecule may act independently on the neighboring molecule, doing so some molecules that would appear to be non-polar, such as carbon dioxide, still exhibit a high polarity. The part of the electrical influence of a diluent on a solute that arises from the polarizability of the solvent is represented by the refractive index $n$, more specifically by function of $n$, such as the Lorenz-Lorenz function (also called “polarizability function”$^{[13]}$) $f(n^2)$ given by the equation (4.18)$^{[20][15][13][27]}$.
\[ f(n^2) = \frac{n^2 - 1}{n^2 + 2} = \pi \frac{\rho \cdot N_a}{3 \cdot M \cdot \varepsilon_0} \]  \hspace{1cm} (4.18)

where \( n \) is the refractive index of the diluent of the \( n \)-line from a sodium light, \( \pi \) the polarizability, \( \rho \) the density of the diluent, \( N_a \) the Avogadro number, \( M \) the molecular weight and \( \varepsilon_0 \) the dielectric permittivity of the vacuum. The correlation between the variation of the Gibbs energy of europium extraction in different diluents (relative to carbon tetrachloride) and the polarizability of the diluent calculated from the Lorenz-Lorenz function calculated using the equation (4.18) is shown in Figure 4.6. The correlation shows that increasing the polarizability of a diluent seems to proportionally increase the Gibbs energy of extraction of the metal chelate. However, Gibbs energy for decalin and 1,3-diisopropylbenzene are lower than expected.
Figure 4-5. Correlation between the variation of the Gibbs energy of europium extraction in different diluents by HEH[EHP] (results from the extraction from the Chapter 3, Table 3.1, results relative to carbon tetrachloride) and the polarizability of the diluent calculated from the Lorenz-Lorenz function calculated using the equation (4.18)

### 4.3.2.3 Dipole moment

The difference between Debye function $f(\varepsilon_r)$ and the Lorenz-Lorenz function $f(n^2)$ can be used to describe a polarity that is distinct from the polarizability.$^{[20][15][28]}$ This function obtained is called the dipolar field function, $f(\varepsilon_r,n^2)$.$^{[15]}$

$$f(n^2,\varepsilon_r) = \frac{\varepsilon_r - 1}{\varepsilon_r + 2} - \frac{n^2 - 1}{n^2 + 2} = \mu^2 \frac{\rho \cdot N_a}{9 \cdot M \cdot \varepsilon_0 \cdot k \cdot T}$$  \hspace{1cm} (4.19)
where \( \varepsilon_r \) is the relative dielectric permittivity of the diluent, \( \mu \) the dipole moment, \( k \) the Boltzmann constant and \( T \) the absolute temperature. The difference is mostly dependent on the dipole moment.

The **Figure 4-6** represents the correlation between the variation of the Gibbs energy of europium extraction by HEH[EHP] in different diluents (relative to carbon tetrachloride) and the polarity of the diluent based on the dipole moment using the dipolar field function calculated with equation (4.19). Based on this figure it seems that the Gibbs energy of extraction is independent of the dipole moment of the diluent molecules. Also, the group of diluents that are completely non-polar (have no dipole moment) seem to correspond to the group of diluents showing a linear fit with the Debye function. Based on the **Figure 4-6**, it seem that the variation of the Gibbs energy of extraction to be completely independent of the dipole moment.
Figure 4-6. Correlation between the variation of the Gibbs energy of europium extraction in different diluents by HEH[EHP] (results from the extraction from the Chapter 3, Table 3.1, results relative to carbon tetrachloride) and the polarity of the diluent based on the dipole moment using the dipolar field function calculated with equation (4.19)

4.3.3 Hansen Solubility Parameters

Recently, the cavitation/dispersion property of a diluent and its impact on the solvent extraction processes have been refined by the use of the Hansen solubility parameters according to which:

$$\delta_{Hansen}^2 = \delta_{disp}^2 + \delta_{polar}^2 + \delta_H^2$$  (4.20)
where the Hansen solubility representing the interaction between solute and diluent, and is describe
the addition of various type of cohesive forces. In general, dispersion dominates and are
described as London dispersion parameters. The Hildebrand and the Hansen theory diverge in
the matter that when Hildebrand developed his equation, his theory was mostly based on the
behavior of lower polarity hydrocarbons, without considering the importance of hydrogen bonding
and carboxyl groups. Figure 4-7 demonstrates the correlation between the variation of the
Gibbs energy of europium extraction by HEH[EHP] in different diluents (relative to carbon
tetrachloride) and tabulated Hansen solubility parameters from reference [30].

Figure 4-7. Correlation between the variation of the Gibbs energy of europium extraction in different diluents by HEH[EHP] (results from the extraction from the Chapter 3, Table 3.1, results relative to carbon tetrachloride) and tabulated Hansen solubility parameters from reference [30].
The inert family of diluents (red in the Figure 4-7) shows a correlation between the $\delta^2_{\text{Hansen}}$ and the Gibbs free energy of extraction of europium (slope = 0.0380 ± 0.0021 kJ·mol$^{-1}$·MPa$^{-1}$, $R^2 = 0.971$). However, the other families of diluents do not show any correlation. Interestingly, nitrobenzene and 1,3-diisopropylbenzene are aligned on the inert diluent trend.

4.4 Specific Interactions: Solvatochromic parameters

The solvatochromism is the ability of a chemical substance to change color due to a change in the solvent properties, such as polarity, or acidity and basicity.$^{[31]}$ The solvatochromic effect or solvatochromic shift refers to a strong dependence of absorption and emission spectra with the solvent properties. Since polarities of the ground and excited state of a chromophore are different, a change in the solvent polarity will lead to different stabilization of the ground and excited states, and thus, a change in the energy gap between these electronic states. Consequently, variations in the position, intensity, and shape of the absorption spectra can be direct measures of the specific interactions between the solute and solvent molecules.$^{[32]}$

![Figure 4-8. Schematic representation of a ground state property of a solvatochromic molecule](image)
The solvatochromic molecules are interesting in the context of this study because they can probe specific solvent interactions with the solute (rather than a solvent-solvent interactions such as the Hildebrand solubility parameter). According to Drago, the solvatochromic diluent effect is a good tool to study different SI depending on the probe used to characterize it.

4.4.1 Diluent Basicity (DN, β, and SB scales)

The SI of a diluent can be described in a large part to their ability to interact in a specific manner with the solute. This may take place by the donation of a non-bonding pair of electrons from a donor atom of the diluent toward an accepting group in the solute. This interaction of often referred as Lewis basicity.

Several methods have been proposed over the years to express this Lewis basicity property, however very few have been proven to show any utility. In the early studies of the diluent basicity, the donor number scale (DN) has been developed in the 60’s by Gutman et al. This DN scale was determined calorimetrically, using the heat of reaction of the diluent with antimony pentachloride in dilute solution. This scale has been “largely” expanded using spectroscopic methods with diacetylacetonatooxovanadium(IV) as an accepting probe - Figure 4-9.

![Figure 4-9](image-url) Schematic representation of diacetylacetonatooxovanadium(IV) used as DN probe by Gutman et al.
For this chromophore, it is assumed that the donating group of a diluent molecule in going to coordinate in the base of the square pyramidal of the diacetylacetonatooxovanadium(IV) (indicated by the arrow in the Figure 4-9) to form an octahedral vanadium(IV) complex. Figure 4-10 represents the correlation between the variations of the Gibbs energy of europium extraction in different diluents (relative to carbon tetrachloride) and tabulated DN\cite{33}.

![Graph](image)

**Figure 4-10.** Correlation between the variations of the Gibbs free energy of europium extraction in different diluents by HEH[EHP] (results from the extraction from the Chapter 3, Table 3.1, results relative to carbon tetrachloride) and tabulated DN from reference [33]. The slope is the fit result, excluding the inert diluents.
On the DN scale, the inert diluents all have a DN of 0, implying, as expected that the inert diluent family does not give any electrons, showing no Lewis basicity character. The remaining diluents show a DN > 0, where the variations of the Gibbs energy of extraction of Eu\(^{3+}\) by HEH[EHP] becomes more favorable (\(\Delta G < 0\)) proportionally to DN, with a slope of \(-1.30 \pm 0.20\) (\(R^2 = 0.648\)). Another solvatochromic scale has been created by Kamlet and Taft, the \(\beta\) scale. This scale is based on the averaged quantity, for which that wavenumber of different protic chromophores shift in function of the diluent. The interesting feature of this scale is that the effect the diluent on a chromophore can be impacted by specific interactions but also nonspecific interactions, especially from the polarizability. The chromophore used was studied in parallel with aprotic equivalent, to correct for the polarizability - Figure 4-11.\(^{[17][33]}\)

![Chemical Structures](image)

**Figure 4-11.** Schematic representation of the solvatochromic chromophore used for the determination of the \(\beta\) scale. Top left 4-nitrophenol, top right 4-nitroanisol, bottom left 4-nitroaniline, bottom right 4-nitro-N,N-diethylaniline

This \(\beta\) scale is by far the most popular scale of diluent hydrogen donor properties. Figure 4-12 represent the correlation between the variations of the Gibbs energy of europium extraction in different diluents (relative to carbon tetrachloride) and tabulated \(\beta\).\(^{[33]}\) Based on the average of
multiple probes used and the inconsistency on the number of probes used by diluent, it is advised to use a uncertainty of ± 0.04 units on this scale.[33] One of the first interesting features to be observed is that, according to this scale, chlorinated diluents are classified as electron donors.

