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## Advancements in solvent extraction of metal ions: Mechanisms, kinetics, and efficiency with diverse extractants

Muhammad Saidur Rahman \*

*Department of Electrical & Electronic Engineering, Pundra University of Science & Technology, Gokul, Bogura-5800, Bangladesh.*

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### Abstract

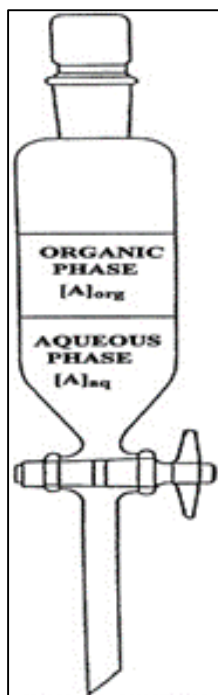
This study illustrates the most recent developments and evolution of solvent extraction techniques for metal ion separation. It emphasizes the replacement of conventional extractants, such as TBP and  $\beta$ -diketones, with modern ones, including LIX reagents, D2EHPA, TOPO, and Cyanex reagents, as a result of enhanced design and process optimization. Recent research has demonstrated the efficacy of novel extractants in selectively targeting metal ions from complex matrices, illustrating the continuous advancements in solvent extraction techniques. In hydrometallurgy, solvent extraction is essential for the recovery, purification, and separation of both high-value and low-value metals. The review examines the history, principles, and applications of solvent extraction, with a particular emphasis on the mechanism of metal ion transfer and the characteristics of extractants such as Cyanex 272. It includes research on Mn(II) and Ni(II), as well as extractants' physicochemical properties and efficacy in selective separations. Additionally, it addresses extraction kinetics. The research also investigates surfactant properties, ligand exchange processes, and interfacial phenomena, all of which contribute to the development of environmentally benign metal extraction methods. Furthermore, it analyzes the commercial and selective separation value of extractants such as Cyanex 272, the limitations of traditional methods, the necessity for inventive alternatives, as well as historical innovations. The versatility and ongoing significance of solvent extraction in hydrometallurgical technology are underscored by mechanistic studies, which improve our comprehension of the stability constants and extraction behaviors of Mn(II) and Ni(II).

**Keywords:** Solvent extraction; Metal ion separation; Extractant optimization; Extractants; Hydrometallurgy; Sustainable metal recovery

### 1. Introduction

In hydrometallurgy, solvent extraction is an essential technique that uses a solvent typically one that isn't based on water to extract and recover metals from solutions. Liquid-liquid extraction allows solutes (metal ions) to be transferred into the second solvent phase, which is essential for hydrometallurgy recovery and purification. This process involves mixing a metal-ion-containing solution with an organic phase. The principle of solvent extraction is deployed in Fig. 1. The vessel (a separatory funnel) contains two layers of liquids, one that is generally water ( $S_{aq}$ ) and the other generally an organic solvent ( $S_{org}$ ). In the example shown, the organic solvent is lighter (i.e., has a lower density) than water, but the opposite situation is also possible. The solute A, which initially is dissolved in only one of the two liquids, eventually distributes between the two phases. When this distribution reaches equilibrium, the solute is at concentration  $[A]_{aq}$  in the aqueous layer and at concentration  $[A]_{org}$  in the organic layer [1]. The distribution ratio (D) of the solute;  $D = [A]_{org}/[A]_{aq}$

\* Corresponding author: Muhammad Saidur Rahman; E- mail: [saeed\\_hamim@yahoo.com](mailto:saeed_hamim@yahoo.com)



**Figure 1** A Schematic Representation of Solvent Extraction (Liquid-Liquid extraction) upper phase containing Organic Solvent, and the lower phase containing, an Aqueous solvent (Separatory funnel)

In solvent extraction, metal ions are separated from contaminants in the aqueous phase by an extractant that forms a compound with them. Reversing this reaction with an acidic or basic solution is required to recover the metals. Solvent extraction, which was once limited to high-value metals like uranium, is now applicable to a wide range of low-value metals because to advancements in equipment and extractants. The material being distributed that has been dissolved by the solvent is known as the distribuend. Extractants use a variety of techniques to communicate with the distribuend. Although they don't have the power to extract, diluents enhance extractant characteristics. In order to obtain pure substances, solvent extraction is used in analytical chemistry, waste purification, medicines, and other chemical industries [2].

