DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

THE INVESTIGATION OF KINETICS OF SOLVENT EXTRACTION METHOD FOR RARE EARTH ELEMENTS

by
Haydar GÜNEŞ

November, 2020
İZMİR

THE INVESTIGATION OF KINETICS OF SOLVENT EXTRACTION METHOD FOR RARE EARTH ELEMENTS

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M.Sc. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"THE INVESTIGATION OF KINETICS OF SOLVENT EXTRACTION METHOD FOR RARE EARTH ELEMENTS"** completed by **HAYDAR GÜNEŞ** under the supervision of **ASST. PROF. Dr. MURAT ALKAN,** and we certify that in our opinion, it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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THE INVESTIGATION OF KINETICS OF SOLVENT EXTRACTION METHOD FOR RARE EARTH ELEMENTS

ABSTRACT

In this study, the equilibrium conditions and kinetic studies of solvent extraction processes were investigated for lanthanum, cerium, praseodymium, and neodymium. In the equilibrium studies, effects of extractant, acid and metal concentrations on the solvent extraction of light rare earth elements were examined. Then a single drop apparatus was used for the determination of the reaction kinetics of the solvent extraction process. Column height, extractant concentration, acid concentration, metal concentration, and temperature were the main parameters effecting the reaction kinetics of SX and they were investigated. In conclusion, the rate formulas of the SX reactions were obtained by flux calculations. In addition, thermodynamic properties were determined by using the Arrhenius Equation and Activated Complex Theory. According to thermodynamic properties, the diffusion of the metal-ligand complex into the organic phase was the rate-determining step for the lanthanum and cerium. Besides, both diffusion and chemical reactions were determined as rate-determining steps for praseodymium and neodymium. Reactions at the interface were realized with nucleophilic bimolecular substitution.

Keywords: Solvent extraction, reaction kinetics, rare earth elements

NADİR TOPRAK ELEMENTLERİNİN SOLVENT EKSTRAKSİYON YÖNTEMİ İLE DEĞERLENDİRİLME KİNETİĞİNİN İNCELENMESİ

ÖZ

Bu çalışmada, lantan, seryum, praseodim ve neodim elementlerinin solvent ekstraksiyon yöntemi ile değerlendirilmesindeki denge koşulları ve kinetik özellikleri incelenmiştir. Denge çalışmalarında, ekstraktant, asit ve metal derişiminin hafif nadir toprak elementlerinin solvent ekstraksiyonuna etkisi incelenmiştir. Daha sonra tek damla kolonu ile solvent ekstraksiyon kinetiği incelenmiştir. Kolon yüksekliği, ekstraktant derişimi, asit derişimi, metal derişimi ve sıcaklık parametreleri kullanılan ana parametrelerdir. Sonuç olarak, akı formülleri kullanılarak reaksiyonların hız denklemleri hesaplanmıştır. Ayrıca Arrhenius eşitliği ve aktifleşmiş kompleks teorisi kullanılarak termodinamik özellikler belirlenmiştir. Termodinamik özelliklere göre, metal-ligand kompleksinin organik faza difüzyonu lantan ve seryum için hız belirleyici adım olarak saptanmıştır. Bunun yanında, praseodim ve neodim için hem difüzyon hem kimyasal reaksiyonların hız belirleyici adım olduğu saptanmıştır. Ayrıca arayüzeyde gerçekleşen reaksiyonların nükleofilik bimoleküler yer değiştirme mekanizması ile gerçekleştiği saptanmıştır.

Anahtar Kelimeler: Solvent ekstraksiyon, reaksiyon kinetiği, nadir toprak elementleri

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CHAPTER ONE
INTRODUCTION

Rare earth elements (REEs) have gained worldwide importance in recent years due to their usage in the critical areas. Although, these critical areas are mainly related to technology, the usage of REEs in health, metallurgy, petrochemistry, and similar fields has also opened a road for significant developments in these fields. REEs are able to found their role in daily life of every person that uses technological equipment like automobiles, mobile phones, televisions, and computers (Gschneidner, 2011).

After 2009, the world's REEs leader, China has changed the global REEs trade by production and trade quotas. After that, the criticality of REEs has been increased because of the supply problems (Voncken, 2016). According to the European Commission's Report on the Critical Raw Materials published in 2011 and revised in 2014, 2017, and 2020, REEs are always a critical raw material (European Comission, 2017, 2020). Besides of their supply challenges, the production of individual REEs is also one of the most challenging topics in hydrometallurgy. So, the solvent extraction is the most suitable method for the separation of REEs because of the adjustable nature of the process for each REEs (Zhang et al., 2016).

Solvent extraction (SX) is a method based on mass transfer between two immiscible liquid phases. In SX, there are two different phases: aqueous phase, and organic phase. The aqueous phase is mostly a product of the leaching process, and there is generally water in it. The organic phase contains an extractant in a carrier. The extractant has the role of selective separation for the desired solute, and the majority of diluents are crude oil fractions (Zhang et al., 2016).

The kinetics of the solvent extraction can be controlled by chemical reactions, by diffusion of reactants, or diffusion of products. And a four-step extraction can be presented as: (1) dimerization of extractant, (2) diffusion of the extractant dimers to the interface, (3) formation of first metal-ligand coordination bond for complexation, (4) formation of second and other metal-ligand coordination bonds for complexation,

(5) diffusion of formed metal-ligand complex through the interface. These steps are the mainframe of solvent extraction systems. The rate of extraction and the activation properties are used to determine which step controls the extraction process (Qi, 2018).

The single drop technique, Arrhenius equation, and activated complex theory are used for determining which of the above steps is controlling to the kinetics of solvent extraction and rate equations (Laidler, 1984; Laidler & King, 1983).

In this study, solvent extraction kinetics of lanthanum, cerium, praseodymium, and neodymium were investigated in a chloride medium with a single drop technique.

CHAPTER TWO

THEORETICAL BACKGROUND

2.1 Rare-earth Elements (REEs)

Rare-earth elements (REEs) term is used for describing an element group that contains lanthanides with scandium, and yttrium. All REEs, except Promethium (Pm), are occurred in nature, and their physicochemical properties are similar. These similarities have posed some difficulties in the separation and purification of individual REEs, all along with history. In Figure 2.1, the invention timeline of REEs was drawn according to references (Enghag, 2004; Krishnamurthy & Gupta, 2015).

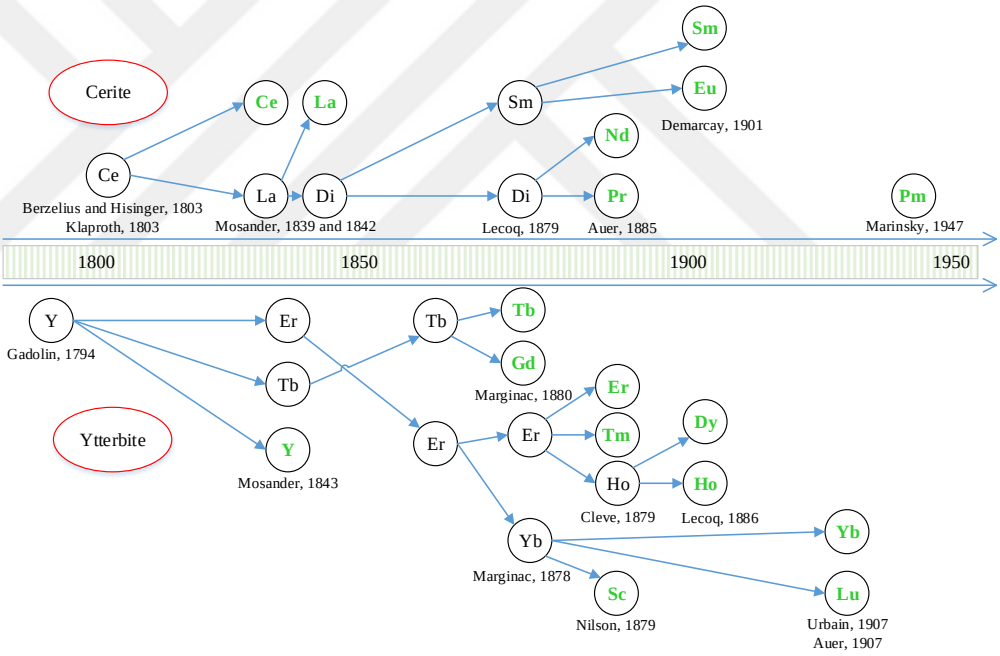

Figure 2.1 Invention timeline of rare-earth elements (Krishnamurthy & Gupta, 2015)

In Figure 2.1, the elements above the timeline are called as light rare-earth elements (LREEs), and the ones below the timeline, except scandium (Sc), are called as heavy rare-earth elements (HREEs). This classification is done according to the atomic mass of the REEs. When REEs are classified as previous statement, some researchers have suggested that samarium (Sm), gadolinium (Gd), and europium (Eu) could be classified as medium rare-earth elements (MREEs) because of their solvent extraction

behavior with acidic extractants (Krishnamurthy & Gupta, 2015; Stone et al., 2016; Zhang et al., 2016).

LREEs are widely used in metallurgy, as misch metal, alloying elements, modifiers, catalysts, etc. For example, some Mg alloys used in the aerospace industry were gain creep resistance with the addition of 2 – 3 wt.% neodymium (Nd) (Yan et al., 2008). In ductile cast iron production, cerium (Ce) was used for making spheroidal graphite (Johnson & Smartt, 1977). Neodymium (Nd), praseodymium (Pr), and Dysprosium (Dy) are used for the production of RE – Fe – permanent magnets, while cerium (Ce), yttrium (Y), samarium (Sm), and praseodymium (Pr) are used for RE – Co permanent magnets. Lanthanum (La) and other LREEs are used in nickel-metal hydride (NiMH) batteries. Europium (Eu), yttrium (Y), and sometimes terbium (Tb) are used in lamp phosphors for their luminescence properties (Emsley, 2011; Voncken, 2016).

Besides these areas, Sm, Eu, and Gd are used in nuclear reactors because of their neutron absorption properties are much higher than other elements (Zhang et al., 2016).

On the other side, most of the HREEs are also used in lasers and magnets for their high optical and magnetic properties. HREEs have many particular usage areas, but usage amounts are low (Voncken, 2016).

2.1.1 Important Properties for Separation of Rare-earths

In the case of REEs, most of the properties that affect the separation process were similar. However, several properties are allowed to separate adjacent REEs, like ionic radius, atomic radius, and valence state electrons. Next to these properties, there is a unique situation for lanthanides, called lanthanide contraction.

2.1.1.1 Lanthanide Contraction

Lanthanide Contraction is an ionic property of REEs (except Sc and Y). In the ionic state, the ionic radii is changed with the atomic number. Most of the physiochemical properties are exhibited a linear behavior with the atomic number. This situation is also valid for ionic radii. A graphical explanation of lanthanide contraction is given in Figure 2.2 (Huang, 2010).

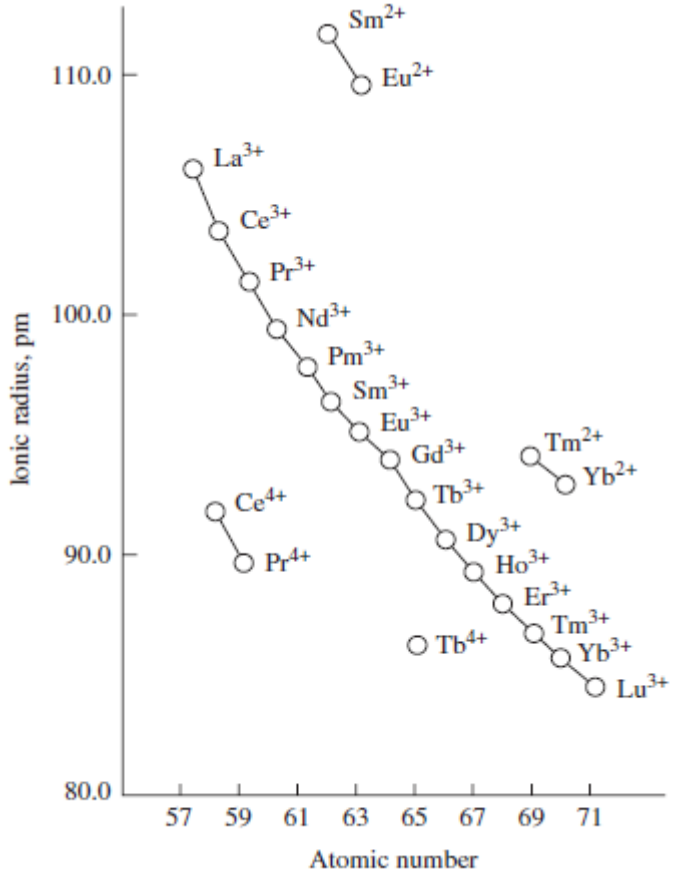

Figure 2.2 Lanthanide contraction with atomic number versus ionic radius (C. Huang, 2010)

Nevertheless, for REEs, when one more proton is added in the nucleus, the reduction in the ionic radii is higher than other elements. This situation only occurred in elements with 4f orbitals (all lanthanides at trivalent state). Lanthanide contraction is caused by poor nuclear charge shielding of 4f orbitals. Nuclear charge shielding can be defined as the collaboration of electrons to prevent collapsing trough the nucleus.

When lanthanides are passed to the ionic state, their outer shell electrons are left from 5s and 6s orbitals, and the total shielding effect of an ion is decreased. So for the lanthanides, when the atomic number is increased, the electrostatic force that affects each electron is also increased more than usual, and ionic radii are decreased more than usual (Krishnamurthy & Gupta, 2015; Platt, 2012; Zhang et al., 2016).

2.1.1.2 Physiochemical Properties of Rare-Earth Elements

Physical and chemical properties are similar for REEs, which are found in the same groups, like light, medium, and heavy rare earth elements. This similarity is giving a chance for separate REE groups to each other quickly, but also it is complicated to separate in-group REEs, like Ce, La, Nd, and Pr. So the separation of REEs is a challenging area, but some processes and approaches were provided to develop some routes for obtaining each REEs at high purity. These routes were benefited from some different properties of REEs like atomic weight, valence electrons, reactivity.

Some of the essential physical and chemical properties of REEs are presented in Table 2.1.

Table 2.1 Physical and Chemical Properties of REEs

Element	Atomic Number	Molecular Weight	Valence Electrons	Electronegativity
Sc	21	44.96	3+	1.36
Y	39	88.91	3+	1.22
La	57	138.91	3+	1.10
Ce	58	140.12	3+, 4+	1.12
Pr	59	140.91	3+, 4+	1.13
Nd	60	144.24	3+	1.14
Sm	62	150.36	2+, 3+	1.17
Eu	63	151.96	2+, 3+	
Gd	64	157.25	3+	1.20
Tb	65	158.93	3+, 4+	
Dy	66	162.5	3+	1.22
Ho	67	164.93	3+	1.23
Er	68	167.26	3+	1.24
Tm	69	168.93	3+	1.25
Yb	70	173.05	2+, 3+	
Lu	71	174.97	3+	1.27

2.1.2 Economic Importance of REEs

After the 1960s, the importance of REEs was highly increased with the purification possibilities, so the research and production of REEs are increased. The production amount of REEs, equivalent to REO (rare-earth oxide), are presented in Figure 2.3. Data in Figure 2.3 are derived from USGS (United States Geological Survey) Mineral Yearbooks, Mineral Commodity Summaries, and Statistics for REEs and visualized. The data until 2012 are taken from DiFrancesco's statistics, and the data after 2012 are taken from the 2015 Mineral Yearbook and 2019 Mineral Commodity Summary (DiFrancesco, Hedrick, Cordier and Gambogi, 2014; Gamboghi, 2019).