For the non-inert diluent family, it appears that the variations of the Gibbs free energy of extraction decreases proportionally to the $\beta$ factor, with a slope of $-10.50 \pm 2.29$ ($R^2 = 0.699$) - **Figure 4-12**. This result shows an improvement from the DN scale (based on the $R^2$). This is probably due to a combination of the higher number of solvents tabulated, presence of error bars on the $\beta$ scale, and...
the stronger basicity character of methyl-isobutyl-ketone, based on the \( \beta \) scale. However, it is interesting to note that the \( R^2 \) decreases to 0.666 if the error bars on the \( \beta \) scale are removed.

The scale developed by Catalán \textit{et al.} is called the SB scale (SB standing for Solvent Basicity).\textsuperscript{[35]} This scale is based on the solvatochromism of 5-nitroindolin compared to 1-methyl-5-nitroindolin (Figure 4-13), with the advantage that the N-H acid function of the 5-nitroindoline probe has only one hydrogen.

![5-nitroindoline 1-methyl-5-nitroindoline](image)

**Figure 4-13.** Schematic representation of the solvatochromic chromophore used for the determination of the SB scale. Left 5-nitroindoline, right 1-methyl-5-nitroindoline

However since this scale has been created recently, the application of this scale is not yet common in the literature. This scale shows a surprising variation in the basic character of the inert alkane diluents, which has not yet been explained. Figure 4-14 represents the correlation between the variations of the Gibbs energy of europium extraction in different diluents (relative to carbon tetrachloride) and tabulated SB.\textsuperscript{[35]} Similar to the DN and \( \beta \) scales, the correlation using the SB scale shows a relatively good dependency for the non-inert diluents, with a slope of \(-9.68 \pm 2.48\) (\( R^2 = 0.49 \)), in red in Figure 4-14. On this correlation, it is clear that chlorobenzene and fluorobenzene are outliers. Catalán already observed surprising results with these diluents, and assimilated this to an electron withdrawing effect. Since this electron withdrawing effect has never
been rationalized and “corrected”, it has also been excluded from a second fit, producing a slope of \(-9.78 \pm 1.56\) \((R^2 = 0.81)\) – in green in **Figure 4-14**.

**Figure 4-14.** Correlation between the variations of the Gibbs free energy of europium extraction by HEH[EHP] in different diluents (relative to carbon tetrachloride) and tabulated SB from reference [35].
4.4.2 Diluent Acidity

Acidic diluents are often described as diluents that express the ability to form a hydrogen bond by accepting an electron pair of a donor atom from a solute molecule. In the early studies of this diluent property, the acceptor number scale (AN) has been developed in the 70’s by Mayer et al.\textsuperscript{[36][33]} This parameter was determined by probing the NMR chemical shift of the $^{31}$P atom of TBP in different diluents. Unfortunately this parameter has a major defect to be also influenced in the same time by the dipolarity and polarizability of the diluent.\textsuperscript{[33]} Kamlet and Taft developed a scale (the α scale) that was designed to be devoid of contribution from the polarity. This scale is based on the average of different solvatochromic probes. Unfortunately, because of the plurality of the probes used, the α scale suffer of a very large uncertainty.\textsuperscript{[17]}

In more recent study, Catalán and co-workers proposed a new scale (SA) using butylstilbazonium solvatochromic dyes.

![Schematic representation of butylstilbazolium molecule](image)

\textbf{Figure 4-15.} Schematic representation of butylstilbazolium molecule used as a solvatochromic chromophore by Catalán to develop the SA scale, where R and R’ can be either –H or –C(CH$_3$)$_3$

Unfortunately, since the number of diluents with tabulated values for those scale very low, it is impossible to draw any usable correlation, but this diluent property was considered pertinent enough to be cited in this dissertation.
4.5 Discussion on the Diluent Effect

4.5.1 Rationalization of the diluent properties on the equilibria

4.5.1.1 Associative properties

The extraction of a trivalent $f$-element by HEH[EHP] equilibrium has been demonstrated to be expressed by the following equilibrium$^{[37]}$:

$$M^{3+} + \frac{3+n}{2}(HA)_2 \rightleftharpoons MA_3(HA)_n + 3H^+ \quad (4.21)$$

with the equilibrium constant for this reaction is written as$^{[37][38]}$:

$$K^*_{ex} = \frac{[MA_3(HA)_n][H^+]^3}{[M^{3+}][(HA)_2]^{(3+n)/2}} \quad (4.22)$$

However, a more precise description of the solvent extraction can be formally written to occur in the following steps$^{[38][25][6]}$:

$$2(HA) \rightleftharpoons (HA)_2 \quad (K_2) \quad (4.23)$$

$$HA \rightleftharpoons HA \quad (K_d) \quad (4.24)$$

$$HA \rightleftharpoons H^+ + A^- \quad (K_a) \quad (4.25)$$

$$M^{3+} + 3A^- \rightleftharpoons MA_3 \quad (\beta_a) \quad (4.26)$$
\[ MA_3 \rightleftharpoons \bar{MA}_3 \quad (K_D) \quad (4.27) \]

\[ \bar{MA}_3 + n(HA) \rightleftharpoons \bar{MA}_3(HA)_n \quad (\beta_o) \quad (4.28) \]

The equilibrium constant of this reaction is connected with those of the different steps as\textsuperscript{[38]}:

\[ K_{ex}^o = \frac{1}{K_{2.15}^D \cdot K_d^3 \cdot K_a^3 \cdot \beta_a \cdot K_D \cdot \beta_o} \quad (4.29) \]

Here the contribution of the dehydration is assumed to be the same in all system, therefore is not taken into account here. However, as mentioned previously, the diluent is capable of influencing markedly the extraction processes. Due to the hydroxyl group and the phosphoryl groups in the HEH[EHP] extractant, the following equilibria could be considered for a Lewis acid/base adduct formation:\textsuperscript{[38][25]}

\[ \bar{HA} + \bar{S} \rightleftharpoons \bar{HA} \cdot \bar{S} \quad (K_s) \quad (4.30) \]

\[ \bar{MA}_3(HA)_n + xS \rightleftharpoons \bar{MA}_3 \cdot (HA)_n \cdot S_x \quad (\beta_x) \quad (4.31) \]

The Figure 4-16 represent the electrostatic potential mapping of the monomer and dimer molecule of HEH[EHP], HA and \((HA)_2\) obtained using Density Function Theory calculation on Gaussian.
The red and blue colors represent the non-zero potential and the green color represent the zero potential. The electrostatic mapping of HA and (HA)$_2$ shows that the hydroxyl (in blue) and the phosphoryl groups (in red) are especially susceptible to Lewis acid base interactions.

Figure 4-16. Molecular electrostatic potential maps of a HEH[EHP], top monomer, bottom dimer. The green surface are the surface with a zero potential, the red regions are hydrogen bonding acceptors, and the blue is hydrogen bonding donor.

However, even if the electrostatic mapping of the MA$_3$(HA)$_3$ has not been calculated, it is possible to assume that the accessible surface of complex would have a mostly zero potential (assuming a
negligible ligand exchange dynamic). This potential will then assume that $\beta_s$ is negligible in comparison of the other stability constants. Even if the $K_s$ is not known but assumed higher than zero, the equilibrium constants $K_2, K_a,$ and $\beta_o$ are apparent constants (henceforth $K_{2*}, K_{a*}$ and $\beta_{o*}$); their relation to the actual constant can be expressed as follow:\(^{25}\):

$$K_{2*} = K_2(K_s[\bar{S}] + 1)^{-2} \quad (4.32)$$

$$K_{a*} = K_a(K_s[\bar{S}] + 1) \quad (4.33)$$

$$\beta_{o*} = \beta_o(K_s[\bar{S}] + 1)^{-n} \quad (4.34)$$

Then, using the actual constant, the $K_{ex}^*$ can be expressed as follow:

$$K_{ex}^* = \frac{1}{K_{2*1.5} K_{a*3} K_{D*}^3 \cdot \beta_a \cdot \beta_{o*}} \quad (4.35)$$

and summarized as the following:\(^{25}\):

$$K_{ex}^* = K_{ex}^o (K_s[\bar{S}] + 1)^n \quad (4.36)$$

Then when adapted to the Gibbs energy of extraction the following equation can be obtained:

$$\Delta G_{ex}^* = -RT \cdot \ln K_{ex}^o - n \cdot RT \cdot \ln(K_s[\bar{S}] + 1) \quad (4.37)$$

Then when derived on the $K_s$ the following equation is obtained:
\[ \frac{d}{dK_s} \Delta G_{ex}^* = -\frac{nRT[S]}{(K_s[S] + 1)} \] (4.38)

From this equation, the variation of the Gibbs energy should decrease when \( K_s \) is larger than zero, which is consistent with the observations made with the associative properties scales – Section 4.4, Figure 4-10, Figure 4-12, and Figure 4-14. Also, according to Kolarik\(^{[39]}\) and Marcus\(^{[6]}\), the product \( K_2K_d \) should be approximatively constant for a given acidic organophosphorus extractant, regardless of the diluent used. This approximation allows a semi quantitative evaluation of the results. The higher \( K_s \) is, the lower the \( K_2^* \) is, and the higher \( K_d^* \) is, and consequently the lower the free ligand “in” the aqueous phase. Doing so there should be a decrease in the extraction of the metal chelate.\(^{[25]}\) The word “in” has been placed within quotation marks, because it has been demonstrated that HEH[EHP] is not soluble in the aqueous phase, but adsorbed at the interphase, with the \( \text{>P(=O)(O)H} \) group in the aqueous phase and the alkyl chains in the organic phase.\(^{[39][40]}\) However regardless of this subtlety, the description of the impact of the \( K_s \) in the extraction stays the same, since the diluents used are not appreciably water soluble. This semi quantitative description of the impact of \( K_s \) on the efficiency of extraction is also in agreement with the experimental values obtained compared to the basicity scales.