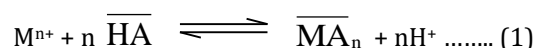
Peligot [3] observed organic solvents extracting metal ions (e.g., uranyl nitrate with diethyl ether), suggesting their use for separating uranium. Another example: extracting Fe(III) from HCl with diethyl ether [4, 5]. Solvent extraction gained traction during WWII for purifying uranium, thorium, lanthanides, and actinides from lean ores. The equipments such as mixer-settlers [6], baffle-cup plate tower [7], sieve-plate tower [8], spray tower [9] etc. used industrially to carry out the technique have been developed in early sixties of the last century. Laboratory performing solvent extraction research usually use convenient-sized reagent vials or stoppered separatory funnels.

These investigations aim to strengthen the field of hydrometallurgical processes, promote metal recovery, and explore the properties of extractants like Cyanex 272, D2EHPA, TBP, and TOPO, including their efficiency for different metal ions and equilibrium constants. Understanding the fundamentals and workings of extraction opens the door to more environmentally friendly methods, long-term, sustainable metal recovery, and improved extraction processes. The optimization of recovery processes is investigated using a combination of theoretical models and empirical research, with a particular emphasis on dynamics, equilibrium kinetics, and molecular interactions. The goal is to increase the selectivity of solvent extraction by assessing the effectiveness of extractants and investigating state-of-the-art methods for the focused separation of metal ions. Developing hydrometallurgical processes that are environmentally friendly is a top priority in order to reduce environmental impact and maximize resource usage. Moreover, this study endeavors to prognosticate the trajectory of solvent extraction within the domain of hydrometallurgy. The kinetics of solvent extraction have been investigated using the following methods or cells: Shake out method [10-16], The static constant interfacial area cell: Hahn cell [17-20], The stirred constant interfacial area cell: Lewis cell [21-24], The stirred tank: AKUFVE apparatus [25, 26], The laminar jet [27], The rotating diffusion cell: RDC [28-32], The single drop technique: rising and falling [33-39], Different hydrodynamics are displayed by each method in relation to the metal transfer from one phase to another. Moreover, the previously mentioned methods aside from the RDC have other drawbacks when it comes to determining rates, including: Relatively very high time consumption for the rate determination in the static constant interfacial area (Hahn) cell, An imperfect interface in the stirred constant interfacial area (Lewis) cell, Fully unknown

interfacial area in the stirred (AKUFVE) tank and shake-out technique, Very short time of contact in the laminar jet and Unknown hydrodynamics in single drop apparatus owing to the internal circulation and the presence of oscillations and wakes [40]. The research is significant due to its comprehensive review of solvent extraction advancements, including modern extractants like LIX reagents and Cyanex 272. It provides valuable insights into the evolution of extraction techniques, highlighting improvements in efficiency, selectivity, and environmental sustainability. By exploring the mechanisms, kinetics, and applications of various extractants, the study addresses both historical developments and current challenges, offering essential knowledge for optimizing metal recovery processes and advancing hydrometallurgical technology.

### 1.1. The theoretical principles of solvent extraction

The theoretical principles of solvent extraction involving chelation have been outlined by Calvin [41]. If the overall reaction involved in transfer of a metal ion ( $M^{n+}$ ) from the aqueous to organic phase by an acidic extractant ( $\overline{HA}$ ) is represented by



where,  $M^{n+}$  = metal ion of oxidation state 'n' in the aqueous phase,  $\overline{HA}$  = organic chelating acid and species under bars represent organic species; then, the equilibrium constant,  $K_{ex}$  for  $M^{n+}$  extraction with  $\overline{HA}$  may be defined as follows:

$$K_{ex} = \frac{[\overline{MA}_n][H^+]^n}{[M^{n+}][\overline{HA}]^n} = \frac{D_M^o [H^+]^n}{[\overline{HA}]^n} \dots\dots\dots (2)$$

where,  $D_M^o$  represents the distribution or extraction ratio of the metal ion (ratio of concentration of metal ion in the organic phase to that in the aqueous phase). Thus, for any given,  $M^{n+}/\overline{HA}$  system, the distribution ratio is given by:

$$D_M^o = \frac{K_{ex} [\overline{HA}]^n}{[H^+]^n} \dots\dots\dots (3)$$

Since the value of  $K_{ex}$  is different for different metal ions [42], it is clear how such a system may be used for the separation of metal ions.