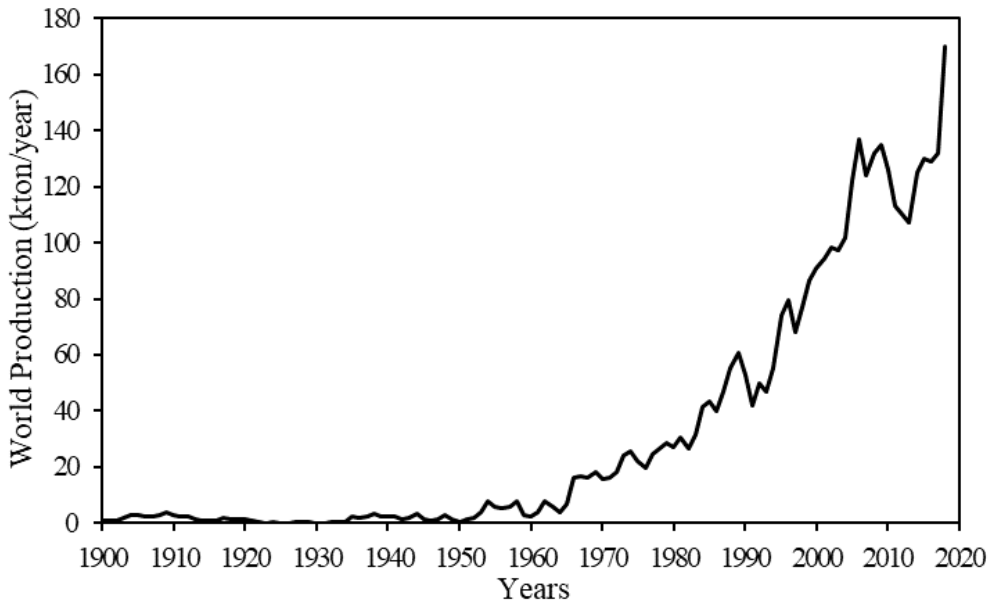

Figure 2.3 World REE production concerning the decades. Production amounts are used as REO equivalent (DiFrancesco, Hedrick, Cordier & Gambogi, 2014; Gamboghi, 2019)

China's policies about REEs production caused the rise in the 1990s, and this period is called as Chinese Era. According to a msineral commodity summary published by USGS in February 2019, China still dominates the worlds' REEs market (Gamboghi, 2019; Jha, 2014). So the criticality of REEs has been increased trough in the last two decades. This can be seen in government reports like the European Commission Critical Raw Materials list and the United States Department of Energy's Criticality Matrices. The criticality of REEs is mostly originated from their supply risk, and for

green energy trends and policies. The world will need REEs (European Comission, 2017; U.S. Department of Energy, 2011).

In 2009, China changed its point to the world's rare earth trade. China announced new production and export limits for REEs with taxes and applied environmental laws. This situation caused worldwide stress among the high tech market. Because many of the high-tech applications are not feasible without using REEs. Notable examples are hard-disk drives, smartphones, flat-screen televisions and monitors, rechargeable batteries (household and automotive), and tiny earphones. This period, starting in 2009, is known as the “Rare Earth Crisis” made many people around the world to be aware of this peculiar group of elements (Gschneidner, 2011; Voncken, 2016).

Production of REEs from secondary sources is more accessible than primary sources, and the percentage of REEs contents in some scraps are getting higher than some minerals and ores. Separation of REEs from transition metals is quicker than the separation of two REEs from each other. So, recovery of REEs from NdFeB hard magnets, rechargeable nickel metal-hydride batteries, and fluorescent lamps have become the most studied topics (Krishnamurthy & Gupta, 2015). This situation is leading to some government foundations and institutions to support the researches about REEs across the world. Meanwhile, in Turkey, the Institute for Rare-Earth Elements (NATEN) was established in early 2019. General Directorate of Mineral Research and Exploration (MTA) and Eti Maden Operations General Directorate have started studies about the feasibility of building a pilot plant that will use the complex ores located in Eskişehir.

2.1.3 General Production Routes for REEs from Primary Sources

The hydrometallurgical processing of REEs ores generally starts with beneficiation with some mining procedures. Ores that crushed down under a determined particle size are roasted. Oxidative roasting is used for oxidizing of Ce (III) to Ce (IV), and then roasted ore are leached for gaining REEs as ionic forms (Krishnamurthy & Gupta, 2015).

REEs contained loaded solutions are used for producing REEs concentrates and for the separation process. It depends on the ore characteristics and process conditions. For separation, ion exchange, solvent extraction, or chemical precipitation procedures are applied to the loaded solutions, and REEs are precipitated as in the form of oxalates, fluorides, chlorides, and hydroxides. Products are calcined or directly fed into reduction procedures. REE compounds are highly stable, so, fused salt electrolysis must be used for reduction of REEs compounds to produce REEs as the metallic forms (Jha, 2014; Krishnamurthy & Gupta, 2015; Zhang et al., 2016).

2.2 Solvent Extraction

Solvent extraction (SX) is a method based on mass transfer of ions between two immiscible liquid phases. In SX, there are two different phases, one is aqueous, and another one is organic. The aqueous phase is mostly a product of the leaching process, and there is generally water in it. The organic phase contains an extractant in a carrier. The extractant has the role of selective separation for the desired solute, and the majority of diluents are crude oil fractions (Zhang et al., 2016).

2.2.1 History of Separation and Solvent Extraction

The alchemy that the art of metallurgy, chemistry, and pharmacy, was probably developed by the Egyptians. Even the word alchemy has Egyptian origins. Alchemy is pronounced as al-Kimiya in Arabic. The “al-” part of the word is the article like “the” in English, and the Kimiya part of the word is a derivation of the word “Kemet” that is used for Egypt in ancient Egyptian (*Al-Kimiya: Notes on Arabic Alchemy | Science History Institute*, 2007). The first step of chemical separation were taken with the fermentation and distillation of alcohol by the early alchemists. Oils and fats were extracted from vegetables and animal parts. Some basic chemical processes like mixing, heating, cooling were applied into the materials that the early alchemists found in nature. They pursued the goal of transmutation of one matter to another for various purposes like making gold, weapons, poisons, and perfumes. The perfume production

process is the first solvent extraction example in the history of chemistry. The odorous leaves were heated and then cooled in alkaline water with fats and oils to enrich the perfumes (Cox & Rydberg, 2004).

The knowledge about distillation was lead that some of the solvents were obtained at their pure forms, like alcohol, ether, and etheric oils. Besides these, only a few pure solvents were known for 200 years ago. The organic solvents were not interested in the alchemists and scientists because of their insolubility in water. This reason could be an answer why solvent extraction is contained some unknown phenomena, among other methods (Cox & Rydberg, 2004).

2.2.2 Solvent Extraction in Modern Chemistry

In the early nineteenth century, the chemistry has made significant progress. The dissolution and recrystallization of many metallic salts in an alcohol and others were studied in this period, and these studied had formed the basis of the solvent extraction (Cox & Rydberg, 2004).

The solvent extraction order is expressed as four main steps:

1. The movement of solvent molecules (ligands) in the organic phase into the interface.
2. The diffusion of solvent molecules through the interface.
3. The formation of solute – solvent complexes due to the interface reactions.
4. The diffusion of hydrophobic complexes into the organic phase.

In the practical use of solvent extraction, the distribution ratio (*D*) is the primary parameter and it is defined by Walther Nernst in 1898. The distribution ratio can be defined as the ratio of a solute's equilibrium concentration in the organic phase ($[A]_{org}$) to equilibrium concentration in the aqueous phase ($[A]_{aq}$). The distribution ratio of the solute is defined by the Nernst distribution law given in Eq. 2.1 (Cox & Rydberg, 2004).

$$D_A = [A]_{org}/[A]_{aq} \quad (2.1)$$

For two or more different solutes, there must be two or more distribution ratio values, D_A, D_B, etc. If D values of two solutes are different, one of the solutes can be separated from the other one. The separation can be realized in a single stage or multiple stages, but after all, the solutes were separated (Cox & Rydberg, 2004).

In industry, the extraction factor ($\%E$) is more popular than the distribution ratio. The extraction factor can be calculated from the D value of a solute given in Eq. 2.2 (Cox & Rydberg, 2004).

$$\%E = 100D/(1 + D) \quad (2.2)$$

2.2.3 Solvent Extraction in Practice

The practical application of solvent extraction is mostly realized in three steps. These steps are extraction, scrubbing, and stripping. In brief, solute ions in the aqueous phase are transferred into the organic phase in the extraction step, some impurities or targeted solute ions are removed or washed in the scrubbing step, and the targeted solute ions are transferred into the aqueous phase as the purified form in the stripping step (Rydberg, Cox, et al., 2004).

2.2.3.1 Extraction

In the extraction step, a loaded solution is used as aqueous phase and contracted with the unloaded organic phase. The aqueous phase contains metal ions, free acids, and impurities, while the organic phase contains nonbonding extractants, carriers, and modifiers (Zhang et al., 2016).

In some cases, a multi-stage extraction may be required for the effective extraction. The multi-stage extraction is achieved by contact phases more than one time with

unprocessed aqueous and organic phases. This requirement can be understood by calculating the D values (Ritcey & Ashbrook, 1979; Zhang et al., 2016).

2.2.3.2 Scrubbing

Scrubbing is defined as washing of the loaded organic phase with water or weak acids. In some processes, scrubbing is necessary before stripping for the make stripping possible, and on the other hand, it is used for removal of the undesired ions. (Ritcey & Ashbrook, 1979).

Scrubbing also decreases the acid consumption in the stripping step. In the case of REEs, some LREEs are separated at scrubbing step when producing HREEs, and the scrubbing solution can be fed back to the feed solution (Erdem et al., 2020).

2.2.3.3 Stripping

Stripping (back extraction) is the last step of the solvent extraction process. The basic definition of stripping is taking the desired ions into the aqueous phase from the loaded or scrubbed organic phase. Mostly, mineral acids (HCl, HNO_3, H_2SO_4) are used in this step. Acid concentration can be varied from weak to strong by the stability of ion – solvent complex (Zhang et al., 2016).

Stripping is necessary for obtaining the product. Most of the solutes are useless in the organic phase. For further applications like precipitation, most of the solute ions are in the aqueous phase.

2.2.4 Solvent Extraction of Metals

Metals in a solution are found as hydrated ions, like in Figure 2.4. Anionic species and hydrated molecules can be form of a compound, an ion association, or solvated with extractants. The compound formation is realized with chelating or acidic extractants and the stable complexes are formed with hydrated metal cations. In the

case of ion association, most of the extractants are salts, and other names of this type of extractants are basic or anionic extractants. Besides these mechanisms, when solvation occurs, there are two possible situations are obtained a water-soluble metal anion or an organic soluble electron-donating functional group (Dong et al., 2016).

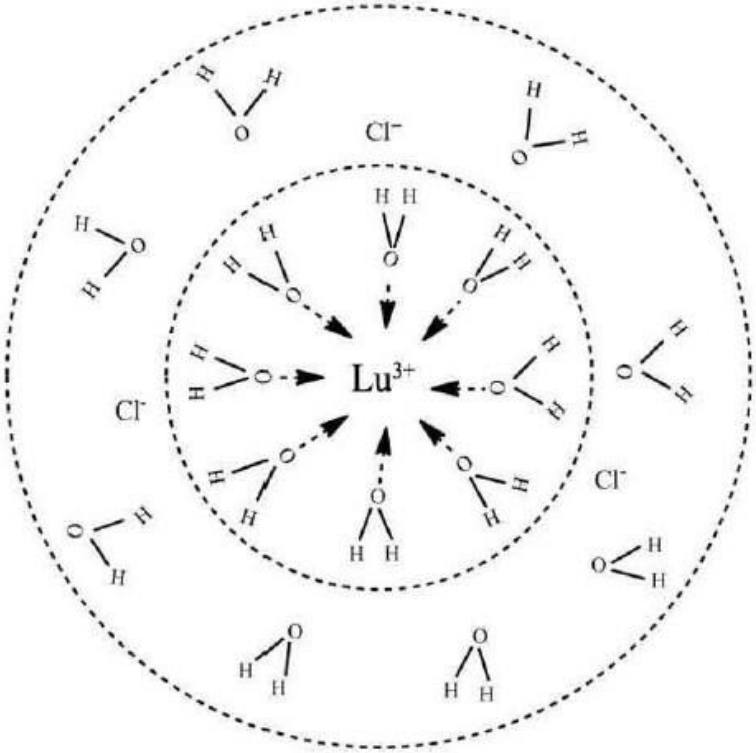

Figure 2.4 Hydrated form of Lu in chloride solutions (Dong et al., 2016)

2.2.4.1 Cation Exchangers (Acidic Extractants)

This type of interaction is based on the formation of a water-insoluble cation – ligand complex. Positively charged solutes (M) from aqueous solution and negatively charged ligand (L) from the organic phase have interacted at the interface. Typical reactions that take place at the interface are presented in Eq. 2.3. “n” can be called the coordination number of solute (Cox, 2004; Qi, 2018; Zhang et al., 2016).

$$\begin{aligned} M + L &= ML \\ ML + L &= ML_2 \\ ML_{n-1} + L &= ML_n \end{aligned} \tag{2.3}$$

This type is also called as acidic extractants, because of the donation of H^+ when they are disassociated. So the practically acceptable version of interface reaction presented in Eq. 2.4.

$$M_{(a)}^{z+} + zHL_{(o)} = ML_{z\,(o)} + zH_{(a)}^{+} \tag{2.4}$$

If the extractant has a dimeric structure (e.g., phosphoric and phosphonic acids, D2EHPA, Cyanex 272), the interface reaction must be indicated as Eq. (2.5).

$$M_{(a)}^{z+} + zH_2L_{2\,(o)} = M(HL_2)_{z\,(o)} + zH_{(a)}^{+} \tag{2.5}$$

The dimeric form of di-2-ethylhexyl phosphoric acid (D2EHPA) is seen in non-polar solvents, like kerosene. The diagram of D2EHPA dimer is presented in Figure 2.5 (Qi, 2018).

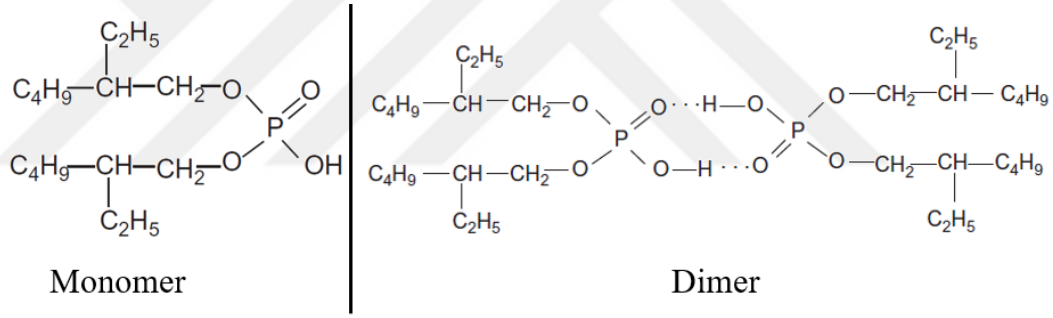

Figure 2.5 Monomeric ve Dimeric form of D2EHPA (Qi, 2018)

2.2.4.2 Ion Association (Ion Pair) Extractants

The extractants that have ion-pair mechanisms are typically amine compounds. The characteristic of this type of solvent extraction system is that, metals react with inorganic ligands to form negatively charged complexes in the aqueous phase, and these complexes can be extracted into the organic phase. This mechanism is simply said as liquid anion exchange. The general reaction of this mechanism is given in Eq. 2.6 (Cox, 2004; Ritcey & Ashbrook, 1979).

$$MX_p^{(n-p)}{}_{(a)} + (n-p)R_3NH^+X^-{}_{(o)} = R_3NH_{(n-p)}MX_p{}_{(o)} + (n-p)X^-_{(a)} \quad (2.6)$$

X^- is the ionic species (Cl^-, SO_4^{2-}, and NO_3^-) that make complexes with amines, and R_3N is the tertiary amine (Cox, 2004; Ritcey & Ashbrook, 1979).

2.2.4.3 Solvating Extractants (Neutral Extractants)

The mechanism of solvating extractants is that, neutral hydrated species are formed with organics and metal salts. These extractants also extract water, mineral acids, and hydrated species. The most common solvating extractants are Tributyl phosphate (TBP), Trioctyl phosphine oxide (TOPO), MIBK (methyl isobutyl ketone), etc. Phosphates, phosphine oxides, ketones, and esters are also used in this mechanism. A general reaction with solvating extractants was given in Eq. 2.7 (Cox, 2004; Ritcey & Ashbrook, 1979).

$$MY_q.xH_2O_{(a)} + rB_{(o)} = MY_q.B_{r\,(o)} + xH_2O_{(a)} \quad (2.7)$$

2.2.5 Major Uses of Solvent Extraction

With the usage of solvent extraction in the production of uranium in the 1940s, SX has got an essential place among enrichment methods. Today, with this method, sufficient knowledge has been provided to enable the production of various metals from low-grade ores, scraps, wastes, and dilute aqueous solutions. Solvent extraction has simplified by the separation of chemically similar precious metals such as REEs, Zr-Hf, Nb-Ta compared to old methods. Other uses of SX in metal processing are copper purification before electrowinning, refining of Pt group metals (PGMs), etc. (Cox, 2004).