4.5.1.2 Cohesive properties

A closer look to the stability constants and at the mechanism involving solubility parameters (assuming that the swelling of a solute is negligible between both sides of a monophasic equation), it is possible to assume that the energy of cavitation for a monophasic equation is essentially zero in comparison to a biphasic system. Then, it is possible to assume that the percent swelling of the HEH[EHP] extractant without a proton or metal cation (so an EH[EHP]\(^-\) anion) is again close to
zero in the same phase, regardless of the cation bonded to the extractant. With all of these assumptions, it is possible to deduce that the energy of cavitation on the overall mechanism is probably driven by the difference of volume between a trivalent \( f \)-element cation\[^{41}\] (between +3.59 Å\(^3\) and +8.58 Å\(^3\) on the entire \( f \)-element series) and three protons\[^{41}\] (\(3 \times 0.23 \text{ Å}^3 = 0.69 \text{ Å}^3\)). The Gibbs energy of cavitation equation adapted to the overall system can be summarized as in the following equation:

\[
\Delta_{\text{cav-ex}} G = A_{\text{cav}} \cdot \Delta V_{\text{solute}} \cdot \delta^2
\]  

(4.39)

where \( \Delta V_{\text{solute}} \) is the difference of volume of solute in the same phase before and after the extraction. Using this equation, and assuming the \( \Delta V_{\text{solute}} \) being comprised between +4.28 Å\(^3\) and +9.27Å\(^3\), it is obvious that higher the cohesive energy of a phase and higher the energy of cavitation, the lower the distribution constant of a solute. This behavior has been summarized (at equi-volume) by Nilsson using the Hansen partial solubility parameter\[^{23}\][\(^{42}\)]:

\[
\Delta_d G_X = RT \ln K_{D,X} = V_X \left[ (\delta_{\text{aq}} - \delta_X)^2 - (\delta_{\text{org}} - \delta_X)^2 \right]
\]  

(4.40)

Using this equation to the variation of Gibbs energy from a standard diluent the variation of energy of cavitation can be summarized as in the following equation\[^{42}\]:

\[
\Delta\Delta_d G_X = V_X \left[ \delta_{\text{org}}^2 - \delta_{\text{org}}^o \right]^2 + 2\delta_X (\delta_{\text{org}}^o - \delta_{\text{org}})
\]  

(4.41)
Then when derived on the solubility parameter of the organic phase:

\[
\frac{d}{d\delta_{org}} \Delta \Delta G_X = 2V_X(\delta_{org} - \delta_X)
\]  

(4.42)

Assuming then that \(\delta_X\) is always smaller than \(\delta_{org}\) (due to the Coulombic repulsion of a charged particle) it is safe to assume that this derivative is always positive. This behavior seems to be in accord with the experimental observations in the variation of \(\Delta\Delta G_{ex}\) as a function of the cohesive parameters (Hildebrand and Hansen solubility parameters and the polarizability parameters).

4.5.2 Assumptions made and Future Work.

4.5.2.1 Assumptions

For the objective of this chapter, a couple of assumptions had to be made to be able to use the different scales from literature applied to this research. One major assumption was that even if the scales values used in this chapter were determined as a pure diluent value, the scale would still be valid in the presence of solute. However this assumption is most likely to be wrong since most of the non-inert diluents can extract water by themselves; HEH[EHP] can also extract water. Doing so the fraction of water is most likely to change the bulk properties of the solvent creating extra interferences with the model of the system.\(^4\) The same assumption has been made with the solute itself. In some cases (especially the non-inert diluent) the volume fraction of HEH[EHP] was comparable to the total volume of the organic phase, doing so it also interferes with the bulk diluent scale value used for this analysis (at the larger concentrations, the volume fraction of HEH[EHP] was about 30%).

\(^4\) Personal correspondence with professor Christian Ekberg from the Chalmers University of Technology (Sweden)
Furthermore, one most important concern that comes from those scales is to know if the values of compound determined in bulk, when acting as a diluent, are the same when they are in dilute solution, acting as a solute. This question is especially important when HBA and HBS scales of diluent are compared with association constant similar to the $K_s$ used earlier and used to explain reactions.$^{[33]}$

Another concern from those scales is that it has been demonstrated that significant systematic differences between similar values on the same scale have been observed as a function of the probe used on a same chromophore (meaning P=O, C=CO, S=O, N=O or –O–).$^{[43]}$ In an attempt to accommodate their scales Kamlet and Taft proposed a new “covalency” parameter, $\zeta$, to take in account this probe dependency problem.$^{[44]}$ Since this parameter was not determined for enough diluents, its influence on the results observed in this study was not investigated.

In her dissertation, Krahn studied the influence of the diluent on the ligand exchange dynamics on Ln-HEH[EHP] metal chelate.$^{[45]}$ This study demonstrated that the characteristic associative or dissociative nature of the ligand exchange dynamic was dependent on the metal center$^{[46]}$, but also extremely dependent of the diluent used. This effect has not been taken into account, and is likely have an influence on the system, especially in the case of an inner-sphere interaction (dissociative exchange)$^{[47]}$, which could reveal for a short time, a polar area in the core of the metal available for electron donor diluent (such as MIBK).

4.5.2.2 Future Work

As stated in the previous section, one of the main problems of these empirical and pseudo empirical scales are the fact that they are based on a pure medium diluent property, and is more likely to differ from the medium properties in a solvent extraction system (wet solvents, presence of solute
in relatively high volume fraction, etc.). Some of those parameters could be simply redefined as described below

4.1.1.1 Characterization of the solvent polarizability (n)

As described in the section 4.2.2, the Lorenz-Lorenz function can be used to describe a medium polarizability. This function is based on the standard refractive index of the medium. The wavelength used for the determination of this standard refractive index is the one obtained at the yellow doublet of the sodium D line, at precisely 589 nm (transition from the orbit \( \psi_{3/2} \) to the \( \psi_{1/2} \)).[20] In the simplest matter, this 589 nm ray is sent to an air/solvent interface and by measuring the entry angle, \( \theta_{\text{air}} \) (in air) at the interface and the exit angle, \( \theta_{\text{solute}} \), at the interface (solvent). The refractive index of the solvent can be determined (goniometric method) using the Snell-Descartes equation (4.43):

\[
n_{\text{air}} \cdot \sin(\theta_{\text{air}}) = n_{\text{solute}} \cdot \sin(\theta_{\text{solute}})
\]

Other and more precise methods exist, especially the ones using interferometry method.[48]

4.5.2.2.1 Characterization of the of the Solvent Polarity (\( \varepsilon_r \))

As described in the section 4.2.2, the Debye function can be used to describe a medium’s polarity. This function is based on the relative permittivity of the medium. This parameter can be measured using a static electric field. Measuring the capacitance \( (C_k) \) of a capacitor with a known medium between its two plates (with a known relative permittivity \( \varepsilon_k \)). Then the medium is replaced by the solvent and the capacity is measured \( (C) \). Using the flowing equation the relative permittivity of the solvent can be calculated.
4.5.2.2.2 Interactive Scale Based on HEH[EHP]

Based on the work of Mayer et al\textsuperscript{[36]}, Elias et al\textsuperscript{[49]}, and Kamlet and Taft\textsuperscript{[50]} it could be possible to create interactive scale based on the interaction in HEH[EHP] with its diluent (especially interesting since HEH[EHP] is an electron donor through the P=O group and acceptor through the P-O-H group). To do so this scale can be based the limiting value of the NMR chemical shift $\delta_P$ of the $^{31}$P atom and the chemical shift $\delta_H$ of the acidic proton at infinite dilution. Then this value would be relativized to a reference value obtained from a reference diluent (both corrected for diamagnetic susceptibility of the solvent). It has already been demonstrated that the $^{31}$P shift changes as a function of the diluent used ($n$-octane vs. toluene) but also in the presence of alcoholic phase modifier ($t$-octanol)\textsuperscript{[51]} Knowing that it is possible to predict a feasibility for the development of this scale. Also, if a tri-alkyl phosphine oxide is added to the system, it could be possible to differentiate the basic interaction from acidic ones (interactions with P=O vs. interactions with P-O-H).
4.6 Conclusion