The Eq. (2) is valid for the extraction of non-hydrolyzed metal ions. Kolthoff and Sandell [43] have described a modified form of the equation for distribution ratio taking into account the hydrolysis of the metal ion in the aqueous phase. If hydrolysis occurs, it is seen that the dependence of distribution ratio on  $[\overline{HA}]$  is not affected but the exponent of  $[H^+]$  in Eq. (3) is decreased and in the extreme case involving the complete hydrolyzed metal ion,  $D_M^o$  is independent of pH. Thus, when hydrolysis occurs, Eq. (3) should be rewritten as:

$$D_M^o = \frac{K_{ex} [\overline{HA}]^n}{[H^+]^m} \dots\dots\dots (4)$$


Where,  $n - m$  = number of hydroxyl group attached to the metal ion in the aqueous phase prior to extraction. The approximate equation developed above for the distribution ratio,  $D_M^o$  for the solvent extraction of a metal chelate, offers a valuable method for studying the composition of the chelate, the nature of the metal ion in solution and then the overall extraction equilibrium reaction i.e., mechanism.

The history, guiding theories, and real-world applications of solvent extraction techniques in metal ion separation were all intended to be covered in this research article. To determine the basic mechanisms underlying metal ion transport, the study looks at theoretical concepts, experimental methods, and historical turning points. In addition, it evaluates the characteristics of specific extractants, like TOPO, TBP, D2EHPA, and Cyanex 272, to ascertain how well they perform in selective separations. Our focus is on advancing hydrometallurgical technology and promoting sustainability in metal extraction. We aim to explore the properties and classification of various metal ions in solvent extraction, offering

insights into challenges, advancements, and potential pathways forward. Extraction of  $M^{2+}$  cations of the base metals by the commercial reagent Cyanex 272 and related phosphoric, phosphonic and phosphinic acids (Table 1), usually provides complexes with 4 : 1 ligand metal stoichiometry,  $[M(L)_2(LH)_2]$  [44]. The following table shows some extractants' structures and typical trade names.

The table 1 & table 2 classify various metal cationic extractants derived from phosphorus (V) acids into distinct groups, each characterized by specific substituents and associated commercial names. These extractants encompass monoalkylphosphoric acids as well as different varieties of dialkylphosphonic acids featuring diverse alkyl and functional group substitutions. Each commercial name is linked to a precise chemical structure, offering researchers and industrial users a range of choices tailored to their specific extraction requirements.

**Table 1** The structures and common commercial names of metal cationic extractants based on phosphorus (V) acids [44]

Monoalkylphosphoric acids		
Substituents		Commercial names
R	n-C <sub>4</sub> H <sub>9</sub> (C <sub>2</sub> H <sub>5</sub> )CHCH <sub>2</sub>	MEHPA
Dialkylphosphonic acids		
Substituents		Commercial names
R	n-C <sub>4</sub> H <sub>9</sub> (C <sub>2</sub> H <sub>5</sub> )CHCH <sub>2</sub>	PC 88A, P507, Ionquest 801
R	t-C <sub>4</sub> H <sub>9</sub> CH <sub>2</sub> (CH <sub>3</sub> )CHCH <sub>2</sub> O	Cyanex 272
X = X'		
R	t-C <sub>4</sub> H <sub>9</sub> CH <sub>2</sub> (CH <sub>3</sub> )CHCH <sub>2</sub>	Cyanex 302
X	O	
X	S	
R	t-C <sub>4</sub> H <sub>9</sub> CH <sub>2</sub> (CH <sub>3</sub> )CHCH <sub>2</sub>	Cyanex 301
X = X'	S	
Substituents		Commercial names
R	n-C <sub>4</sub> H <sub>9</sub> (C <sub>2</sub> H <sub>5</sub> )CHCH <sub>2</sub> O	D2EHPA, DEHPA, P204, Baysolvex DEDP
X = X'		
R	n-C <sub>4</sub> H <sub>9</sub> (C <sub>2</sub> H <sub>5</sub> )CHCH <sub>2</sub>	Hoe F 3787
X	O	
X	S	
R	n-C <sub>4</sub> H <sub>9</sub> (C <sub>2</sub> H <sub>5</sub> )CHCH <sub>2</sub>	DEHTPA
X = X'	S	