Besides these, decaffeination and separation of essential oils can be done with SX for the food industry (Marcus, 2004), washing of polar compounds and recovery of valuable chemicals for the chemistry industry (Ritcey & Ashbrook, 1979), purification

of vitamins (Kislik, 2011) and recovery of active materials and wastewater treatment applications (Cox, 2004).

2.3 Psyhiochemistry of Solvent Extraction

Solvent extraction is an equilibrium process, so, its kinetic investigations must be done in the equilibrium conditions. The process is related to liquids, coordination chemistry, interactions between molecules, and thermodynamics.

2.3.1 Properties of Liquids

2.3.1.1 Phase rule in liquids

In a chemical system that was thermodynamically in an equilibrium, the number of independent thermodynamics variables (temperature and pressure) at equilibrium conditions was called as the degree of freedom of a system. The degree of freedom of a system can be expressed by the Gibbs Phase Rule by J.W. Gibbs. The number of substances (solutes in solvent extraction), number phases (aqueous phase, organic phase, or third phases), and other parameters (temperature and pressure) can affect the degree of freedom of the system with the way in Equation 2.8 (Gibbs, 1878).

$$F = C - P + 2 \tag{2.8}$$

In liquid systems, the phase rule can be applied for predicting the effects of substances that are added or removed. The substances are presented as a component, C in Eq. 2.8 and different phases like organic and liquid are presented with P. Temperature and pressure are parameters that can be independent or dependent. In solvent extraction systems, the entropy change is referred to as the degree of freedom (Choppin, 2004).

2.3.1.2 Polarity of liquids

In chemistry, the polarity refers to the way of forming bonds between atoms. Polar molecules arise when one of their atoms creates a more powerful force on the electrons in the bond. Electrons are drawn towards this atom more than others, and charge unbalance occurs in the molecule (Pauling, 1960).

The polarity of a molecule can be determined with electronegativity difference between atoms that formed the molecule. If the electronegativity difference is higher than 2, the molecule has ionic nature, and it is lower than the molecule has covalent bonding. Covalent bonding is spread into two subclasses, according to electronegativity differences. Polar molecules have an electronegativity values of difference between 0.5 and 2 when non-polar molecules lower than 0.5 (Pauling, 1960).

In liquids, polarity differences between two different phases make it possible to build a system like solvent extraction. The polar and non-polar solvents, e.g., water and organic phase, were not miscible in each other, and dimerization or polymerization is related to the polarity of the solvent. Also, some metal-ligand complexes have high non-polarity, according to others, and this feature can be utilized in separation technology (Rydberg, Choppin, et al., 2004).

2.3.2 Metal Ligand Complexes

The term ligand is described as a molecule that donates its electron pair when bonding according to the acid-base theory proposed by Lewis. Metal – ligand complexations are defined as a Lewis acid – Lewis base reaction because of the sharing of an electron pair between metal and ligand. In these reactions, metal is a Lewis acid; in other words, acceptor of the lone electron pair, while ligand is a Lewis base and donor of the lone electron pair. In the case of hydration, the metals in aqueous solutions are surrounded by water molecules, and water is acts as a Lewis base, so a ligand (Lawrance, 2010).

In this complexation, the stoichiometry of a complex is not easily calculated with the counting of valance electrons. Lone electron pair sharing is calculated with experimental methods, so the stoichiometry of a complex can be specified. In solvent extraction, extractants are electron-pair donors, and complexes of extractants are soluble in organic solvents, like kerosene. So extractants are forming a stable complex with metals in the aqueous phase or interface, then shift into the organic phase. In the case of REEs, the higher coordination numbers are usually obtained because of the f-orbitals, and with chelating ligands, so, REEs are forming their most stable complexes (Lawrance, 2010).

2.3.3 Thermodynamics in Solvent Extraction

Solvent extraction thermodynamics is related to the complexation of metal by water, anion, or ligand. The thermodynamic properties of a process can be determined with enthalpy and entropy changes (Choppin, 2004).

Enthalpy and entropy changes were evaluated as total enthalpy and entropy changes in dehydration and complexation. In the metal extraction, two different models can be suggested for bond formation: inner-sphere and outer-sphere complexation. In the inner-sphere complexation, water molecules around the metal cation are disturbed, and a metal-ligand bond is formed. Contrary to this, in the outer-sphere complexation, water molecules cannot be displaced, and metal and ligand are separated with water molecules (Choppin, 2004).

In the inner-sphere complexation, the displacement of water molecules increases the randomness, so entropy change is positive, and degrees of freedom are increasing. In oppose to this, solvation of metal with hydrates explained with two molecules are gathered together and form one stable complex, so degrees of freedom are decreased (Choppin & Morgenstern, 2000).

2.3.4 Rate of Reaction

The reaction rate is the ratio of the conversion during the observation period. Conversion ratio calculations can be changed according to the process and determination method. For all processes, the area, where the reaction took place, has an essential role on the determination of the rate. In solvent extraction, the conversion ratio is the amount of the mass that is passed through the interface at the observation period. To make consistent predictions about solvent extraction kinetics, the interface area must be known during the reaction (Danesi, 2004).

2.4 Solvent Extraction Kinetics

In the kinetics of the solvent extraction, whether it is controlled by chemical reactions or by diffusion of reactants or diffusion of products, a five-step extraction can be presented as;

1. Dimerization of extractant
2. Diffusion of the extractant dimers to interface
3. Formation of first metal-ligand coordination bond for complexation
4. Formation of second and other metal-ligand coordination bond for complexation
5. Diffusion of formed metal-ligand complex through the interface (Qi, 2018).

These steps are the mainframe of solvent extraction systems. The rate of extraction and the activation properties are used for determining which step controls the extraction process (Qi, 2018).

2.4.1 Reaction Mechanisms

Reactions in the solvent extraction systems are the nucleophilic substitution reactions. This reaction mechanism is defined as the subtraction of a complex maker

group with another group. Substitution is listed in two classes, S_N1 (nucleophilic unimolecular substitution) and S_N2 (nucleophilic bimolecular substitution) (Lawrance, 2010).

For S_N1 reactions, the leaving group departs firstly then, the entering group locates in empty spaces in the complex. Contrary to this, in S_N2, entering and leaving are realized at the same time, so the coordination numbers are preserved. These the only limiting mechanisms, but some intermediate complex formation mechanisms that depends on S_N1 and S_N2 can be determined (Lawrance, 2010).

2.4.2 Interface Properties

The liquid-liquid interface is a result of polar and non-polar interactions. Molecules in the organic phase are non-polar (hydrophobic) therefore, there is an interfacial tension between water molecules and ligand molecules. There are two Nernst diffusion layers: the aqueous phase-interface and interface-organic phase. During the stirring, these layers are getting thin but do not disappear. There is a finite thickness of these layers, and it's still adequate at its minimum thickness (Danesi, 2004).

For the single drop systems, a schematic of the layers and interface on a drop is given in Figure 2.6.

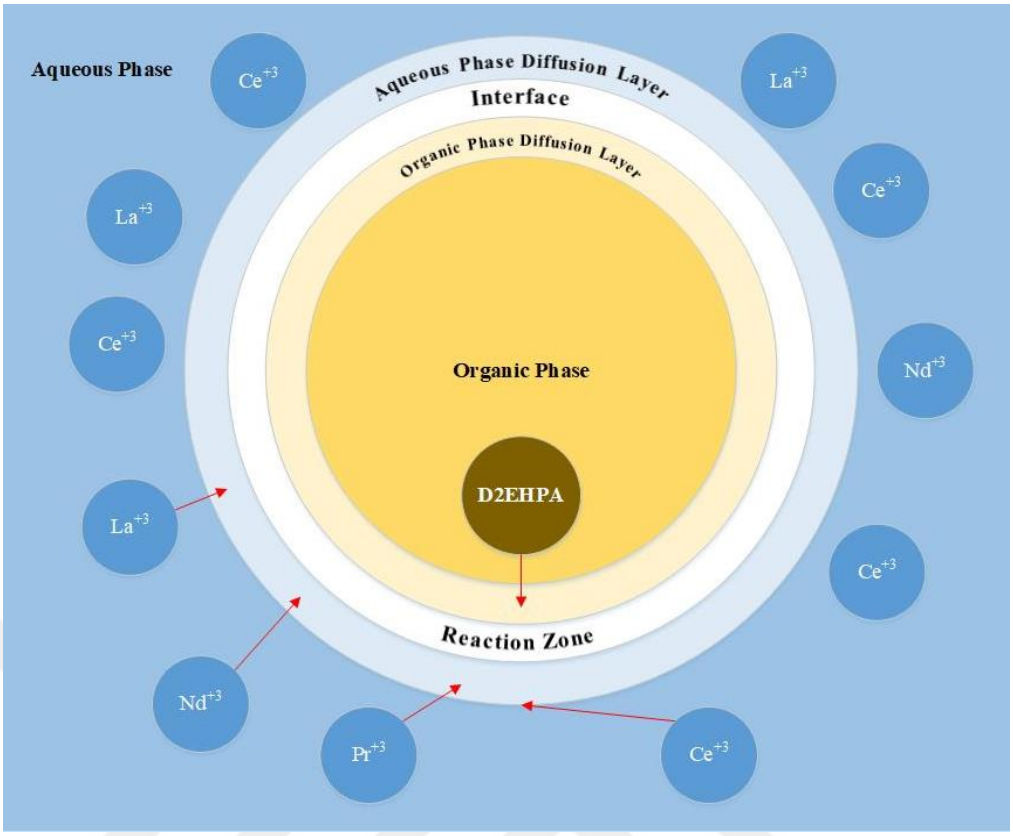

Figure 2.6 Schematic of the zones in a single drop and interface (Yin et al., 2016)

2.4.3 Identification Methods

There are four different comparisons for the determination of solvent extraction kinetics. These are;

1. Comparison of the heat transfer coefficient and the diffusion coefficient
2. Classification of the reaction by the activation energy
3. Addition of inert reference species and compare with the desired solute
4. Individually stirring of two phases and investigate the rate of extraction (Danesi, 2004).

Most of the solvent extraction kinetic investigations were focused on comparison of 2 and 4. Applying the comparison of 1 and 3 are more difficult, according to 2 and 4. Besides, a comparison of the Arrhenius energies of the system does not give a clear conclusion always, because the activation energies of the solvent extraction reaction

can be low as diffusion regimes. The stirring of two phases also does not give accurate conclusions (Danesi et al., 1980; Danesi, 2004).

2.4.4 Experimental Techniques for the Determination of Solvent Extraction Kinetics

Five different methods can provide the necessary hydrodynamic conditions. These are;

1. Highly stirred vessels; in this equipment, two-phase are vigorously stirred, and one of the phases are dispersed in other. Kinetics are determined with the immediate analysis of the aqueous phase at different time intervals.
2. Constant interfacial area stirred cells; Two-phase are stirred individually at a range of stirring speed in a cell that the interfacial area is known and constant. Kinetics are determined with the effect of the different stirring speeds.
3. Rotating diffusion cells; a rotating cylinder microporous membrane filter, is filled with organic phase is dipped into an aqueous phase container, and the thickness of the diffusion film was calculated as a function of rotation speed. In this apparatus, too many unknown parameters are involved.
4. Moving drops; a rising drop of organic phase in the aqueous phase or a falling drop of the aqueous phase in the organic phase is investigated in a column, concentration dependency and temperature dependency are analyzed. The circulation of liquids in this technique is presented in Figure 2.7.
5. Short time phase contact method; phases are not stirred, and conductivity change of the aqueous phase at short time intervals is considered to determined kinetics (Danesi et al., 1980; Danesi, 2004).

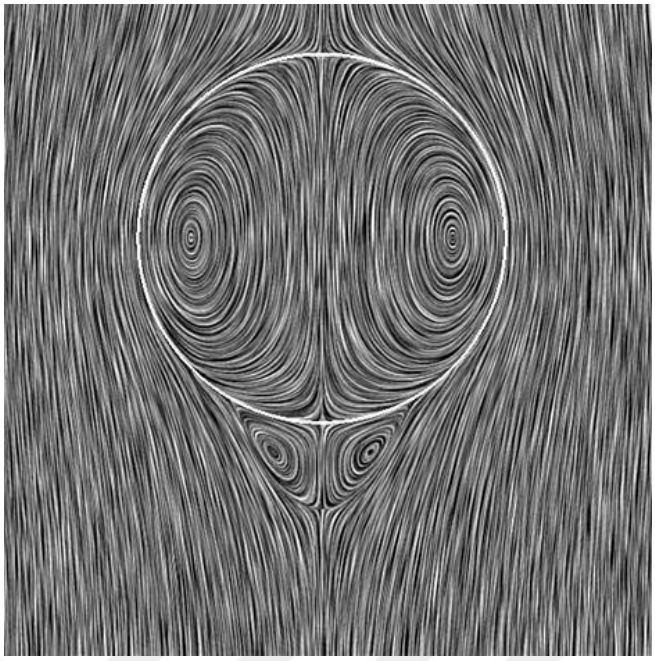

Figure 2.7 Circulations in a rising drop (Bäumler, 2014)

A simple comparison is made with accessible techniques in solvent extraction kinetics are given in Table 2.2 (Aparicio & Muhammed, 1989; Biswas et al., 2004; Biswas & Mondal, 2003; Chen & Wang, 2018; Danesi et al., 1982).

Table 2.2 Methods and apparatus from literature

Apparatus	Method	Advantage	Disadvantage	References
AKUFVE	Highly stirred vessel	Allows sampling at different times	Unknown hydrodynamics	(Chen & Wang, 2018)
Armollex	Constant interfacial area stirred cells	Known interfacial area	The unstable interface at stirring	(Danesi et al., 1982)
Hahn cell	Cylindrical transfer cell without stirring	Known interfacial area	Just for fast kinetics	(Biswas & Mondal, 2003)
Single drop technique	Moving drops in column	Simple construction, easy to modify	Sometimes long columns are necessary	(Biswas et al., 2004; Torkaman et al., 2014)

In this study, a single drop technique is used to determine the kinetics of solvent extraction.

2.5 Determination of Thermodynamic Properties

2.5.1 The Arrhenius Equation

The Arrhenius equation is used to measure of the temperature dependency of the rate of a reaction, with the activation energy. Activation energy can be obtained from the slope of the logarithm of the rate constant vs. 1/T graphs, like in Figure 2.8. The activation energy is the kinetic energy required for the reactants to cross the energy barrier for the reaction that can occur. If the activation energy is higher than 40 kJ/mol, the reaction needs more energy than diffusion, so the system is a chemical controlled system. If the activation energy is lower than 20 kJ/mol, the reaction is faster than diffusion, so the system is diffusion-controlled. In between 20 – 40 kJ/mol, there is not a sharp difference between the two mechanisms. The mathematical expression of the Arrhenius equation is given in the experimental section (Laidler, 1984).