In this chapter, coefficient of extraction of europium by HEH[EHP] in various diluents have been compared to multiple diluent properties scales. Based on the results it seems that the cohesive properties of a diluent (described by the solubility parameters) and the dispersive properties of a diluent work against the extraction process by increasing the Gibbs energy of extraction mechanism in the organic phase. This mechanism has been attributed to the change in cavitation and dispersion energy between \((3+n)/2(HA)_2\) dimers and the \(MA_3(HA)_n\) metal chelate. Based on the observation made in the interactive forces dependency, it seems that the higher the electron donor and or acceptor capability of a diluent, higher is the interaction between the diluent and the free monomer in solution, creating a stronger Lewis acid/base abduct. Doing so, the concentration of free monomer available (not involved in a diluent-solute or solute-solute adduct) for the exaction is reduced and therefore a decrease in the extraction. Understanding that, it seems that the diluent effect on solvent extraction follow the general schematic behavior described in the solvation process of a solute in a liquid.
4.7 References


(22) Allard, B. The Coordination of Tetravalent Actinide Chelate Complexes with [Beta]-Diketones, Chalmers university of technology, 1975.


5.1 Preface.

Of particular interest in this investigation is to assess the role of the diluent in controlling the progress of the extraction of trivalent lanthanide and actinide metal ions from dilute nitric acid media into solutions containing cation exchanging organophosphorus extractants. As the research results described in the previous chapters have sought to develop insight into the contribution of the diluent to the overall driving force of such reactions (Gibbs energy, $\Delta G$), it is the purpose of this chapter to assess the relative importance of the thermal heat change (Enthalpy, $\Delta H$) and disorder (entropy, $T\Delta S$) on these same reactions. To broaden the scope of the investigation, the extractant studied herein was bis(2-ethyl(hexyl)) phosphoric acid, HDEHP; the van’t Hoff method was selected to enable the thermometric analysis.

5.2 Introduction

Thermodynamics is the study of thermal, electrical, chemical, and mechanical forms of energy. The study of thermodynamics crosses many disciplines, including physics, engineering, chemistry and even biology. Of the various branches of thermodynamics, the most important to chemistry is the study of the change in the energetic state of the system that occurs during a chemical reaction. Such diagnostic evidence can reveal important details about the features of the chemistry that drive a reaction of interest. In the context of this research, the methods of thermometric analysis will be
applied to gain additional insight into the effect of the diluent on lanthanide and actinide extraction by acidic organophosphorus reagents.

It is possible to obtain critical parameters when using thermometric methods including van’t Hoff analysis and calorimetry to study a chemical reaction including the change of entropy ($\Delta S$) and enthalpy ($\Delta H$) of a reaction. Knowledge of these parameters is vital for increased understanding of a chemical equilibrium. The focus of this chapter is on characterizing those thermodynamic parameters ($\Delta G$, $\Delta H$ and $\Delta S$) for the solvent extraction of $\text{Am}^{3+}$ and $\text{Nd}^{3+}$ from mildly acidic nitrate media, by HDEHP using van’t Hoff analysis within selected diluent ($n$-octane, toluene, nitrobenzene and chloroform). These diluents are taken as representative of the four principal subgroups (aliphatic, aromatic, polar, and H-donor).

5.3 Principle of Thermochemical Analysis

The first law of thermodynamic states that when a quantity of heat $Q$ is absorbed by a system, at the exact same time the system performs a quantity of work $W$ against mechanical, gravitational, electrical or magnetic forces. The increase of energy of the system on passing from an initial state to a final state is given by the function:

$$\Delta E = Q - W = E_{\text{final}} - E_{\text{initial}}$$ (5.1)

In most thermochemical considerations, the work done on and/or by the system is mechanical and is given by the expression (when reversible).
\[ W = \int_{V_{\text{initial}}}^{V_{\text{final}}} PdV \]  

(5.2)

where \( P \) and \( V \) represent respectively the pressure and the volume of the system. Substituting equation (5.2) into equation (5.1) and integrating for a constant pressure process yields the equation:

\[
Q = \Delta E + P\Delta V = (E + PV)_{\text{final}} - (E + PV)_{\text{initial}}
\]

(5.3)

The function of state represented by \( E+PV \) is called the enthalpy or heat content, and is represented by \( H \). In general, the increase in enthalpy for processes occurring under any conditions of temperature and pressure are given by the equation:

\[
\Delta H = \Delta E + \Delta(PV)
\]

[5.1]

When a quantity of heat, \( dQ \), is absorbed at the absolute temperature \( T \), under reversible conditions the increase of entropy is given by the relation:

\[
dS = \frac{dQ}{T}
\]

(5.4)

As in the case of energy and enthalpy, entropy is a point function, depending only on the state of the system and not how the system reaches that state. Substituting equation (5.3) into equation (5.1) gives the following equation.
\[ dE = TdS - PdV \]

This equation is valid for processes involving mechanical work only. Another function of the state of a system exists which is of major interest to chemists since it permits the prediction of equilibrium conditions for physical and chemical changes. It represents the maximum non-mechanical work theoretically obtainable for processes occurring at constant temperature and pressure. This function is called the Gibbs energy. The increase in Gibbs energy in going from the initial to the final state of the system is given by the equation:

\[ \Delta G = \Delta H - T\Delta S \]

The quantity \( T\Delta S \) represents the heat that must be absorbed or given up to the surroundings during the reversible process, in order to maintain isothermal conditions.

The determination of these energetic parameters are essential for solvent extraction chemists. Choppin demonstrated the importance of the knowledge of those factors, and gave a thoughtful description of the thermodynamics in a metal chelate formation, ionic medium effect, hydration, solvation, Lewis acid base interaction, and complexation.\[1\]

These thermodynamic quantities may be obtained accurately from direct calorimetric measurement.\[2][3][4\] However exceptions need to be made for more “challenging” systems.\[5\] For examples where slow reaction occurs, where low vapor pressures makes the PV parameter non-constant though the measurements, or where low solubilities or non available material (as is often

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\[5\] Personal conversation with Cecilia Eiroa Lledo (WSU): “OMG, I can’t use our calorimeter with Tc, because the concentrations are too low, it is almost insoluble, it is too radioactive and it is too slow! I hate it...”
true with radioactive isotopes) require work with trace quantities. To overcome the limitations of calorimetry, the use of the van’t Hoff analysis is a relatively good method, and has been shown to give results similar to the calorimetric ones.[3] Analysis by van’t Hoff plot has been used in the past by solvent extraction chemists.[5][6][7]

The van’t Hoff equation relates the change in the equilibrium constant, $K_{eq}$, of a chemical reaction, as a function of the temperature $T$ (K), given the standard enthalpy change $\Delta H$ for a given process.[8] The van’t Hoff equation is expressed under standard conditions as:

$$\frac{d}{dT} \ln K_{eq} = \frac{1}{RT^2} \Delta H$$

(5.7)

where $R$ is the ideal gas constant. This equation is exact at any one temperature. In practice, the equation is often integrated between two temperatures under the assumption that the reaction enthalpy $\Delta H$ is constant. Since in reality $\Delta H$ and $\Delta S$ do vary with temperature for most processes, the integrated equation is only an approximation.[9] To obtain the integrated equation, it is convenient to first rewrite the van’t Hoff equation as:

$$\frac{d}{d\frac{1}{T}} \ln K_{eq} = -\frac{1}{R} \Delta H$$

(5.8)

The definite integral between temperatures $T_1$ and $T_2$ is then defined by:

$$\ln \frac{K_2}{K_1} = -\frac{1}{R} \Delta H \left( \frac{T_1 - T_2}{T_1 T_2} \right)$$

(5.9)
The equilibrium constant can be measured over a range of temperatures for a reversible reaction. These measured $K_{eq}$ can be plotted on a natural logarithm scale, against the inverse of the absolute temperature. In the most basic case the data should yield a linear relationship, the equation for which can be found fitting the linearized form of the van’t Hoff equation:

$$\ln K_{eq} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

This type of plot/fitting is called the van’t Hoff plot analysis and is widely used to estimate the enthalpy and entropy of a chemical reaction at equilibrium. For an endothermic reaction, heat is absorbed, making the net enthalpy change positive. Thus, the slope of a van’t Hoff plot analysis should be negative. For an exothermic reaction, heat is released, making the net enthalpy change negative. Thus, the slope of a van’t Hoff plot analysis should be positive. The entropy term ($\Delta S$) can be calculated from the y-intercept of the linear plot.
5.4 Experimental

5.1.1 Method

The analytical method used in this chapter is adapted from the method described for gamma emitters in chapter 2. However, the method has been adapted for the van’t Hoff analysis and must be described further.

The following experimental method is used:

1. In a 25 mL disposable glass vial, 9.8 mL of acidic solution without any metal, \( \mu = 0.1 \text{ mol·L}^{-1} \) (Na-H)NO\(_3\) and 10 mL of an organic phase containing the extractant.

2. A sample of 200 \( \mu \text{L} \) of americium-241/ neodymium-147 radiotracers solution is spiked into the vials.

3. The vial is capped with a PTFE cap and PTFE tape is used to seal the vial. Then the vial is placed into three layers of zip-lock bags and lifted with multiple binder clips to assure a complete immersion of the vial in the water bath.

4. The vial is immersed in a constant temperature water bath, and equilibrated 12 hours for the first sampling (overnight), and then for at least 2 hours after changing the temperature. When the sample is left in the bath overnight, the mass of the vial before and after the night is measured to check for evaporation of the diluent.

5. Before removing the sample, the temperature of the bath is measured with an alcohol thermometer.

6. The zip lock bags are removed and disposed into radioactive wastes.
7. A 200 µL sample of the top organic phase is taken and introduced into a gamma counting tube.

8. A 200 µL sample of the aqueous phase is taken and introduced into another gamma counting tube.

9. Steps 3 to 8 are then repeated for each increment of temperature.

10. The gamma tubes then are capped and transported to the gamma counter.

The water bath used for the van’t Hoff analysis was a VWR scientific heated refrigerated circulating water bath 1180’s.

The Gamma counter is a Packard Model 5003 Cobra II Auto Gamma Counter with an energy window between 15 – 2000 keV. Americium-241 is counted between 60-80 keV; neodymium-147 is counted between 85-120 keV.
5.1.2 Results

The extractant chosen for this study was di-(2-ethylhexyl)phosphoric acid (HDEHP), with concentration adjusted as a function of the diluent used. The extraction experiments were done with an ionic strength of 0.1 mol·L\(^{-1}\) (Na-H)NO\(_3\) and pH = 2. For this chapter, the extractant HDEHP has been used instead of the HEH[EHP]. This choice has been made because in the past HDEHP has been observed to be more convenient to study in thermometric condition. The reason of the difficulty to apply thermometric analysis to HEH[EHP] has never been fully understood, however it was hypothesized that the heat of extraction was too small for classical method of thermometric analysis. With the objective to simplify the method, a graphic slope analysis has a function of the temperature, diluent and cation extracted has not been performed. It has been assumed that the stoichiometry between the metal and the extractant are constants regardless of the temperatures of the media. Considering the mixed stoichiometry observed in chapter 3 for HEH[EHP] and the stoichiometry observed by Kolarik with HDOP\(^{[10]}\), it has been assumed that the stoichiometry of the metal chelate for toluene, chloroform and nitrobenzene were \(MA_3(HA)_3\) and \(MA_3(HA)_2\) for \(n\)-octane. Then the calculations used for the \(\log K_{ex}\) were adapted as a function of the stoichiometry used.

\[
\log K_{ex} = \log D - 3 \cdot \log[(HA)_2] + 3 \cdot \log[H^+] \quad (5.11)
\]

\[
\log K_{ex} = \log D - 2.5 \cdot \log[(HA)_2] + 3 \cdot \log[H^+] \quad (5.12)
\]
Since the common calculated value for solvent extraction is the base 10 logarithm instead of the natural logarithm needed for the van’t Hoff plot analysis, it is possible to use the following approximation of base change:

\[
\ln x = 2.303 \cdot \log x
\]  \hspace{1cm} (5.13)

Then substituting equation (5.13) into the equation (5.10), it is possible to obtain this adapted van’t Hoff relation:

\[
\log K_{ex} = -\frac{\Delta H}{2.303 \cdot R} \cdot \frac{1}{T} + \frac{\Delta S}{2.303 \cdot R}
\]  \hspace{1cm} (5.14)

**Figure 5-2.** Change in \( \log K_{ex} \) for Nd (red) Am (black) extractions with HDEHP, within different diluents (top left toluene, top right chloroform, bottom left n-octane, bottom right nitrobenzene) as a function of the temperature.
The log $K_{ex}$ for neodymium and for americium in all four diluents ($n$-octane, toluene, nitrobenzene and chloroform) as function of the temperature have been plotted in Figure 5-2. The first thing to observe is that the variation in the extraction of $\text{Am}^{3+}$ and $\text{Nd}^{3+}$ as a function of the temperature are always parallel to each other, suggesting that in this system the changing diluent is primarily responsible for the net changes in enthalpy that is observed. The extraction using $n$-octane as a diluent is exothermic, the extraction from nitrobenzene is close to be athermic and the extraction from toluene and chloroform are both endothermic (chloroform being more endothermic than toluene). The thermodynamic parameters determined from the plot in Figure 5-2 using equation (5.14) are shown in Table 5-1.

<table>
<thead>
<tr>
<th>Diluent</th>
<th>$\Delta G$ (298.15 K) (kJ·mol$^{-1}$)</th>
<th>$\Delta H$ (kJ·mol$^{-1}$)</th>
<th>$T\Delta S$ (kJ·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd n-octane</td>
<td>13.53 ± 0.37</td>
<td>-8.29 ± 0.27</td>
<td>-21.82 ± 0.26</td>
</tr>
<tr>
<td>toluene</td>
<td>15.66 ± 0.72</td>
<td>8.98 ± 0.52</td>
<td>-6.68 ± 0.51</td>
</tr>
<tr>
<td>chloroform</td>
<td>21.07 ± 1.36</td>
<td>26.90 ± 0.96</td>
<td>5.83 ± 0.96</td>
</tr>
<tr>
<td>nitrobenzene</td>
<td>14.57 ± 0.54</td>
<td>0.11 ± 0.38</td>
<td>-14.46 ± 0.38</td>
</tr>
<tr>
<td>Am n-octane</td>
<td>11.84 ± 0.62</td>
<td>-9.43 ± 0.26</td>
<td>-21.27 ± 0.57</td>
</tr>
<tr>
<td>toluene</td>
<td>14.11 ± 0.57</td>
<td>7.59 ± 0.35</td>
<td>-6.52 ± 0.45</td>
</tr>
<tr>
<td>chloroform</td>
<td>19.86 ± 1.71</td>
<td>26.15 ± 1.69</td>
<td>6.30 ± 0.26</td>
</tr>
<tr>
<td>nitrobenzene</td>
<td>13.19 ± 5.25</td>
<td>-0.98 ± 0.04</td>
<td>-14.17 ± 5.24</td>
</tr>
</tbody>
</table>

Table 5-1. Calculated thermodynamic parameters, $\Delta G$ (calculated for 298.15 K), $\Delta H$, and $T\Delta S$ for the extraction of Nd(III) and Am(III) by HDEHP in various diluents ($n$-octane, toluene, chloroform, nitrobenzene) from acidic nitrate media, $\mu = 0.1$ mol·L$^{-1}$ (Na-H)NO$_3$ at pH=2. Values calculated from equation (5.14), uncertainties in $\Delta H$ and $T\Delta S$ calculated from the unweighted linear regression and the 95% confidence interval of the fitting. (T = 298.15 K)
The Gibbs energy values for both Am and Nd become increasingly unfavorable (more positive) following the order: \( n \)-octane (strongest extraction) < nitrobenzene < toluene < chloroform (weakest extraction). The measured enthalpy for extraction from \( n \)-octane is exothermic, from toluene endothermic (and of similar magnitude to \( n \)-octane), three to four times more unfavorable for extraction into chloroform, with nitrobenzene characterized by near zero enthalpy. The extraction entropy term is most unfavorable in \( n \)-octane, though the exothermic heat cancels enough of the unfavorable entropy to give \( n \)-octane the least unfavorable Gibbs energy of the four diluents. The entropy term is only favorable in the chloroform system, which suffers the most unfavorable enthalpy. The minimal difference seen between Nd and Am extraction thermodynamics data is as expected.

5.5 Discussion

The thermochemistry of a solvent extraction process can be considered as a first approximation to be a balancing act between the endothermic\(^\text{[1]}\) heat associated with metal ion dehydration\(^\text{[11]}\) in the aqueous phase and the exothermic formation of lipophilic complexes in the organic phase. The thermodynamic results of extractions indicate a \( T \Delta S < \Delta H \) regardless of the diluent, per consequent \( \Delta G \) is positive and \( \log K_{ex} \) negative. Also, the relation \( T \Delta S < \Delta H \) indicates an enthalpy driven reaction\(^\text{[1]}\), regardless of the diluent used. This conclusion is consistent with the heat diagram determined by Marcus, where he noted that these processes dominate the enthalpy level diagrams for every liquid-liquid distribution process.\(^\text{[2]}\) Though entropy can exert a significant influence on the net free energy of extraction, the final outcome of this enthalpic ‘‘tug of war’’ is often the driving force of a separation process.\(^\text{[3]}\) The thermodynamic results obtained of \( n \)-octane are consistent extraction of lanthanides from nitrate media by HDEHP in \( n \)-dodecane data published by Zalupski and Nash (measured calorimetrically)\(^\text{[3]}\).
Choppin correlated $\Delta S$ and $\Delta H$, attributing a linear correlation to a change in the dehydration/hydration processes of the cations.\textsuperscript{[12]} Here since the cation is constant, and the dehydration of the metal and the hydration of the proton are invariant, the difference is attributed to solvation.\textsuperscript{[1][12]} Marcus demonstrated that entropy of the reactions dehydration/hydration + desolvation/solvation + dissociation/complexation should give by default either a small positive (diluent with cohesive interaction) or a negative (inert diluent).\textsuperscript{[2]} This demonstration is in agreement with the results from Table 5-1. The especially positive value for the extraction in chloroform may be due to the breaking of a ligand-diluent hydrogen bonding adduct $\{(RO)_2(OH)P=O--HCCl_3\}$. The small value of the change in enthalpy for the nitrobenzene is lower than expected. This could be explained by a weak hydrogen bonding between the ligand and the diluent $\{(RO)_2P(=O)OH--ONO-bnz\}$, or by an interaction/complexation between the diluent and the metal.