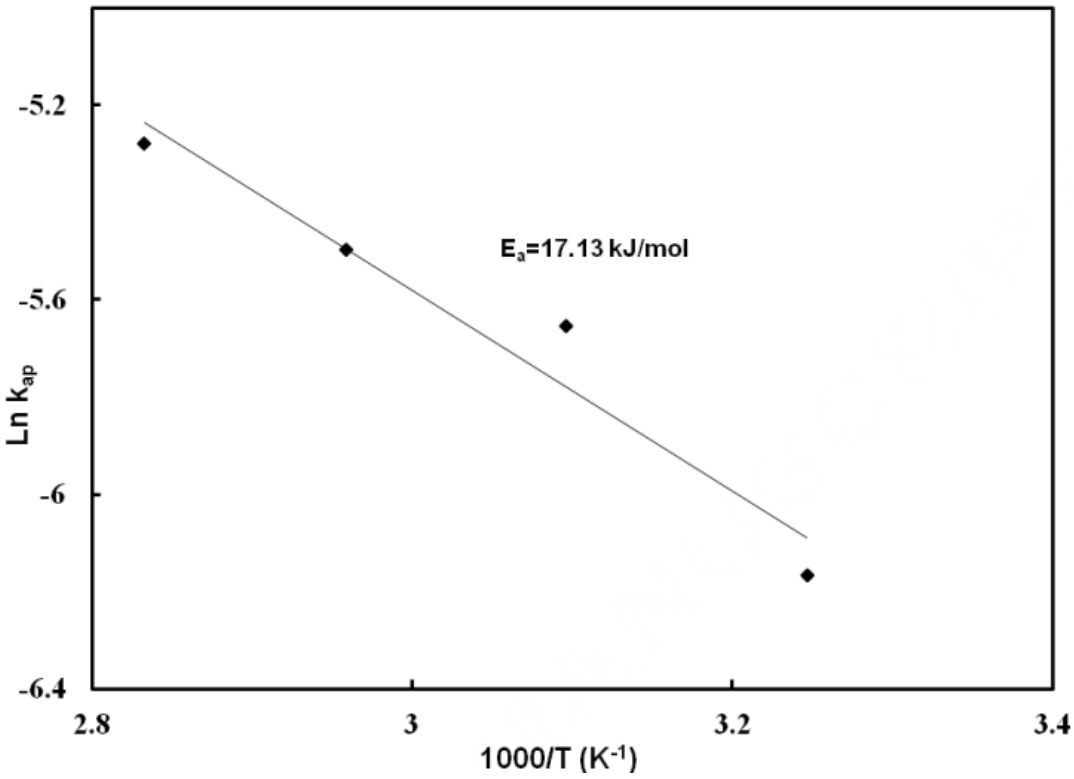

Figure 2.8 An example of using the Arrhenius equation for a leaching system (Behera & Parhi, 2016)

2.5.2 Activated Complex Theory

The activated complex is a theory for the calculation of absolute reaction rate with the help of the vibrational properties. The activated complex theory was developed with the help of the statistical mechanics and emphasized a quasi-equilibrium state with reactants. In Figure 2.9, energy diagrams of the S_N1 and S_N2 mechanism with the quasi-equilibrium products are given. The mathematical expression of the activated complex theory is given in the experimental section (Laidler & King, 1983).

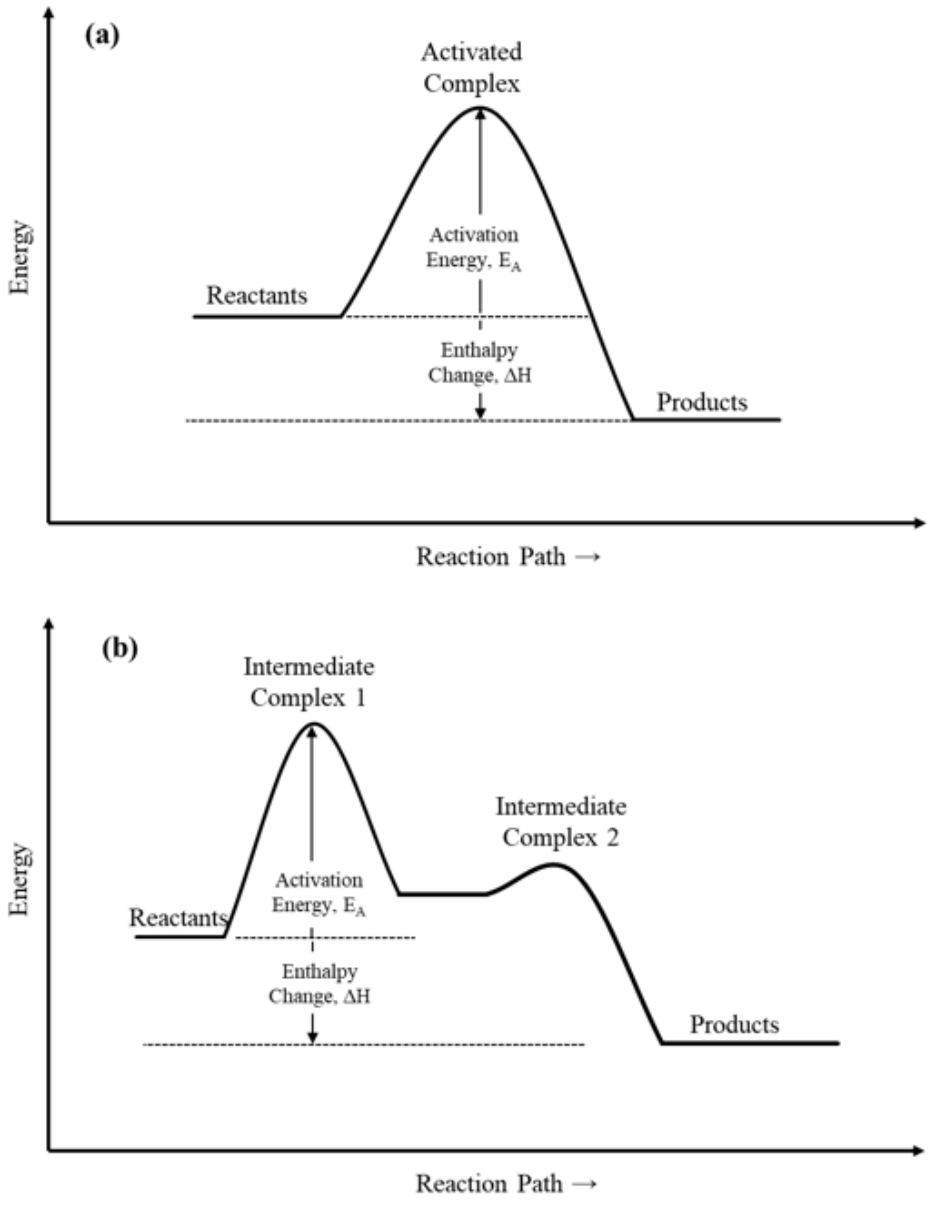

Figure 2.9 Energy diagrams of activated complexes (a) with S_N2 mechanism and (b) with S_N1 mechanism (Soderberg, 2019)

2.6 Literature Review

Torkaman et al. studied extraction kinetics of samarium from nitrate medium with D2EHPA and dialkyldithiophosphinic acid (Cyanex 301) by using single drop technique. In the study, the extraction rate of Sm with D2EHPA at pH 3 was obtained higher than Cyanex 301. The rate equation was different nozzle diameters were compared for the determining the rate-controlled step and diffusion was found as the slowest step. The rate equation of the interface reactions were indicated as $J=10^{4.035}[Sm(III)][D2EHPA][H^+]^{-0.8}$ for D2EHPA and $J=10^{4,035}[Sm(III)][Cyanex301]^{0.65}[H^+]^{-0.5}$ for Cyanex 301. The stripping kinetic was also studied in their study and the results showed that the stripping of Sm from D2EHPA or Cyanex 301 was directly proportional to the acid concentration (Torkaman et al., 2014).

Khanramaki et al. studied the extraction kinetics of uranium (VI) from a sulfate leach liquor with Alamine 336 in kerosene. The optimum extraction conditions were determined as 5 min equilibrium time, 1.5 initial aqueous pH, 0.12 mol/L Alamine 336 concentration and 0.22 mol/L sulfate ion concentration. The enthalpy change and the Gibbs free energy change were found to be negative, so the reaction was exothermic and spontaneous. The rate equation of the process was determined as $2.65x10^{-5}[UO_2^{2+}]^{1.5}[R_3N]^{0.5}[SO_4^{2-}]^{-0.5}[H^+]^{-0.2}$ and the activation energy was measured as 10 kJ/mol. So the extraction rate of the system was controlled by diffusion mechanism (Khanramaki et al., 2017).

Nasser S. Awwad studied the solvent extraction of uranium (VI) from nitrate medium with triphenyl phosphine oxide (TPPO). The rate equation of U(VI) extraction was found as $J = K_F[U(VI)]^1[HNO_3]^1[TPPO]^1$ and the research indicated that the reaction was controlled by diffusion. Thermodynamic investigations revealed that the extraction of uranium with TPPO in toluene has an enthalpy change as 12 kJ/mol and an entropy change as -348 J/mol.K. So reaction between U (VI) and TPPO was found as exothermic and ordered according to enthalpy and entropy changes (Awwad, 2004).

Awwad and Ibrahium studied the extraction of Ti (IV) from chloride solutions that contains Fe (III), Cr (III), and V (V) by D2EHPA. According to the equilibrium studies, the distribution ratio of Ti (IV) were higher at high D2EHPA concentration, high acidity, and low Ti (IV) concentration. In the kinetic experiments, flow rate was investigated with the extractant concentration, acid concentration, and metal concentration. The rate equation for Ti (IV) was found as $J = K_F[Ti(IV)][HCl][D2EHPA]$ and rate was controlled by mainly diffusion for Ti and other metal ions. Rate of other metal ions were just proportional with HCl concentration at the selected range, other parameters did not have any significant effect on extraction of Fe (III), Cr (III), and V (V) by D2EHPA (Awwad & Ibrahium, 2013).

Wang et al. studied the differences between extraction kinetics of Nd and Pr from aqueous solutions by trialkylmethylammonium nitrate [A336][NO_3] and they investigated that the effects of the addition of the diethylenetriaminepentaacetic acid (DTPA). Ratio of the rate constants of Pr and Nd was found as 2.04 with no DTPA and 2.21 with the addition of DTPA. The activation energies were found as 9 kJ/mol and 11.6 kJ/mol for Pr and Nd, respectively. The reaction was controlled by diffusion and reactions obey S_N2 mechanism (Wang et al., 2020).

Bardestani et al. investigated the kinetics of the solvent extraction of cerium (IV) with di-2,4,4-trimethylpentyl phosphinic acid (Cyanex 272) and 301 from sulfate medium. The rate equation of Ce (IV) was found as $J = 3\times10^{-8}[Ce^{4+}]^1[Cyanex\ 272]^1[H^+]^{-1}$ and $J = 3\times10^{-7}[Ce^{4+}]^{1.1}[Cyanex\ 301]^{1.2}[H^+]^{-0.6}$ for the Cyanex 272 and Cyanex 301, respectively. Rate-controlling step of the reactions were determined by the surface area of droplet and diffusion was found as the controlling mechanism (Bardestani et al., 2019).

Biswas and Begum investigated the extraction of Ti (IV) from chloride medium with D2EHPA. The extraction kinetics were changed at low and high concentration of Ti (IV). The forward rate equations were found as $J = 10^{-4.02}[Ti^{4+}][D2EHPA][H^+]^{-1}$ and $J = 10^{-6.06}\ [D2EHPA][H^+]^{-1}$ for the low and high concentration of Ti (IV), respectively. According to the activation energies, extraction was controlled by

chemical reactions at low concentration and controlled by both chemical reactions and diffusion at high concentration of Ti (IV). Stripping was also studied and found to be controlled by chemical reactions (Biswas & Begum, 2000).

Saleh et al. investigated the extraction of lanthanum from nitrate medium with the presence of acetate ions. According to the results, the rate equation was $J = 10^{-7}[La^{3+}]^{1}[Cyanex\,272]^{1}[H^{+}]^{-1}$ and the process was controlled by chemical reaction. The controlling reactions occurred with SN_2 mechanism as a result of the activated complex theory (Saleh et al., 2002).

CHAPTER THREE

EXPERIMENTAL STUDIES

3.1 Material

In this study, the synthetic leaching solutions were used for kinetic investigations of light rare earth elements. The certified standard solutions (CSS) of La, Ce, Pr, and Nd (1000 mg/L) from PerkinElmer were used for adjusting the concentrations of the synthetic leaching solutions. Glass equipment for the experimental setup was obtained from Pyrex. The extractant, D2EHPA (97%), was purchased from Sigma Aldrich, and kerosene for diluting the extractant was obtained from local sources. Hydrochloric acid solution (37% v/v) for pH adjustments was purchased from ISOLAB Chemicals.

3.2 Method

The method was briefly described in four stages: preparation of the synthetic leaching solutions, experimental setup, equilibrium studies, and single drop experiments.

3.2.1 Preparation of the synthetic leaching solutions

Compositions of LREEs in the synthetic leaching solutions were simulated from original leach liquor. The ratio of the individual REEs to total REEs (REE/TREE) in the synthetic solution was kept constant according to the kinetic calculations and the ratios of REEs was given in Table 3.1.

Table 3.1 The ratios of the individual REEs to total REEs in the synthetic solutions

Element	La	Ce	Pr	Nd
REE/TREE ratio (%)	27	53	3	17

Compositions and free acid contents of the synthetic leaching solutions were adjusted according to Eq. 3.1.

$$C_1 \times V_1 = C_2 \times V_2 \tag{3.1}$$

In Eq. 3.1, C_1, and V_1 were initial concentration, and the required volume of CSS and acid, C_2, and V_2 were desired concentration and final volume of the synthetic solution.

The free acid contents of the synthetic solution was adjusted with the addition of the required volume of HCl acid solution into synthetic solutions, according to Eq. 3.1.

For the organic phase, D2EHPA concentration was adjusted with diluting of pure D2EHPA with kerosene. One liter of pure D2EHPA contained 3 mol of extractants, the molarity of extractant in the organic phase was tuned according to Eq. 3.1.

The effect of initial metal concentration on the kinetics was determined with three different metal concentrations. The selected concentrations were given in Table 3.2.

Table 3.2. REEs concentration of the synthetic leaching solutions used for the kinetic investigation

Metal Concentrations	La mg/L	Ce mg/L	Pr mg/L	Nd mg/L	Total mg/L	Total mol/L
High (ME1)	160	250	15	60	485	$3.84x10^{-3}$
Medium (ME2)	80	125	8	30	243	$2.17x10^{-3}$
Low (ME3)	40	60	4	15	119	$9.77x10^{-4}$

3.2.2 Experimental Setup

The experimental setup that was used in single drop experiments was presented in Figure 3.1. The design of the single drop apparatus for this work was originated in previous works (R. K. Biswas et al., 1996; R. K. Biswas & Begum, 1999; Saleh et al., 2002; Torkaman et al., 2014; Whewell et al., 1975).

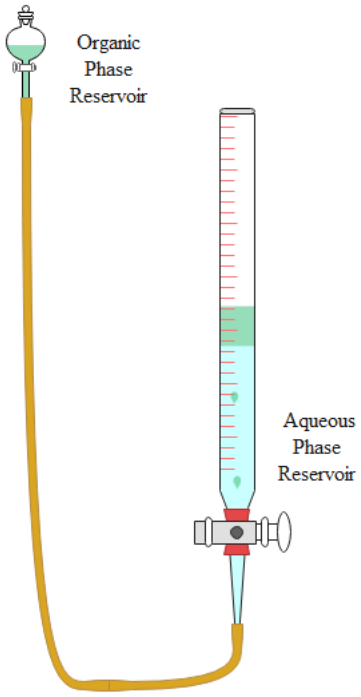

Figure 3.1 The experimental setup for single drop technique

For the experiments, firstly, the aqueous phase was fed into the column from a determined height. Then, the organic phase in the reservoir was transferred to the column, and the flow rate was arranged with a stopcock. Drops were formed with the effect of the height difference between the organic phase reservoir and column. The interface was controlled at a certain height, and the collected volume of the organic phase was measured. All experiments were continued until 100-120 drops collected. Drops were assumed as spherical, so volume (V_d) and surface area (A_d) of one drop can be calculated. The rising time of one drop (t_d) was the time elapsed between the formation of drop and arrival to the interface.

3.2.3 Equilibrium Studies

In the equilibrium studies, the exponential coefficients of the ions were determined at the selected conditions. For the determination of the coefficient of extractant concentration, different D2EHPA concentrations (0.1, 0.2, 0.3, and 0.4M) were studied when 0.1 M HCl concentration and 243 ppm of total REEs contents were constants. For the determination of the coefficient of initial metal concentration, different REEs concentrations (total amount of 119, 243 and 485 ppm) were studied

when 0.1 M HCl acid concentration and 0.3 M D2EHPA concentration were constants. For the determination of the coefficient of acid concentration, different HCl concentrations (0.001, 0.01, 0.1, and 0.316 M) were studied when 0.3 M D2EHPA concentration and 243 ppm of total REEs contents were constants.