It has been shown that for many thermochemical systems, there is a linear correlation between an experimental $\Delta H$ and a $\Delta T \Delta S$ values.
Figure 5.3. Correlation of $\Delta H$ and $T\Delta S$ of extraction of a series of diluent (where $T = 298.15^\circ$K). Black squares: neodymium data, red spheres: americium data.

Figure 5-1 show the experimental correlation for Nd and Am extraction from Table 5-1. Such correlation between $\Delta H$ and $T\Delta S$ is called the enthalpy-entropy compensation effect.$^{[13]}$[14] The general phenomenon of enthalpy-entropy compensation in essence refers to the experimental observation of a linear scaling between enthalpy ($\Delta H$) and entropy ($\Delta S$) for a set of related reactions.

$$\Delta H = \alpha + \beta \cdot \Delta S$$

(5.15)

where $\alpha$ and $\beta$ are constants, with $\beta$ called the “compensation” temperature, as well as a common isoequilibrium temperature for all van’t Hoff plots.$^{[14]}$ Considerable controversy surrounds the subject of this phenomenon. Some scientists, such as Choppin or Freed, from puzzlement and
amazement at its occurrence, investigated its origins, without finding any definitive answers\textsuperscript{[1]}\textsuperscript{[14]}. Others, such as Zolotnitsky \textit{et al.} claim that the effect is either spurious or an artifact from a limited amount of data.\textsuperscript{[15]}

<table>
<thead>
<tr>
<th></th>
<th>( \alpha ) (kJ·mol(^{-1}))</th>
<th>( \beta ) (mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd</td>
<td>17.8 ± 0.49</td>
<td>360 ± 82</td>
</tr>
<tr>
<td>Am</td>
<td>15.7 ± 0.39</td>
<td>352 ± 8</td>
</tr>
</tbody>
</table>

Even if the real meaning of the thermodynamic parameters of the compensation effect still remains obscure, this effect is sufficiently interesting to present here. One the major problems of this effect is due to the fact that the isoequilibria temperature is inapproachable experimentally, due to the much higher freezing point of each phase. However the \( \alpha \) parameter could be interpreted as an enthalpy potential of the solvent extraction of a metal by HDEHP.

5.6 Future Work

The van’t Hoff linear plot analysis is based on the assumption that \( \Delta H \) does not depend on the temperature. However, the enthalpy \( \Delta H \) depends on \( T \) via the heat capacity \( C_P \) (at fixed pressure \( P \)) as expressed by the fundamental thermodynamic relation:

\[
H - H^\circ = \int C_P dT
\]  

(5.16)

Using the polynomial heat capacity fit:

\[
C_P = a + b \cdot T + c \cdot T^2
\]  

(5.17)
It is possible to develop the following equation:

\[
\ln K = cst + \frac{\Delta H_0}{R} \cdot \frac{1}{T} + \frac{\Delta a}{R} \ln T + \frac{\Delta b}{R} T + \frac{\Delta c}{R} T^2
\]  

(5.18)

It also is possible to obtain these parameters measuring the \(Cp\) for the system as a function of the temperature, using calorimetry. Doing so it could be possible to refine the determination of the standard enthalpy change and standard entropy change.

Also with the objective to increase the degree of precision of the analysis, increasing the number of diluents in the correlation of \(\Delta H\) and \(T\Delta S\) and increasing the number of trivalent cations studied with the same method are probably needed.

5.7 Conclusion

This study represents the preliminary investigation of a van’t Hoff analysis of the diluent effect on the solvent extraction of trivalent \(f\)-elements by HDEHP. The Gibbs energy, the enthalpy and the entropy change as function of the diluent has been found to increase as follows: \(n\)-octane < nitrobenzene < toluene < chloroform. With these thermodynamic parameters, a linear enthalpy-entropy compensation diagram has been obtained, allowing to determine the iso-equilibria temperature as well as an enthalpy potential of the mechanism. Such diagram can be attributed to the change in the desolvation and solvation processes in the organic phase.
5.8 References


(8) Van’t Hoff, J. H. Etudes de Dynamique Chimique, first.; Frederik Muller & Co: Amsterdam, 1884.


CHAPTER SIX
GENERAL CONCLUSIONS

This study has reported the results of work improving the understanding of the fundamental chemistry of solvent extraction of f-elements by acidic di-alkyl organophosphorus extractants, 2-ethylhexyl phosphoric acid 2-ethylhexyl ester (HEH[EHP]) and bis-2-ethylhexyl phosphoric acid (HDEHP). The focus of this study reported on the influence of the organic phase, in which the extractants were dissolved, on the solvent extraction equilibria and thermochemistry. The results presented emphasized the diluent used had a strong influence on the efficiency of the extraction, the stoichiometry of the metal chelate, and the change in thermodynamic parameters.

In the chapter 3, the results from the extractions of europium, thulium, neodymium and americium as function of the diluent showed, through linear free energy diagrams, that the influence of the diluent on the solvent extraction is strong, and independent of the cation used. The stoichiometry of the metal chelate has been showed to be variable as a function of the diluent used, where low interacting diluents can favor lower stoichiometry, MA₃(HA)₂, and higher interactive diluents can cause higher stoichiometry, with MA₃(HA)₄ observed. Spectrophotometric methods have been used to observe a potential change intro the coordination environment of the cation. This data has shown that the octahedral environment of the metal chelate stayed unchanged from one diluent to another. However, the results also show a small change in the symmetry of the metal chelate (thought the diminution of the pic resolution of the Nd⁺³ UV-Vis spectra, and the apparition of the ⁵D₀ → ⁷F₀ transition of the Eu³⁺ luminescence spectra).
To extend this study, additional diluents could be investigated, especially hydrogen donors such as dichloromethane, bromoform, 1,1-dichloroethene, etc. Also as an extension of this general study done with pure diluents, mixed diluent systems should be studied – see examples in the appendices.

In the chapter 4, the change in Gibbs energy of extraction of Europium by HEH[EHP] obtained from the chapter 3 was studied in this work and was compared to physical and chemical properties of the diluent used. It has been shown that higher cohesive dispersive energies cause a lower efficiency of extraction. The Hansen solubility parameters showed the best correlation with the Gibbs energy of extractions. This effect has been attributed to the lower solubility of the metallic cation in comparison to the three protons exchanged from the extractant during the solvent extraction process. In a second period, the ability of the diluent to associate with the extractant (thought a Lewis acid base abduct formation mechanism), has been investigated. To do so, empirical Lewis acid/base scales have be compared to the change in Gibbs energy of extractions. The results showed interesting correlations between the basicity scales and the efficiency of extraction, which was a strong indication of a potential adduct formation.

To extend this study, additional parameters should be determined, such as association parameter constants, but also redefining/measuring the nonspecific interaction while taking into account the water and nitric acid uptake. In addition, it would be interesting to determine the Hansen solubility parameters of the extracted complexes; this could lead to a new plot of log D vs. solubility parameters, bringing additional insight into diluent effect study.

In the chapter 5, solvent extraction of Am$^{3+}$ and Nd$^{3+}$ by HDEHP with using different diluent have been investigated using van’t Hoff thermometric analysis. The results from the thermometric analysis of the extraction Nd$^{3+}$ and Am$^{3+}$ by HDEHP showed a variation of the Gibbs
energy, the change in enthalpy and entropy a function of the diluent. The $\Delta G$ and $\Delta H$ have been found to increase as following: $n$-octane < nitrobenzene < toluene < chloroform. $\Delta S$ have been found to increase as follows: chloroform < toluene < nitrobenzene < $n$-octane. A linear enthalpy-entropy compensation effect was also plotted. This plot allowed us to find the iso-equilibrium temperature $\beta$, Nd: 360 mK ± 82 mK, Am: 352 mK ± 8 mK. A second parameter $\alpha$ has been determined, Nd: 17.8 kJ·mol$^{-1}$ ± 0.49 kJ·mol$^{-1}$, Am: 15.7 kJ·mol$^{-1}$ ± 0.39 kJ·mol$^{-1}$.

To extend this study, additional cations and diluents could be investigated (especially to extend the thermochemical data to complete the entropy-enthalpy compensation diagram). If a trend was observed, it would help to attribute enthalpic and entropic behavior to family of diluents but also help to understand the meaning behind the parameter $\alpha$.

The overall impact of this work on the broader scientific community is an increased understanding of the chemistry of acidic di-alkyl organophosphorus extractant during the solvent extraction of an $f$-element. Included in this work is the first extensive study of slope analysis with various cation (Nd$^{3+}$, Eu$^{3+}$, Tm$^{3+}$ and Am$^{3+}$), cross-compared with diluent physical and chemical properties. The overall conclusion is that the diluent has a strong impact on the solvent extraction mechanism, mostly due to the cohesive and interactive properties of the diluent with the solutes.
APPENDIX
A.1. The Need of Energy and the Impact of its Production

A.1.1. Energy and Quality of Life

At the most basic level, energy is required to cook our food, warm people from the cold, and light the dark. Moving beyond survival, energy becomes an essential component to every aspect of enhanced development: providing motive force for industry, refrigerating medicines, lighting schools, preserving food, transporting products, and communication. When those goals are achieved, the excess of energy can be used to fulfilling basic social needs, driving economic growth, and fueling human development. This is because energy services have an effect on productivity, health, education, safe water, and communication services. Also, modern services such as electricity, natural gas, modern cooking fuel, and mechanical power are necessary for improved health and education, better access to information, and agricultural productivity.[1]

Figure A-1 shows the energy needs related to this living standard. It is also very important to notice that in 2016 there are 1.1 billion people that are living without access to electricity (this number fell from 1.7 billion in 2000) and 2.7 billion have only a limited access[2]

In Figure A-2 the recent Per Capita[6] Energy Consumption (PCEC) patterns[3] are compared with recent quality of life data (UNDP, 2014[4]) from the UN Human Development Index to isolate those nations that have a favorable HDI compared with moderate energy consumption at different stages of development.

---

[6] Per Capita means Per Person, from the Latin capita = head.
Published on 4 November 2010 (and updated on 10 June 2011), the 2010 Human Development Report (HDI) combines three dimensions\cite{5}: A long and healthy life: Life expectancy at birth, Education index (Mean years of schooling and Expected years of schooling), and decent standard of living (GNI per capita):

\[
LEI = \frac{LE - 20}{85 - 20}
\]  

(A.1)
where LEI is the Life Expectancy Index, and LE is the Life Expectancy. LEI is 1 when Life expectancy at birth is 85 and 0 when Life expectancy at birth is 20.

\[ EI = \frac{MYSI + EYSI}{2} \]  \hspace{1cm} (A.2)

\[ MYSI = \frac{MYS}{15} \]  \hspace{1cm} (A.3)

\[ EYSI = \frac{EYS}{18} \]  \hspace{1cm} (A.4)

where EI is the Education Index, MYSI is the Mean Years of Schooling Index, MYS is the Mean Years of Schooling (fifteen is the projected maximum of this indicator for year 2031), EYSI is the Expected Years of Schooling Index, and EYS is the Expected Years of Schooling (eighteen is equivalent to achieving a master's degree in most countries).

\[ II = \frac{\ln(GNI) - \ln(100)}{\ln(75000) - \ln(100)} \]  \hspace{1cm} (A.5)

where II is the Income Index, GNI is the Gross National Income per capita. II is one when GNI is $75,000 and 0 when GNI is $100.

Finally, the HDI is the geometric mean of the previous three normalized indices:

\[ HDI = \sqrt[3]{LEI \cdot EI \cdot II} \]  \hspace{1cm} (A.6)
The comparison of PCEC to HDI is becoming the most common type of analysis in the energy production industry. Indeed, as depicted in Figure A-2, a moderately satisfactory and commonly applied fit may be made using a logarithmic trend. This logarithmic representation shows that there is a first order relation between the energy production of a country and the quality of life. An HDI between 0.3 and 0.7 means there is an extremely strong dependence of HDI and PCEC. The second region, located near the point of inflection (HDI 0.7–0.9), represents transitioning nations and indicates a threshold from very poor human development to very high development. In the third region, the higher energy consumption (above 5 000 kOE), there is a saturation phenomenon, where a higher consumption of energy does not increase the quality of life. A final assumption from Figure A-2 could be that the countries in region 2 (HDI > 0.7 and PCEC < 5 000 kOE) would have difficulty to reduce their PCEC without risking a reduction in their HDI. The results in terms of energy footprint show that the generalization of the living standards from the so-called highly developed countries to the rest of the world would require a substantial increase in the global energy use rates.
A.1.2. Energy and World Population Growth

“Is there a sustainable solution for the world and the resources it needs to maintain a decent standard of living for everybody, at a population very much higher than today’s? Clearly, there cannot be both a permanent growth in the use of materials and a sustainable future.”

~John Sheffield

If the earth is considered as a closed system where the amount of critical resources available are limited (clear water, food, clean air, living space), it is easy to understand that the growth of the human population needs to be monitored. The world population was estimated to be around 7.6 billion in December 2018 and is expected to increase to 8.8 Billion in 2050 for the most optimistic
projections or to 11 Billion the same year for the most pessimists’ projections\cite{7} - Figure A-3. However, if we want to maintain our level of life while giving the opportunity to humanity to achieve same sustainable HDI than the more developed countries, the world population needs to achieve an equilibrium.

In 1998, Sheffield related the world population growth and the annual energy use per capita.\cite{6} In this study he demonstrated that the most “developed” countries have a lower population growth rate, and also likened this population growth rate to the annual energy use per capita. As demonstrated previously, the higher the per capita energy consumption, the more likely the standard of living is going to increase - Figure A-2.

<table>
<thead>
<tr>
<th>Years</th>
<th>Total Population (both sexes combined) (thousands)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1800</td>
<td>1.2x10^7</td>
</tr>
<tr>
<td>1850</td>
<td>1.4x10^7</td>
</tr>
<tr>
<td>1900</td>
<td>1.6x10^7</td>
</tr>
<tr>
<td>1950</td>
<td>1.8x10^7</td>
</tr>
<tr>
<td>2000</td>
<td>2.0x10^7</td>
</tr>
<tr>
<td>2050</td>
<td>2.2x10^7</td>
</tr>
<tr>
<td>2100</td>
<td>2.4x10^7</td>
</tr>
</tbody>
</table>

**Figure A-3.** World population estimates from 1800 to 2100, based on "high", "medium" and "low" United Nations projections in 2017\cite{7}
Also with increasing standard of living comes more extensive education for both men and women, increasing literacy, and the availability of information (print, television, internet), better access the health care, greater availability and use of contraception, more opportunities for women, lower early mortality, less need for parents to want a large number of children to support them in their old age, etc. By understanding that, it is logic that the access to a sustainable source of energy is a key factor for the survival of our planet.

A.1.3 Production of Energy and Gaseous Emission Footprints

In the last 20 years it has been largely demonstrated that the current energy consumption patterns are both physically and socially unsustainable. While the industrialized world faces sweeping energy transitions imposed by an impending decline of petroleum production, much of the non-industrialized world already faces significant energy shortages\[8\]. There is discussion about the nature of an overall transition to more sustainable energy systems (such as the COP21 in Paris in 2017). In recent years, progress has been made in developing cleaner, more efficient energy technologies. Indeed, we are seeing signs that economic growth and energy-related emissions – which have historically moved in the same direction – are starting to decouple. It seems unlikely that any single source will succeed in claiming a market share comparable to that currently owned by petroleum, let alone the collective fossil fuels. It will be critical in planning for the transition to understand the energy demand and potential production from various sources in terms of carbon footprint of each source\[9\], but also the emission of NO\(_2\) and SO\(_2\), responsible for the acid rains.
In 2015, Turconi et al published a critical review on the emission through the life cycle assessment (LCA) reviewing over 167 LCA case of the major electricity generation technology. Figure A-4 and Figure A-5 show a graphic comparison of those emissions in function of the technology.

**Figure A-4.** CO\textsubscript{2} gas pollutant emission per unit of energy used (integrated though the LCA, in function of the energy source.

The CO\textsubscript{2} emissions, in Figure A-4, could be devised in 3 different families of technologies, the high emission technologies (caused in general by the combustion of carbohydrate fuels during the operation), including coal, oils, gas and biomass (organic wastes, wood, sugar, ethanol, etc); the medium emission technologies, solar (thermal and photovoltaic), marine current, and photovoltaic; and the low emission technologies including geothermal, nuclear and hydrolytic\textsuperscript{[10]}.
Figure A-5. NO\textsubscript{x} (left) and SO\textsubscript{2} (right) pollutant emission per unit of energy used (integrated though the LCA, in function of the energy source.