3.2.4 Single Drop Experiments

The first run of the experiments was done for determining the column height that was used in further experiments. At this step, a rising time correction must be done for the determination of the excess time that has passed during the drop formation and coalescence. This excess time can be calculated by the Farbu plot (Farbu et al., 1974).

Farbu plot represents the mass transfer per drop with time, and it is determined with column height. The mass transfer per drop due to time has resulted in a straight line that does not pass through the origin. So the intercept of the straight line is equal to the time elapsed in drop formation. This value must be added to the rising time for the correct results.

After determining the column height, the remaining experiments were done for investigating the effect of different parameters on kinetics. The parameters were used in single drop experiments were given in Table 3.3.

Table 3.3 The parameters that were used in kinetic studies

Parameter	D2EHPA (M)	LREEs Concentration (mol/L)	HCl (M)
Extractant Concentration	0.1 0.2 0.3 0.4	2.17×10^{-3} (ME2)	0.316 0.1 0.01 0.001
Metal Concentration	0.1 0.2 0.3 0.4	3.84×10^{-3} (ME1) 2.17×10^{-3} (ME2) 9.77×10^{-4} (ME3)	0.1
HCl Concentration	0.3	3.84×10^{-3} (ME1) 2.17×10^{-3} (ME2) 9.77×10^{-4} (ME3)	0.316 0.1 0.01 0.001

The effect of the parameters was investigated for each of REEs. Changes in the logarithm of the fluxes depended on the changing parameters that were graphed and analyzed with linear regression. The slope and intercept values were utilized in kinetic formulas, and the rate of the reactions were calculated.

3.2.5 Thermodynamic Investigations

The Arrhenius equation and the transition state theory were applied in investigations for temperature dependency. Thermodynamic investigations were done with three different metal concentrations at different temperatures. The experiments were represented in Table 3.4.

Table 3.4 Parameters that were used in thermodynamic investigations

Parameter	Temperature (°C)	D2EHPA (M)	LREEs Concentration (mol/L)	HCl (M)
Temperatures	20 30 40 50	0.3	3.84×10^{-3} 2.17×10^{-3} 9.77×10^{-4}	0.1

3.3 Data Treatment

3.3.1 Equilibrium Experiments

Equilibrium constants were calculated with stoichiometric constants that obtained by logD versus log[H^+], logD versus log[M^{3+}], and logD versus log[D2EHPA] graphics. A general reaction of rare earth elements with dimeric D2EHPA was given in Eq. 3.2.

$$RE^{3+}_{(aq)} + bH_2A_2 \overset{K_{ex}}{\leftrightarrow} RE(HA_2)_b + bH^+ \tag{3.2}$$

When this reaction is in the equilibrium, the equilibrium constant, K_{ex}, can be calculated according to Eq. 3.3.

$$K_{ex} = \frac{[RE(HA_2)_b][H^+]^b}{[RE^{3+}][H_2A_2]^b} \tag{3.3}$$

When using Eq. 2.1 in Eq. 3.3, Eq. 3.4 was written as:

$$K_{ex} = D_{RE} \frac{[H^+]^b}{[H_2A_2]^b} \tag{3.4}$$

H_2A_2 and H^+ in Eq. 3.4 are the initial extractant concentration and hydrogen ion concentration, respectively. According to data, the logarithm of K_{ex} was the measure of the affinity between D2EHPA and mentioned ions at the equilibrium.

3.3.2 Kinetic Experiments

The rate equation shows the effects of reactants to the reaction rate, and it was presented in Eq. 3.5.

$$reaction\ rate\ = k[A]^a[B]^b[C]^c \tag{3.5}$$

In Eq. 3.5, k is the forward rate constant, [A] is the concentration of reactant A, and a is the degree of rate. k in the equation was determined with values of a, b, and c, and the rate equation can be entirely written. For determining the kinetics of solvent extraction with a single drop technique, the reaction rate was replaced with flux.

Total flux calculation can be derived from the flux, volume, and surface area of one drop. Flux for a single drop was given in Eq. 3.6.

$$J\left(\frac{kmol}{m^2.s}\right) = \frac{V\ (L) \times dC\ (\frac{kmol}{L})}{A\ (m^2) \times dt\ (s)} \tag{3.6}$$

J : Flux of one drop
V : Volume of one drop
dC : Concentration change for one drop
A : Surface area for one drop
dt : Time for rising of one drop

For the single drop technique, the radii of drops are not stable, so the surface areas are different for each drop. Because of this, flux formulation must be corrected for calculation of the total flux. Eq. 3.7 and 3.8 show the total volume and total surface area of all drops and Eq. 3.9 is the combined form of Eq. 3.7 and Eq. 3.8.

$$V_T = N.\frac{4}{3}\pi r^3 \tag{3.7}$$

$$A_T = N.4\pi r^2 \tag{3.8}$$

$$\frac{V_T}{A_T} = \frac{r}{3} = \frac{1}{3} \times \sqrt[3]{\frac{3V_T}{4\pi N}} = 0{,}2068 \times \frac{V_T^{1/3}}{N^{1/3}} \tag{3.9}$$

V_T : Volume of the collected drops
A_T : Surface area of all drops
N : Number of the collected drops
r : Radius of one drop

The total flux equation is obtained by replacing the $\frac{V_T}{A_T}$ in Eq. 3.9 with Eq. 3.6 and Eq. 3.10 shows the combined form of these two equations.

$$J = 0{,}2068 \times \frac{V_T^{\frac{1}{3}} \times 10\ (L \times \frac{mL}{L})}{N^{1/3}} \times \frac{dC \div M_{A\,(RE)} \times 10^6\ (\frac{kmol}{L} \times \frac{mg}{kmol})}{dt\ (s)} \tag{3.10}$$

Units of volume and concentration are changed according to units in the experiments. REEs concentrations are used as ppm (mg/L), so the molecular weight (M_A) is multiplied with concentration as kmol/L. Eq. 3.10 is arranged for La, Ce, Pr, and Nd and Eq. 3.11 is obtained.

La $$J_{La}\left(\frac{kmol}{m^2.s}\right) = \frac{V_T\ (mL) \times dC\ (\frac{mg}{L})}{(6{,}71\ \times 10^7) \times dt\ (s)}$$

Ce $$J_{Ce}\left(\frac{kmol}{m^2.s}\right) = \frac{V_T\ (mL) \times dC\ (\frac{mg}{L})}{(6{,}78\ \times 10^7) \times dt\ (s)}$$

Pr $$J_{Pr}\left(\frac{kmol}{m^2.s}\right) = \frac{V_T\ (mL) \times dC\ (\frac{mg}{L})}{(6{,}81\ \times 10^7) \times dt\ (s)}$$

Nd $$J_{Nd}\left(\frac{kmol}{m^2.s}\right) = \frac{V_T\ (mL) \times dC\ (\frac{mg}{L})}{(6{,}98\ \times 10^7) \times dt\ (s)}$$

(3.11)

Fluxes that were calculated with Eq. 3.11 was used in the reaction rate equation and Eq. 3.12 was obtained from Eq. 3.5.

$$J_{RE} = k_F[A]^a[B]^b[C]^c \quad (3.12)$$

The rate order for each reactant, a, b, and c, can be determined experimentally when the logarithm of both sides was taken in Eq. 3.12. Logarithmic form of Eq. 3.12 was given in Eq. 3.13.

$$logJ_{RE} = logk_F + a.log[A] + b.\log[B] + c.\log[C] \quad (3.13)$$

[A], [B], and [C] were the metal concentration, D2EHPA concentration, and H^+ concentration, respectively. In this method, the slope analyses of the logJ-log[RE], logJ-log[D2EHPA], and logJ-log[H^+] give a, b, and c values, respectively.

After determining orders a, b, and c, the forward rate constant (k_F) was obtained by the intercepts of each parameter, and the reaction rate equation is obtained. These steps were applied for four REEs, and differences were criticized.

3.3.3 Thermodynamic Experiments

The thermodynamics of a solvent extraction system is determined with the Arrhenius equation and the activated complex theory, which gives the thermodynamic constants of the reaction. The Arrhenius equation is used for obtaining the activation energy of reaction, and it is a measure of how temperature affects the reaction. So the kinetic regime of the reaction can be revealed as chemical controlled or diffusion controlled. After that, the activated complex theory takes place, and the thermodynamic constants are calculated. The values of the thermodynamic constants show the rate-controlling step and mechanism. The formulas of the Arrhenius equation and activated complex theory were given in Eq. 3.14 and 3.15.

$$k = A\,exp[-E_A\ /(RT)] \quad (3.14)$$

$$log\frac{J.h}{k^*.T} = \frac{-\Delta H^{\pm}}{2{,}303RT} + \frac{\Delta S^{\pm}}{2{,}303R} + logJ_{RE} \quad (3.15)$$

J: flux
A: integration constant
E_A: activation energy
R: gas constant
T: temperature

h: Planck constant
k*: Boltzmann constant
$\Delta H^{\pm}$: enthalpy change
$\Delta S^{\pm}$: entropy change

In the Arrhenius equation, the logarithm of the determined rate constants at different temperatures makes a straight line with the reciprocals of the temperatures. The slope of the straight line is the $-E_A/R$, and the activation energy can be calculated. The values of the activation energy represent the temperature dependency of the reaction. The Activation energy values and pairing control mechanism are given in Table 3.5.

Table 3.5 Activation energy and control mechanism relationship

Activation Energy	Slow step	Control mechanism
<20 kJ/mol	Diffusion	Diffusion controlled
20 – 40 kJ/mol	Cannot be determined	Mixed controlled
>40 kJ/mol	Reaction	Reaction controlled

In a chemical reaction-controlled process, the reaction at the interface is slower than the diffusion of the reactants to the interface. In this regime, the solute concentration on the interface is increased, and the diffusion loses its effect. The reaction rate can be increased with increases in the temperature because of the high-temperature dependency of the reaction control mechanism.

In a diffusion-controlled processes, since the reactions taking place at the interface are very fast, solutes entering the interface are reacted faster than the diffusion of solutes. In this regime, diffusion and hydrodynamics are sufficient enough for reaction, and the determining factor is the diffusion coefficient. Although the temperature is also a factor that accelerates diffusion, in these processes, it is more effective for interface reactions. When temperature increases, the transport coefficient increases at the same ratio, but the "rate constant" of the reaction increases more than a hundred times of temperature increase.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Equilibrium Studies

4.1.1 Effect of Metal Concentration

The effect of metal concentration on the equilibrium at constant D2EHPA and HCl concentrations were studied for light rare earth elements, and results were drawn in Figure 4.1.

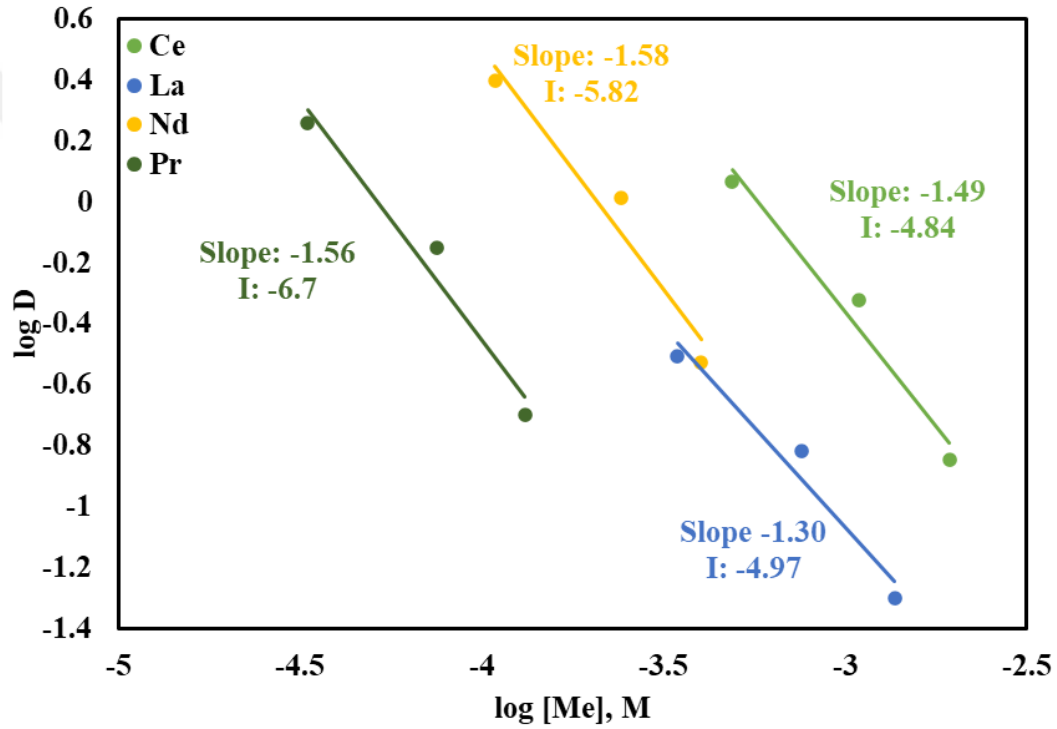

Figure 4.1 Effects of REEs concentration on the distribution ratios in SX process using of 0.3 M D2EHPA containing organic phase and 0.1 M HCl acid solution

According to experimental results, the logarithm of the distribution ratio (Eq. 2.1) shows a linear relationship with the logarithm of metal concentration (R^2>0.97). The negative slope of the linear regression lines indicates that the distribution ratio decreased with the increasing metal concentrations. The reason for this, the metal concentration in the organic phase was almost constant when the metal concentration in the aqueous phase was increased. Therefore, this situation was only valid for the constant extractant concentrations.

4.1.2 Effect of HCl Concentration

It can be seen in Figure 4.2, the HCl concentration affected the equilibrium at two different molarity ranges.

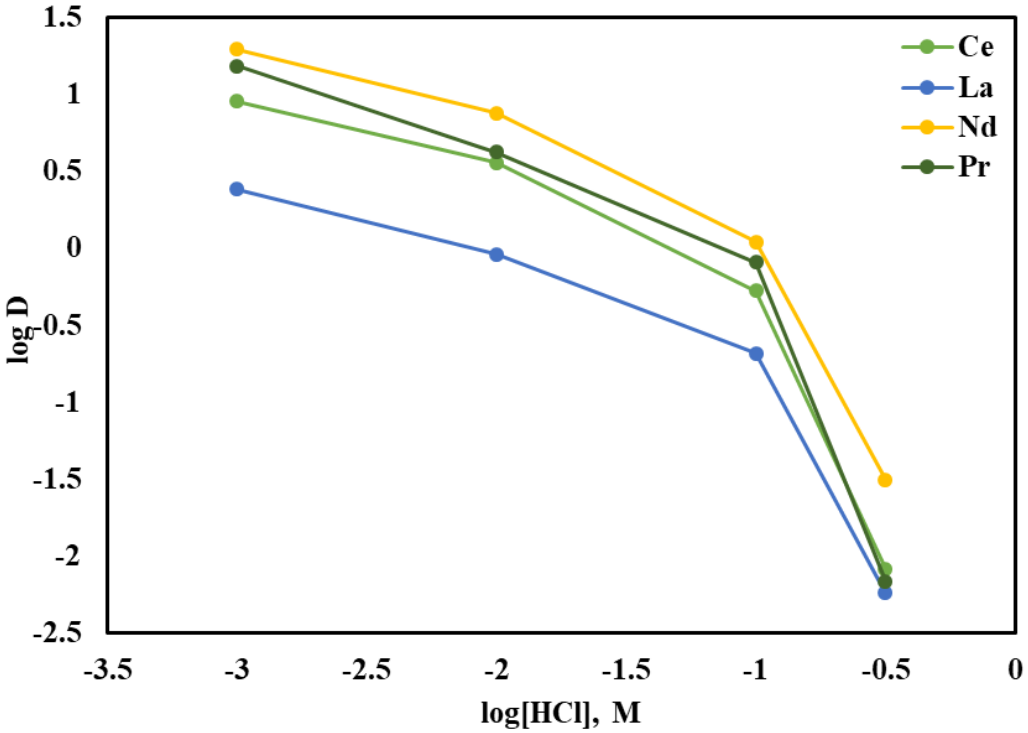

Figure 4.2 Effects of acid concentration on the distribution ratios in SX process using of 0.3 M D2EHPA containing organic phase and 2.17 $x10^{-3}$ M REEs containing acid solution

According to Figure 4.2, the correct slope analysis can be done between 0.001 – 0.1 M of HCl. In the region of 0.1 M – 0.316 M, the distribution ratios sharply decreased. At high acid concentrations, the dimeric D2EHPA was not released its proton and act as a neutral extractant. This situation can be seen in the slope analysis that was done in Figure 4.3, and Figure 4.4. So the concentration of HCl lower than 0.1 M is useful for single drop studies.