Figure A-5 left shows that the flame technologies (coal, lignite, gas, and oil) are extremely polluting in terms of NO\textsubscript{x} emission. Figure A-5 right shows that the coal, lignite, and oil technologies are extremely more polluting in terms of SO\textsubscript{2}. The main problem of those gas emissions is that they are diluted in the atmosphere, and doing so, the choice of using an extremely polluting technology (such as coal) is going to affect also not only the local environment, but also neighborhoods on thousands of kilometers away (as function of the winds), and in a certain measure the entire planet.
A.1.4. Energy and Resources

A.1.4.1. Raw Materials

Regardless of the nature of the source of energy used for the production of energy (sun, wind, water, uranium, etc.), all energy technologies require material to support the production. However, in function of the technology installed, the type and amount of material consumed can vary widely. Some technologies require only common, plentiful material, such as steel and concrete, but some other may consume various quantities of more critical material, such as noble metal and rare earth elements.\textsuperscript{11} Since the earth is still a closed and limited system, is seem obvious that the quantities of material is also limited and can become critical as a function of the market value and availability.\textsuperscript{12} In addition, for the moment, the technologies that require the largest amount of material for their construction are not supported by any sustainable recycling program. This is especially true for the photovoltaic technology, were after deconditioning the solar panel join the classic waste streams.\textsuperscript{7,13} Figure A-6 is a graphic representation of the key materials by mass per energy technology lifetime.\textsuperscript{14}

Recycling, reuse, and more efficient use of critical materials could significantly lower the demand for new material. In 2015, it has been estimated by the US Department of Energy that only 1\% of critical materials are recycled in the end of life of the electricity generator.\textsuperscript{11} Finally, it is interesting to point out that the technology that require the lower amount of materials are the technology using heat from various fuel as a source of energy (coal, gas, biomass and nuclear).

\textsuperscript{7} France opened the first solar panel recycling plant in 2018 see ref [18]
A.1.4.2. Land Footprint

In the same manner of any other industry, the energy industry requires land area. Comparing the required land area for each technology can inform the decision making for the choice of a technology as function of the land available and the process footprint. One of the major challenges to compare each technology as function of the land use is the absence of a universally accepted definition of the land use and per consequence, of any universal metric. A US Department of Energy report presented some estimates on the land use requirement per technology in m²·TWh⁻¹, giving a low and a high estimate, and a crop area for the biomass. This data is presented in Figure A-7.
The logarithmic scale in Figure A-7 (right) has been used to visualize all the land use on the same graphic. However, the linear scale used in Figure A-7 left to emphasize the real differences between each technology. A closer look at this data shows that the three technologies that require the larger area of land are the hydraulic (necessary for the water storage), wind (since a large radius is required between each turbine to reduce the wind buffer effect) and biomass (completely dominated by the land needed for the crops used as fuel). The three technologies that are the most land efficient are coal, nuclear, and geothermal. However, it is important to specify that these
estimations do not take into account the mining for the coal and uranium, the storage of ashes, and radioactive wastes.

A.1.5. Energy’s Deathprint

If the environmental footprint is largely discussed, the energy’s deathprint, as it is can be called, is rarely discussed. It could be calculated by the number of people killed per TWh produced. According to the World Health Organization (WHO), the Centers for Disease Control, the National Academy of Science and many health studies over the last decade (NAS 2010), the adverse impacts on health become a significant effect for fossil fuel and biofuel/biomass sources\textsuperscript{18}. The major source of death from coal, oil and biomass are the carbon particulates resulting from burning that cause upper respiratory distress, kind of a second-hand black lung. WHO’s doctors have called biomass burning in developing countries a major global health issue\textsuperscript{19}. Coal and fossil fuel deaths usually do not include deaths caused during transportation of the fuel; there is an increase in deaths due to an increase in trucking and rail transport. The non-air pollution related deathprint are related to occupational health and safety statistics of the deaths of workers in the different industries. The deathprint of hydropower is dominated by a few rare large dam failures like Banqiao in China in 1976 which killed about 171 000 people\textsuperscript{20}. For wind power, workers still regularly fall off wind turbines during maintenance for a relatively little electricity production, which could be simply reduced by increasing the workers’ safety regulation\textsuperscript{21},\textsuperscript{22}. The deathprint of solar energy is mostly dominated by the fall of workers and non-workers installing the rooftop solar panels, but can be divided by two if only solar farms are considered\textsuperscript{23}. The major issue with the rooftop panel is roof worker safety, in the US alone about 1000 construction fatalities are reported per year, with 32 fatality per 100 000 roof workers\textsuperscript{24}. Wind power and solar deaths do not include the deaths caused by mining of rare earth material in China due to its difficulty to integrate percentage of the
mass of ore extracted and used for the production of those technologies. Solar does not include the
death due to maintenance or any electrical shock incidents through a 30 years average lifetime per
solar panel. Nuclear energy is integrated through the entire lifecycle, from mining to storage.
Uranium mining is a lot safer because in-situ leaching (the main method of uranium mining)
involves flushing acid down pipes. This process prevents workers digging underground,
preventing mining accidents. Also due to the very large energy density of uranium less material is
being moved than for coal plants. Before 2008 WHO indicated that 50 people died in the
Chernobyl incident, and 4000 may eventually die (using the Linear No-Threshold Dose hypothesis).
However, it has been recently discussed by health physicists that the LNT model may overestimate
the potential deaths from the Chernobyl’s accident. Furthermore in 2008, the United
Nations’ Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) corrected the
number of deaths caused by Chernobyl to no more than 49. Reconsidering these data, a
correction can be applied to the civilian nuclear deathprint. In 2010, the Agency for the Nuclear
Energy published a cross reference similar the one just developed, including the specific deathprint
of the nuclear energy in the entire OECD. However, it is important to note that in this report the
data were pre-Fukushima, increasing the number to death in the OCDE from 0 to 6 (nota bene: the
6 deaths at Fukushima are non-radioactivity related workplace accident, but should be integrated
for a more objective integration). Considering deathprint as a comparison factor, it is interesting
to point that coal is the more deadly technology and nuclear technology the safest, even after the
major accidents.
Table A-1. Comparison of the deathprint of each electricity production technology.

<table>
<thead>
<tr>
<th>Energy Source</th>
<th>Deathprint (death·TWh⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal (world average)</td>
<td>60</td>
</tr>
<tr>
<td>Coal in China</td>
<td>90</td>
</tr>
<tr>
<td>Oil</td>
<td>36</td>
</tr>
<tr>
<td>Natural Gas</td>
<td>4</td>
</tr>
<tr>
<td>Biofuel/biomass/peat</td>
<td>12</td>
</tr>
<tr>
<td>Solar (including rooftop)</td>
<td>0.44</td>
</tr>
<tr>
<td>Solar (exclusively rooftop)</td>
<td>0.88</td>
</tr>
<tr>
<td>Wind</td>
<td>0.15</td>
</tr>
<tr>
<td>Hydro (excluding Banqiao)</td>
<td>0.1</td>
</tr>
<tr>
<td>Hydro (including Banqiao)</td>
<td>1.4</td>
</tr>
<tr>
<td>Nuclear (including LNT effects)</td>
<td>0.038</td>
</tr>
<tr>
<td>Nuclear (corrected by UNSCEAR)</td>
<td>0.012</td>
</tr>
<tr>
<td>Nuclear (OCDE) before Fukushima*</td>
<td>0</td>
</tr>
<tr>
<td>Nuclear (OCDE) after Fukushima*</td>
<td>0.14 × 10⁻⁶</td>
</tr>
</tbody>
</table>

*Death integrated since 1980

A.1.6. Conclusions

One of the major challenges of the 21st century is obtaining energy to raise the standard of living of the overall population of the earth and to stabilize the population in a more sustainable manner. If the dependence on energy use per capita is a fair measure of the standard of living aspects of population growth, a large portion of the world population needs to raise their energy use rapidly enough to stabilize their populations before energy demand becomes out of reach. However, the production of energy to satisfy this needs to be done in a responsible manner. When the major technologies used for large production of electricity are compared as a function of the greenhouse emissions (CO₂, NOₓ and SO₂), material needed land use and the death rate induce by the utilization of those technology, it appears that not all technologies are equivalent. No energy is perfectly clean or safe, and chasing the perfect technology might cause the ignoring of just improving trading the obvious worse technologies to the better ones. Considering the parameters
presented in this appendix, it appear that the nuclear energy and the hydroelectric are the most reliable. The question of the waste have not been treated here, because the information on the waste management of most of the other technology than nuclear are not necessary available and/or reliable. However, it is important to specify that an intense effort if given by the nuclear industry to reduce the amount of waste (close fuel cycle, fast neutron reactor, molten salt reactor, etc), but also to propose long-term safe and controlled disposal of the final waste. In regards of this information, it seems that two technologies are more sustainable that the others (in term of pollution emission, resources (material and land) and deathprint), hydropower and nuclear energy. Furthermore, one of the major advantage of hydropower as source of energy can be stored and tuned easily in function of the need. However, this energy suffers because of its dependency on the availability of a large quantity of unsalted water, which is already limited due to the lack of access of water and is probably going to be reduced in the context of global warming.

“if we’re going to tackle global warming, nuclear is the only way you can create a massive amount of power”

~ Sting, December 2016
A.1.7 References


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