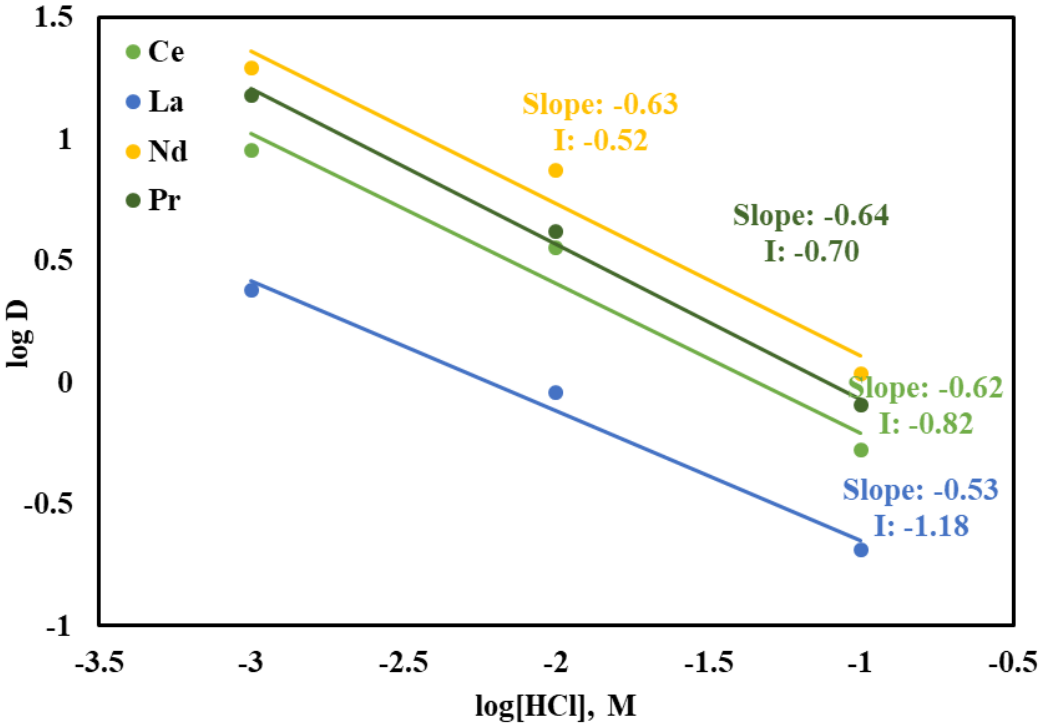

Figure 4.3 Effects of acid concentration (0.1-0.001 M HCl) on the distribution ratios in SX process using of 0.3 M D2EHPA containing organic phase and 2.17 x10^{-3} M REEs containing acid solution

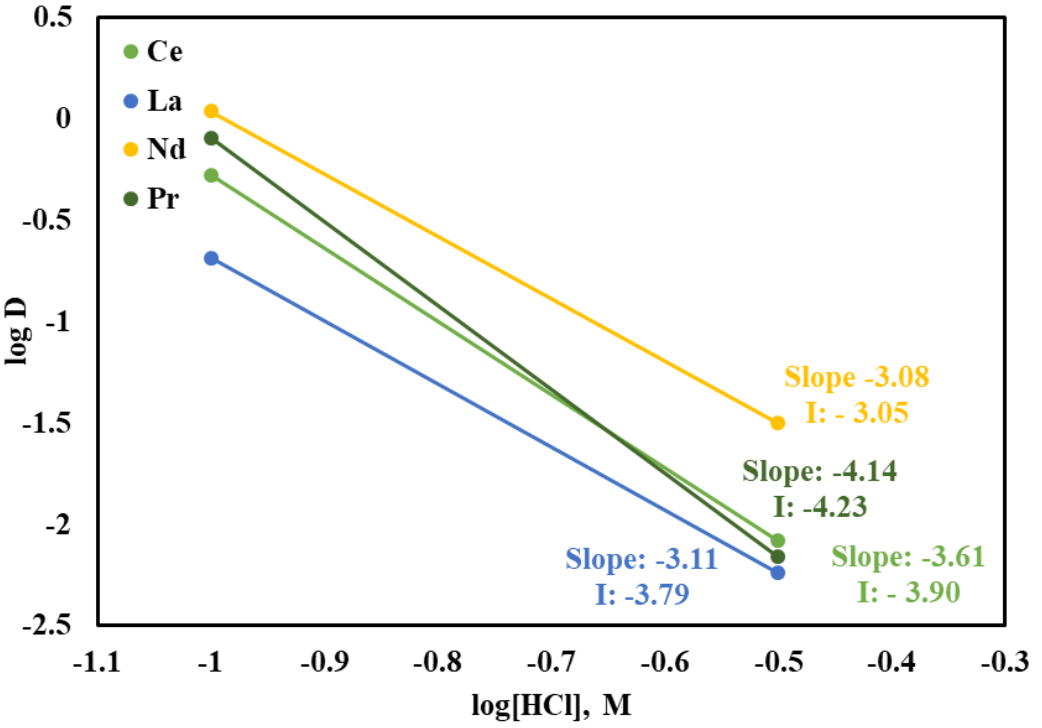

Figure 4.4 Effects of acid concentration (0.1-0.316 M HCl) on the distribution ratios in SX process using of 0.3 M D2EHPA containing organic phase and 2.17 x10^{-3} M REEs containing acid solution

4.1.3 Effect of D2EHPA Concentration

The effect of D2EHPA concentration on the distribution ratios can be seen in Figure 4.5.

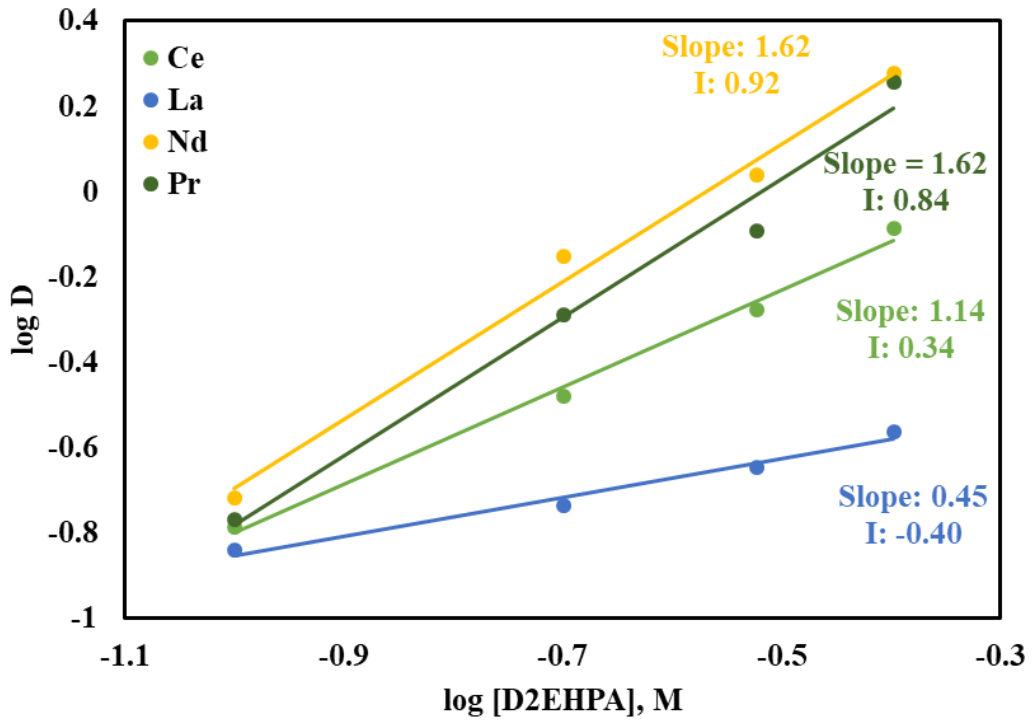

Figure 4.5 Effects of D2EHPA concentration on the distribution ratios in SX process using of 0.1 M HCl and 2.17 x10^{-3} M REEs containing acid solution

According to the linear relationship between the logarithm of D2EHPA and distribution ratios, the slopes were obtained for each LREEs. As can be understood from the slope values, the effect of D2EHPA depended on the atomic number when the metal concentration and HCl concentration is kept constant. In other words, the lanthanide contraction resulted in ionic radius decreases and lead to stronger complex with the chelating agent. Based on this slope analysis, it can be said that the stoichiometric coefficients between metal ions and D2EHPA were measured approximately 2 for Nd and Pr and 1 for Ce, but in the case of La, the slope was below 0.5. This slope value means the extraction of Nd, Pr, and Ce was dependent on D2EHPA concentration while the extraction of La was independent when 0.1 M HCl acid solutions used. Dependence of La to D2EHPA concentration will be valid at lower acidities. The obtained results did not give consistent K_{ex} values according to Eq. 3.4.

4.2 Single Drop Studies

4.2.1 Column Height

Column height was studied for determination of time that passing through the drop formation and coalescence. In this step, different column heights were studied, and the flux equation was calculated with mass transfer per drop. Mass transfer per drop vs. rising time graphs were drawn in Figure 4.6. All the R^2 values are above 0.99, and the relationship between the parameters is linear.

The mass transfer per drop was affected by D2EHPA concentration as usual, but the excess time that passed until the drop was formed for LREEs when single drop experiments were almost the same. Table 4.1 shows that the slopes and intercepts obtained with linear regression equation and excess times were calculated according to Eq. 4.1 for y = 0. The meaning of slope is the measure of the effect of rising time at different D2EHPA concentrations and intercept is the metal amount per drop when rising is started.

$$y = slope \times x + intercept$$
$$excess\ time = -\frac{intercept}{slope} \quad (4.1)$$

Table 4.1 The experimental results of column height studies

Element	D2EHPA Concentration	Slope	Intercept	Excess time (ET)	Average ET.	Standard Deviation
La	0.1 M	0.51	0.17	0.33 s	0.342 s	0.059 s
	0.4 M	1.08	0.39	0.36 s		
Ce	0.1 M	0.71	0.26	0.37 s		
	0.4 M	0.97	0.28	0.29 s		
Pr	0.1 M	0.74	0.26	0.35 s		
	0.4 M	1.53	0.54	0.35 s		
Nd	0.1 M	0.75	0.24	0.32 s		
	0.4 M	1.24	0.45	0.37 s		

The average excess time was calculated as 0.342 seconds with a standard deviation as 0.059 seconds, and this time was added to rising time in flux calculations.

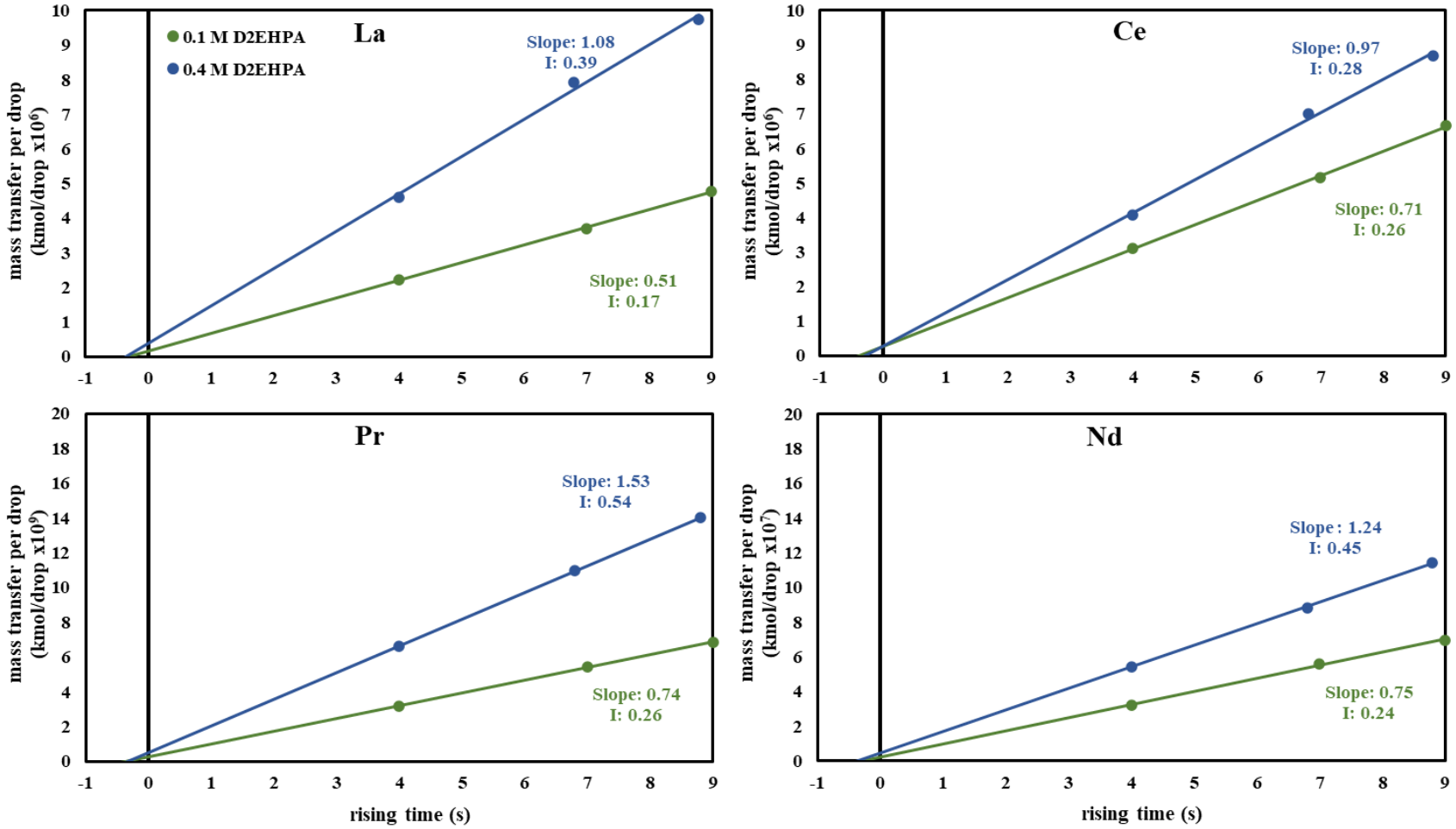

Figure 4.6 The Farbu plots obtained by the experimental studies where 0.1 and 0.4 M D2EHPA containing organic phase with 0.1 M HCl and 2.17 mM REEs containing aqueous solution were used.

4.2.2 Metal Concentration

The extraction rates obtained with different concentrations of LREEs were calculated at different D2EHPA concentrations and given in Figure 4.7. There were linear relationships between the logarithm values of flux and logarithm values of LREEs concentration obtained by different D2EHPA concentrations and R^2 values of these functions are higher than 0.96.

The slopes of the linear regression functions, given in Figure 4.7 are measured as 0.9, 1.0, 1.1, and 1.2 for La, Ce, Nd, and Pr, respectively. This slope values mean that the extraction kinetics of LREE were directly proportional to the metal concentration, and the drop surface was not saturated by the Me^{3+}-D2EHPA complex. If the metal concentration increase, eventually, the drop surface will be saturated with metal ions, and the SX process will be controlled by the chemical reaction. So, after this point, the slopes of the lines will stay constant.

4.2.3 HCl Concentration

HCl concentration in the aqueous phase was used in a range of 0.001 M to 0.1 M because of the sharp decrease after 0.1 M HCl concentration, and log-log graphics were drawn in Figure 4.8. The slope analysis indicates that HCl concentration has a negative effect, but kinetics were almost independent of HCl concentration between 0.001 M and 0.1 M range. Dependencies were changed with atomic number, and it was found that La was more dependent on HCl concentration, while Nd was less dependent.

0.316 M HCl concentration was also used, and according to slope analysis, at 0.316-0.1 M range, HCl dependencies of the kinetics of LREEs were increased.

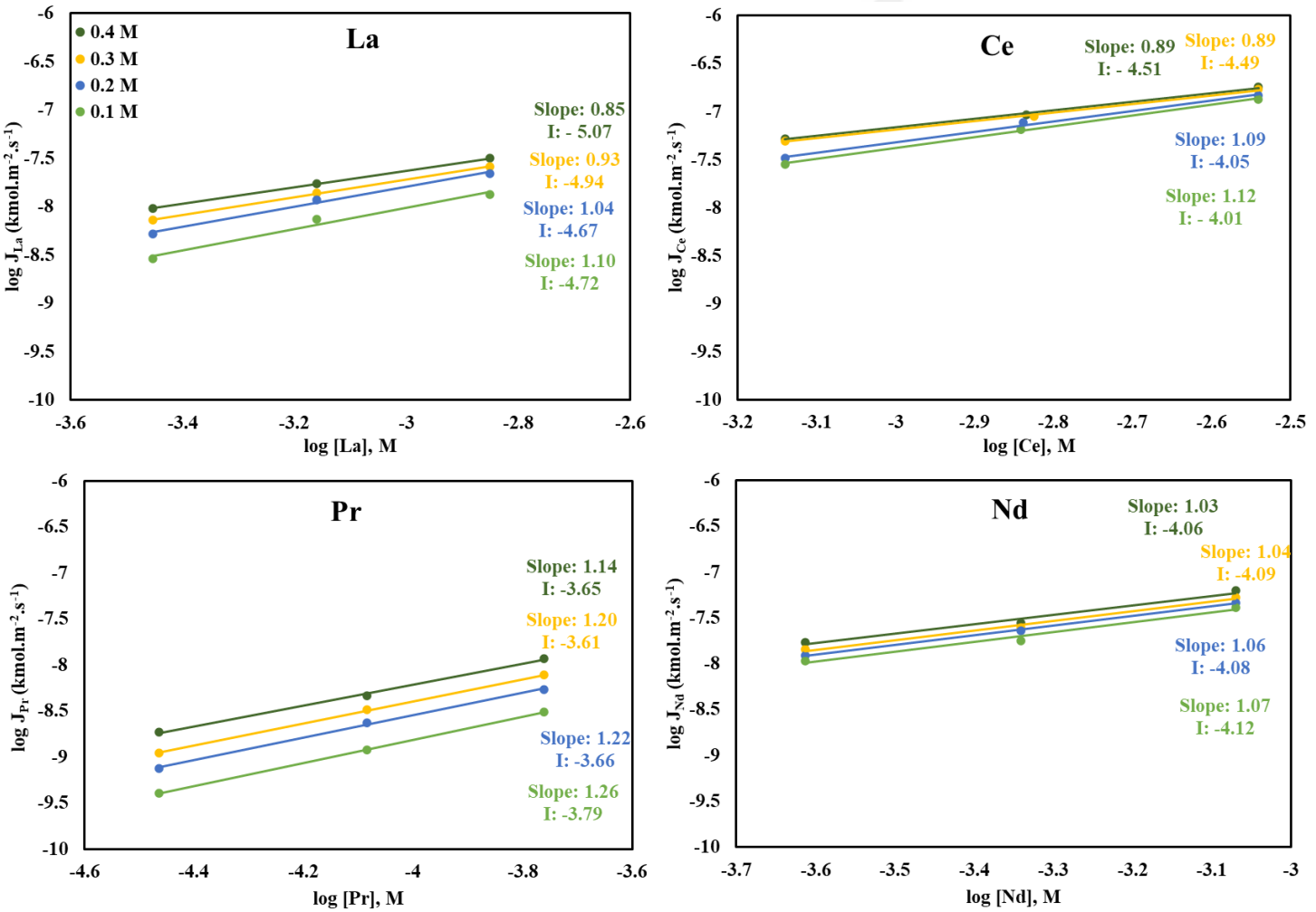

Figure 4.7 Effect of metal concentration on their flux values obtained by using different D2EHPA containing organic solution with 0.1 M HCl and 3.84, 2.17, and 0.977 mM REEs containing aqueous solution.

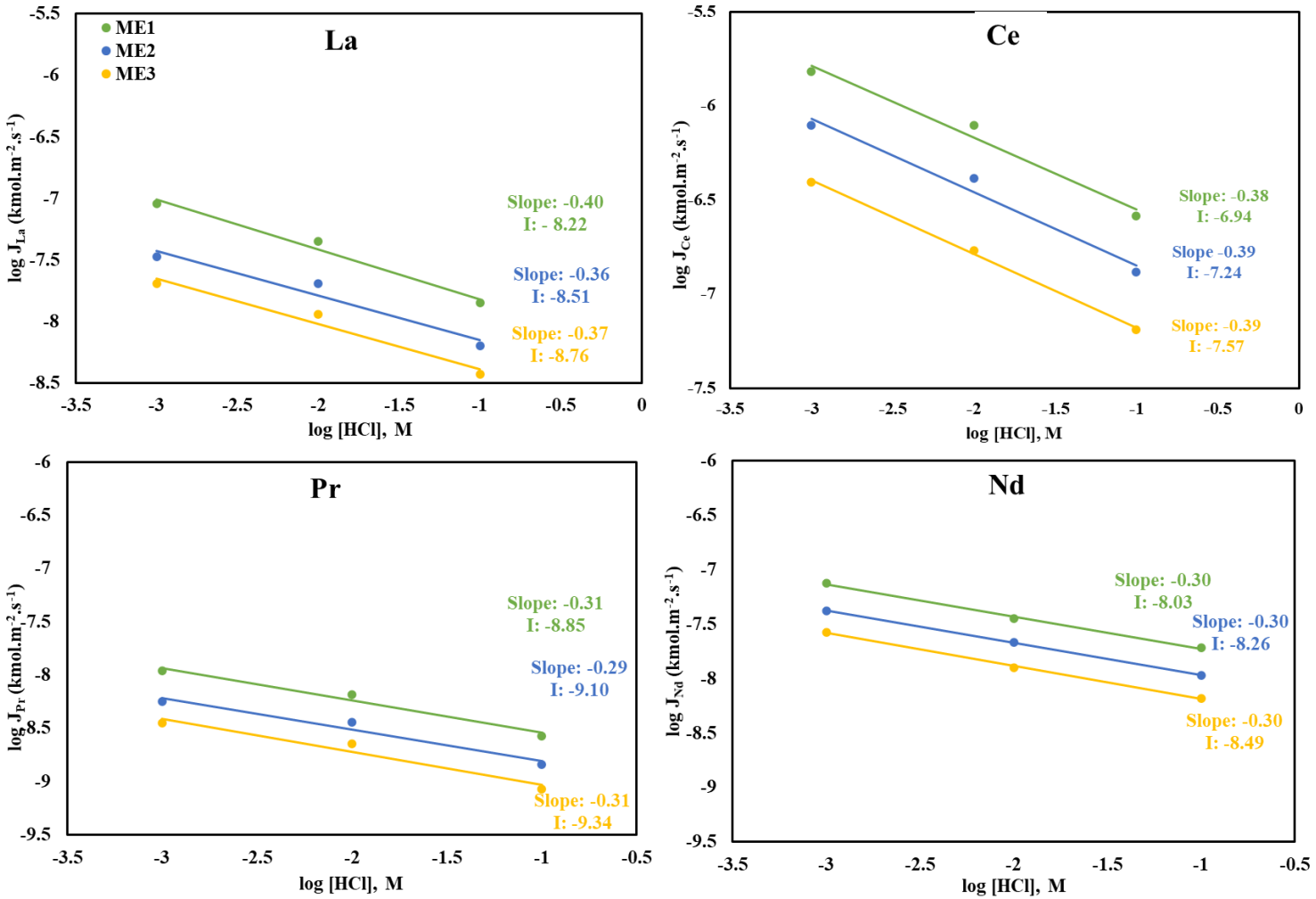

Figure 4.8 Effect of HCl concentration on their flux values obtained by using different REEs containing aqueous solution with 0.3 M D2EHPA containing organic solution.

4.2.4 D2EHPA Concentration

D2EHPA concentration is found to be the most effective parameter that affects the kinetics of LREEs. Log-log graphics of flux of LREEs with changing D2EHPA concentrations at with different HCl concentrations were given in Figure 4.9.

According to slope analysis, the rate was directly affected by D2EHPA concentration, and this effect was valid for different HCl concentrations except for La at 0.1 M HCl. There was a significant change for La with acidity, while other LREEs had almost the same value at different HCl concentrations. So, the results obtained in La at 0.1 M HCl can be neglected for the calculation of average reaction order.

4.3 Kinetic Investigations

After the determination of reaction orders for different parameters, the forward rate constants (k_F) were calculated with the intercepts of all experiments. Eq. 4.2, Eq. 4.3, and Eq. 4.4 were obtained from Eq. 3.13 with slope formulation (y = mx + n) and utilized in the calculations for metal, HCl, and D2EHPA concentration, respectively.

$$\begin{gathered} logJ_{RE} = a.log[RE^{3+}] + (logk_F + b.\log[HCl] + c.\log[D2EHPA]) \\ Intercept = logk_F + b.\log[HCl] + c.\log[D2EHPA] \end{gathered} \tag{4.2}$$

$$\begin{gathered} logJ_{RE} = b.\log[HCl] + (logk_F + a.log[RE^{3+}] + c.\log[D2EHPA]) \\ Intercept = logk_F + a.log[RE^{3+}] + c.\log[D2EHPA] \end{gathered} \tag{4.3}$$

$$\begin{gathered} logJ_{RE} = c.\log[D2EHPA] + (logk_F + a.log[RE^{3+}] + b.\log[HCl]) \\ Intercept = logk_F + a.log[RE^{3+}] + b.\log[HCl] \end{gathered} \tag{4.4}$$

The forward rate constants of La, Ce, Pr, and Nd were calculated according to Eq. 4.2, Eq. 4.3, and Eq. 4.4, and the results were given in Table 4.2, 4.3, 4.4, and 4.5, respectively.

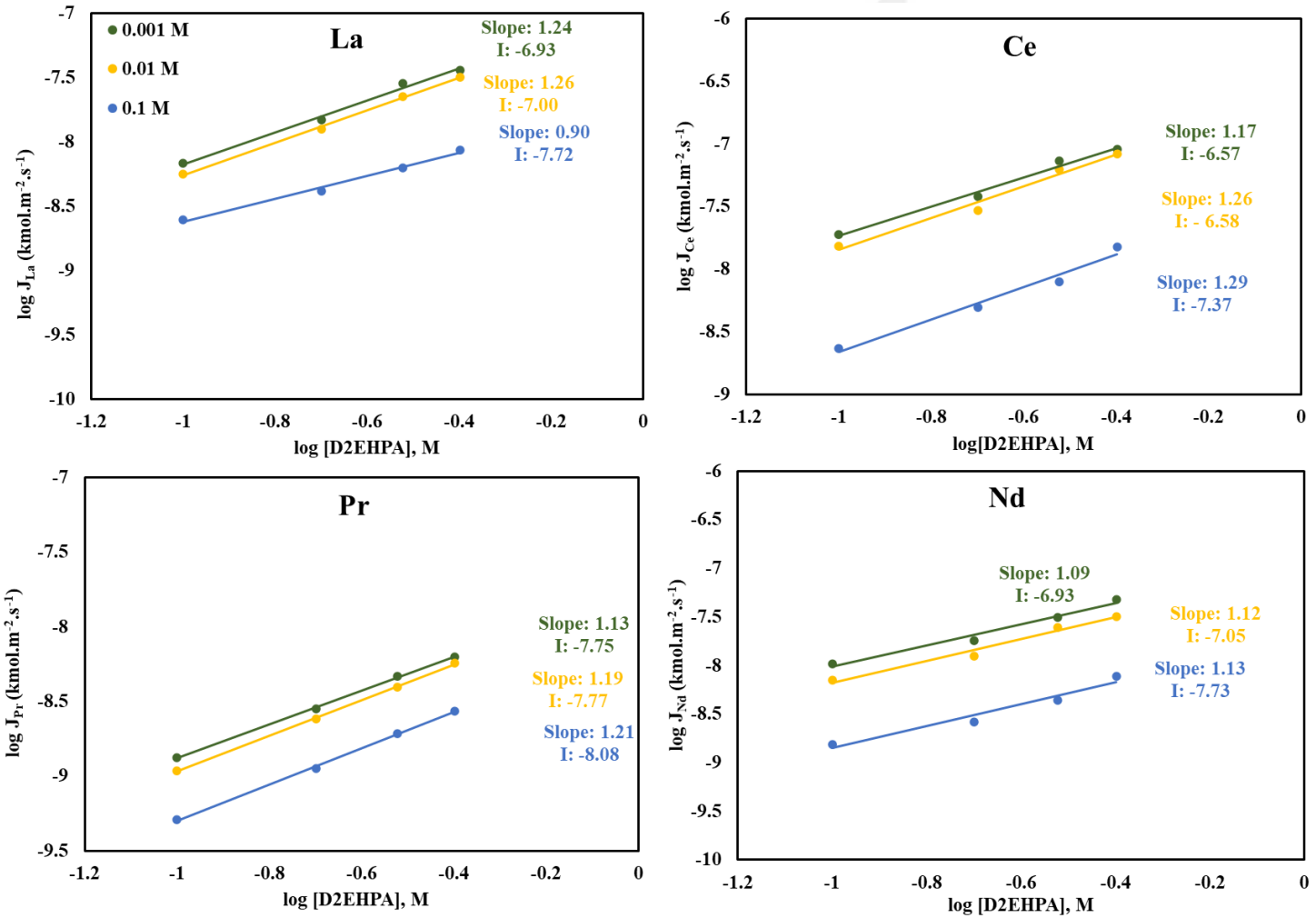

Figure 4.9 Effect of D2EHPA concentration on REEs flux values obtained by using different HCl concentrations with 2.17 mM REEs containing aqueous solutions.

Table 4.2 The results of the forward rate constant calculation for La

Parameter	$[La^{+3}]$	$[H_2A_2]$	HCl	Slope	R^2	Intercept	$\log k_F$	Aver. $\log k_F$
La	-	0.1	0.1	1.10	0.99	-4.72	-3.97	-4.74
		0.2	0.1	1.04	0.99	-4.67	-4.26	
		0.3	0.1	0.93	1.00	-4.94	-4.73	
		0.4	0.1	0.85	0.99	-5.06	-4.99	
HCl	1.35E-03	0.3	-	-0.40	0.98	-8.22	-4.82	
	6.67E-04	0.3		-0.36	0.95	-8.51	-4.81	
	3.38E-04	0.3		-0.37	0.97	-8.76	-4.71	
D2EHPA	6.67E-04	-	0.01	1.26	1.00	-6.99	-4.64	
	6.67E-04		0.001	1.24	0.99	-6.93	-4.96	

Average a: 0.98, b: -0.39, c: 1.25

Table 4.3 The results of the forward rate constant calculation for Ce

Parameter	$[Ce^{+3}]$	$[H_2A_2]$	HCl	Slope	R^2	Intercept	$\log k_F$	Aver. $\log k_F$
Ce	-	0.1	0.1	1.12	1.00	-4.47	-3.62	-4,17
		0.2	0.1	1.08	1.00	-4.45	-3.97	
		0.3	0.1	0.89	1.00	-3.98	-3.72	
		0.4	0.1	0.89	1.00	-3.93	-3.82	
HCl	2.71E-03	0.3	-	-0.38	0.98	-6.93	-3.73	
	1.12E-03	0.3		-0.39	0.98	-7.23	-3.65	
	7.20E-04	0.3		-0.39	1.00	-7.56	-3.79	
D2EHPA	1.14E-03	-	0.1	1.29	0.97	-7.37	-4.83	
	1.14E-03		0.01	1.26	0.98	-6.58	-4.43	
	1.14E-03		0.001	1.17	0.99	-6.57	-4.80	

Average a: 1.00, b: -0.39, c: 1.24

Table 4.4 The results of the forward rate constant calculation for Pr

Parameter	$[Pr^{+3}]$	$[H_2A_2]$	HCl	Slope	R^2	Intercept	$\log k_F$	Aver. $\log k_F$
Pr	-	0.1	0.1	1.26	1.00	-3.79	-3.05	-3.43
		0.2	0.1	1.22	1.00	-3.67	-3.24	
		0.3	0.1	1.20	1.00	-3.61	-3.37	
		0.4	0.1	1.14	1.00	-3.65	-3.54	
HCl	1.72E-04	0.3	-	-0.31	0.98	-8.84	-3.26	
	6.86E-05	0.3		-0.29	0.96	-9.09	-3.35	
	3.85E-05	0.3		-0.31	0.96	-9.33	-3.47	
D2EHPA	7.04E-05	-	0.1	1.21	1.00	-8.08	-3.39	
	7.04E-05		0.01	1.19	1.00	-7.77	-3.38	
	7.04E-05		0.001	1.13	1.00	-7.75	-3.66	

Average a: 1.20, b: -0.30, c: 1.18

Table 4.5 The results of the forward rate constant calculation for Nd

Parameter	$[Nd^{+3}]$	$[H_2A_2]$	HCl	Slope	R^2	Intercept	$\log k_F$	Aver. $\log k_F$
Nd	-	0.1	0.1	1.07	0.98	-4.12	-3.30	-3.93
		0.2	0.1	1.06	0.99	-4.08	-3.60	
		0.3	0.1	1.04	1.00	-4.09	-3.80	
		0.4	0.1	1.03	0.98	-4.06	-3.92	
HCl	8.16E-04	0.3	-	-0.30	1.00	-8.02	-3.66	
	3.85E-04	0.3		-0.30	1.00	-8.26	-3.89	
	2.42E-04	0.3		-0.30	1.00	-8.49	-4.10	
D2EHPA	2.91E-04	-	0.1	1.13	0.96	-7.73	-4.30	
	2.91E-04		0.01	1.12	0.98	-7.05	-3.93	
	2.91E-04		0.001	1.09	0.98	-6.93	-4.10	

Average a: 1.05, b: -0.30, c: 1.11

After determination of the forward rate constants, the rate equations for La, Ce, Pr, and Nd were obtained and given in Eq. 4.5, Eq. 4.6, Eq. 4.7, and Eq. 4.8, respectively.

$$J_{La}\left(\frac{kmol}{m^2 s}\right) = 10^{-4.74}.[La^{3+}]^{0.98}.[HCl]^{-0.39}.[D2EHPA]^{1.25} \quad (4.5)$$

$$J_{Ce}\left(\frac{kmol}{m^2 s}\right) = 10^{-4.17}.[Ce^{3+}]^{1.00}.[HCl]^{-0.39}.[D2EHPA]^{1.24} \quad (4.6)$$

$$J_{Pr}\left(\frac{kmol}{m^2 s}\right) = 10^{-3.43}.[Pr^{3+}]^{1.20}.[HCl]^{-0.30}.[D2EHPA]^{1.18} \quad (4.7)$$

$$J_{Nd}\left(\frac{kmol}{m^2 s}\right) = 10^{-3.93}.[Nd^{3+}]^{1.05}.[HCl]^{-0.30}.[D2EHPA]^{1.11} \quad (4.8)$$

As can be seen in the rate equations, the extraction kinetics of LREEs with D2EHPA was directly dependent on metal and D2EHPA concentrations, while HCl concentration has a negative effect as expected.

4.4 Thermodynamic Investigations

The thermodynamics of the extraction process was revealed with the Arrhenius equation. The single drop studies were realized at different temperatures by using three different metal concentration. According to the Arrhenius equation, the logarithm of flux must have a linear relationship with the reciprocal of the absolute temperature. The obtained results were given in Figure 4.10.

The activated complex theory was applied to flux, and temperature data and slope analysis were done. The results were given in Figure 4.11. Combined results of thermodynamic investigations were given in Table 4.6.

Table 4.6 Thermodynamic data for the LREEs-D2EHPA system for different metal concentrations

Element	Metal Concentration	Activation Energy (kJ/mol)	Entropy Change (J/mol.K)
La	ME1	6.9	-116
	ME2	7.9	-109
	ME3	8.9	-104
Ce	ME1	16.2	-52
	ME2	17.2	-47
	ME3	18.2	-43
Pr	ME1	20.7	-87
	ME2	20.6	-86
	ME3	20.5	-83
Nd	ME1	20.5	-65
	ME2	21.2	-61
	ME3	22.1	-57

The activation energies showed that extraction of La and Ce was controlled by the diffusion at this ranges of parameters while Nd and Pr have a transition to a mixed controlled regime. In the case of Nd and Pr, the activation energies are close to the limit value, so it was just a contribution of chemical reactions to the diffusion-controlled regime. At this point, disassociation of D2EHPA in the organic phase and diffusion through the interface were fast. So, the rate-determining step was the transferring of the complexes to the organic phase for Ce and La. For Nd and Pr, complex formation was slower than Ce and La, so the rate was controlled with the

diffusion, but some interface reactions had effects according to activation energy values.

The decrease in the entropy was explained by the combination of two molecules into one molecule. This situation was compatible with nucleophilic substitutions mechanisms. Therefore, the extraction reaction was followed by the bimolecular reaction mechanism (S_N2). In this mechanism, the dissociation of ligand ions in the organic phase was fast and had no control over the rate-determining step. So extraction has occurred in the interface, and the rate was mainly controlled by the transfer of the metal-ligand complexes from the interface. The diffusion of extractant ions to the interface was negligible because of the different results were seen in four different metal ions. At the interface, reactions were fast, and the product saturates the interface, so the process is limited by the diffusion of the metal-ligand complexes to the organic phase.

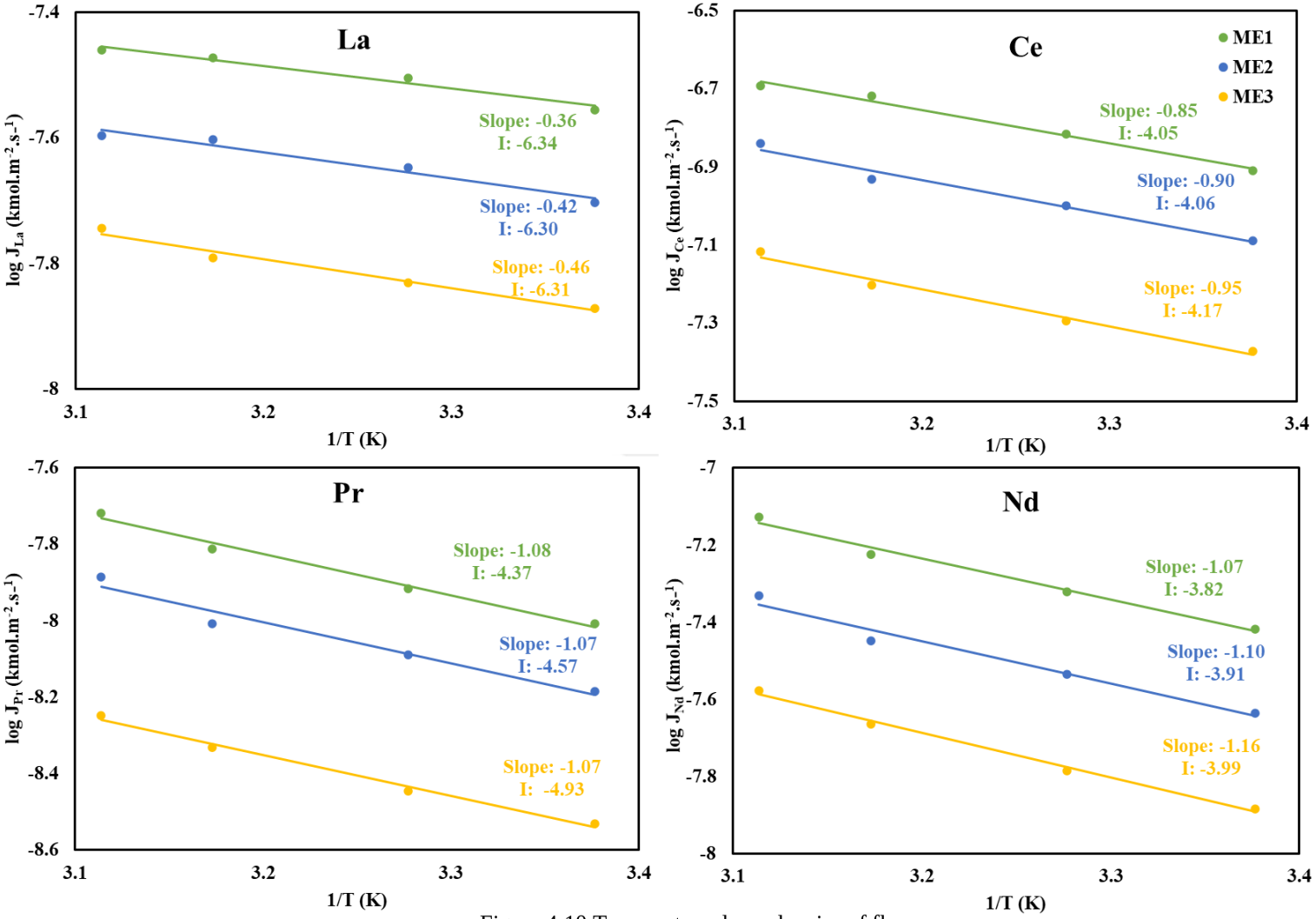

Figure 4.10 Temperature dependencies of flux

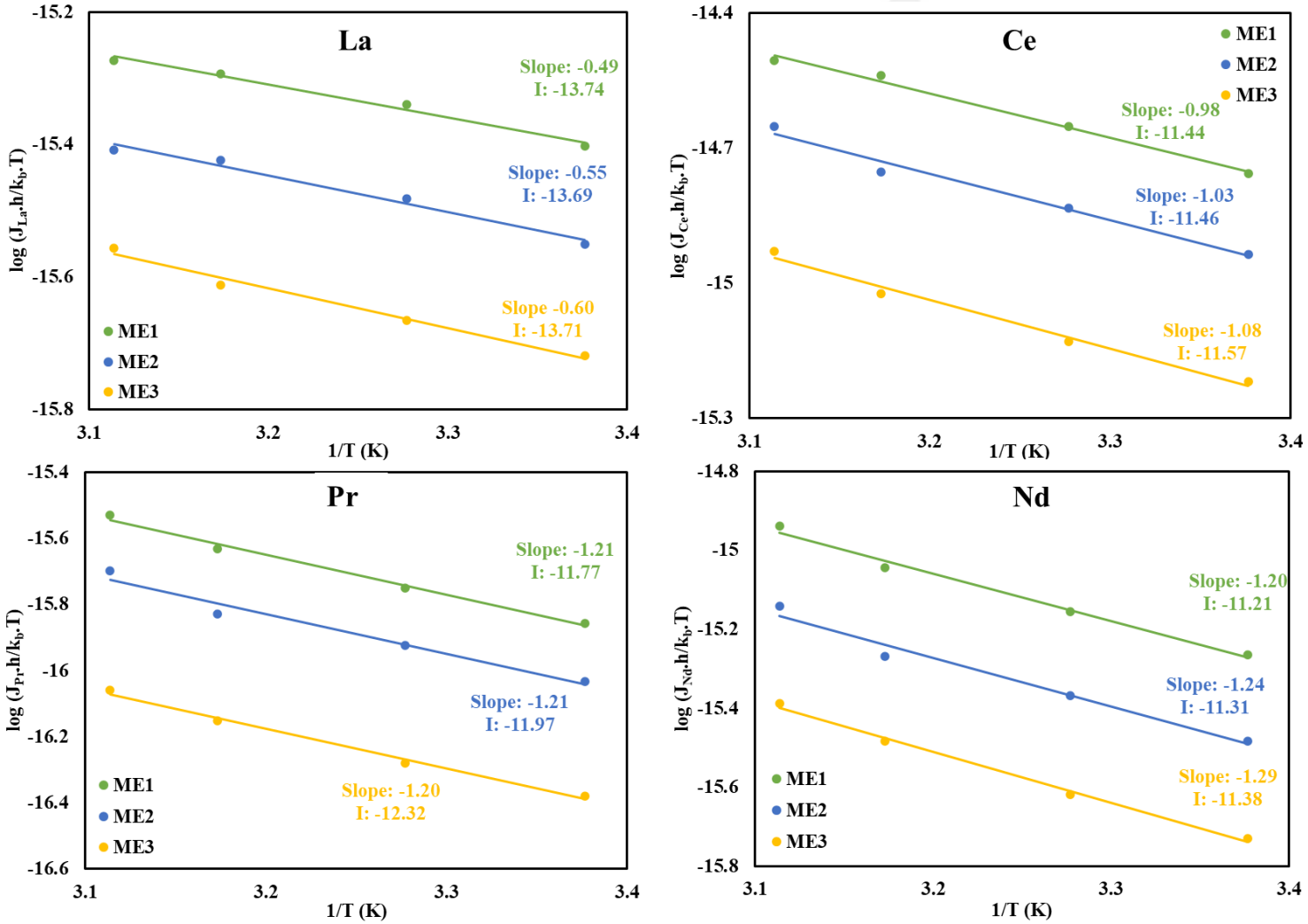

Figure 4.11 Evaluating of temperature dependency data with Activated Complex Theory

CHAPTER FIVE

CONCLUSIONS

1. The rate of the LREEs extraction was directly proportional to [REE^{3+}] and $[D2EHPA]_{(o)}$ when it has a negative relationship with [HCl].
2. According to equilibrium studies, the effect of D2EHPA concentration on the extraction of the LREEs was increasing when the atomic number increases (Pr> Nd> Ce> La). Based on slope analysis, the stoichiometric coefficient between metal ions – D2EHPA was approximately 2 for Nd and Pr and 1 for Ce, but in the case of La, the slope was below 0.5.
3. The rate equations were determined as follows.

$$J_{La}\left(\frac{kmol}{m^2 s}\right) = 10^{-4.74}.[La^{3+}]^{0.98}.[HCl]^{-0.39}.[D2EHPA]^{1.25}$$

$$J_{Ce}\left(\frac{kmol}{m^2 s}\right) = 10^{-4.17}.[Ce^{3+}]^{1.00}.[HCl]^{-0.39}.[D2EHPA]^{1.24}$$

$$J_{Pr}\left(\frac{kmol}{m^2 s}\right) = 10^{-3.43}.[Pr^{3+}]^{1.20}.[HCl]^{-0.30}.[D2EHPA]^{1.18}$$

$$J_{Nd}\left(\frac{kmol}{m^2 s}\right) = 10^{-3.93}.[Nd^{3+}]^{1.05}.[HCl]^{-0.30}.[D2EHPA]^{1.11}$$

4. According to temperature dependency data, the average activation energies (E_A) of the extraction reactions were determined as 7.9, 17.2, 20.6, and 21.3 kJ/mol for La, Ce, Pr, and Nd, respectively. Average entropy changes were determined with activation state theory and calculated as -110 J/mol.k for La, -47 J/mol.k for Ce, -85 J/mol.k for Pr, and -61 J/mol.k for Nd.

5. According to thermodynamic investigations, fast and slow reactions were given in Eq. 5.1 to 5.6.

$$H_2A_{2\,(o)} \overset{fast}{\longleftrightarrow} H_2A_{2\,(i)} \tag{5.1}$$

$$H_2A_{2\,(i)} \overset{fast}{\longleftrightarrow} HA^-_{2(i)} + H^+_{(a)} \tag{5.2}$$

$$REE^{3+}_{(a)} \overset{fast}{\longleftrightarrow} REE^{3+}_{(i)} \tag{5.3}$$

$$REE^{3+} + HA^-_{2(i)} \overset{\substack{fast\ for\ La\ and\ Ce \\ slow\ for\ Pr\ and\ Nd}}{\longleftrightarrow} [REE(HA_2)]^{2+}_{(i)} \tag{5.4}$$

$$[(REE)HA_2]^{2+}_{(i)} + HA^-_{2(i)} \overset{fast}{\longleftrightarrow} [REE(HA_2)_2]^{+}_{(i)} \tag{5.5}$$

$$[REE(HA_2)_2]^{2+}_{(i)} + HA^-_{2(i)} \overset{slow\ for\ all}{\longleftrightarrow} [REE(HA_2)_3]_{(o)} \tag{5.6}$$

6. Extraction was controlled by the transfer of metal-ligand complexes from the interface (Eq. 5.3) for La and Ce, on the other hand both the diffusion and reaction had control over the extraction (Eq. 5.3 and Eq. 5.4) for Pr and Nd.
7. The solvent extraction of LREEs follows to the S_N2 mechanism because of the negative entropy change.

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