**Table 2** Structures and Commercial Names of Some Phosphine Oxide and Phosphine Sulfide Extractants [45, 46]

Phosphine		
$\begin{array}{c} R & R'' \\ & \diagdown \quad / \\ & P \\ & / \quad \diagdown \\ R' & X \end{array}$		
Substituents		Commercial name(s)
R = R' = R'' X	i-C <sub>4</sub> H <sub>9</sub> S	Cyanex 471
R = R' = R'' X	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> O	Cyanex 921, TOPO
R = R' = R'' X	i-CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> O	Cyanex 925
R = R' = R'' X	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> and CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> O	Cyanex 923

### 1.2. Characterization of Select Extractants for Metal Solvent Extraction

These findings (Table 3) indicate that each extractant possesses unique physical and chemical properties, including molecular composition, purity, solubility, density, appearance, and thermal characteristics. These attributes are crucial for evaluating their suitability and effectiveness in solvent extraction processes in hydrometallurgy [Sources: D2EHPA, 47] [Cyanex 272, 48][TOPO, 49][TBP, 50]:

**Table 3** Comparative Analysis of Four Phosphoric Acid Derivatives Used in Solvent Extraction

Characteristics	D2EHPA (di-2-ethylhexylphosphoric acid)	Cyanex 272 bis-(2,4,4-trimethyl pentylphosphinic acid)	Tris-(2, 4, 4-trimethylpentyl) phosphine oxide (TOPO)	Tri butyl phosphate (TBP)
Molecular formula	C <sub>16</sub> H <sub>35</sub> O <sub>4</sub> P	(C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub> PO <sub>2</sub> H	C <sub>24</sub> H <sub>51</sub> OP	C <sub>12</sub> H <sub>27</sub> O <sub>4</sub> P
Purity	98%	87%	93%	99%
Molecular Weight (g/mol)	322.43	290	386.645	266.318
Solubility in water (g/L)	<0.01	0.016	0.88	0.40
Density (g/cm <sup>3</sup> )	0.9758	0.92	0.88	0.9727
Appearance	Odorless yellowish liquid	low viscosity liquid	white, opaque crystals	colorless to light yellow liquid
Melting point	-50 °C	<-32 °C	50-54°C	-80°C
Boiling point	393 °C	>300°C	411.2°C	289°C
Refractive index	1.44	1.46 (n <sub>20</sub> /D 1.460)	-	1.4231 at 20°C
Flash point	150°C	117°C	110°C	146.1°C

The research has been taken into the fundamental principles and practical applications of solvent extraction within hydrometallurgy, an indispensable technique that employs non-aqueous solvents to separate and recover metals from solutions. This method entails the transfer of metal ions from an aqueous phase to an organic phase, facilitated by specialized extractants. Initially developed for purifying high-value metals such as uranium, advancements have expanded its utility to encompass a broader range of low-value metals. The study aims to evaluate the effectiveness and utilization of specific extractants like Cyanex 272, D2EHPA, TBP, and TOPO across various metal ions, with the goal of optimizing extraction processes for sustainable and environmentally sound metal recovery practices.

### 1.3. Purification Method for Dialkyl Phosphoric Extractants

The purification method for Cyanex 272 together with D2EHPA (di-2-ethylhexylphosphoric acid) and HEHEHP (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester) by copper salt precipitation and crystallization has been used for a long time when extraction mechanism and other fundamental studies have been carried out using these extractants [51]. This method is time consuming and costly, consuming large quantities of acetone and ether. Zhengshui et. al., [52] have developed a new purification method for dialkyl phosphoric / phosphonic / phosphinic acid extractants based on the formation a middle microemulsion phase. The later method of purification is easier and cheaper. Like carboxylic, phosphoric and phosphonic acid derivatives; Cyanex 272, also exists in dimeric form in a non-polar solvent as shown below [53].

In recent decades, significant progress has been achieved in understanding the efficient separation of metal ions using organic solvents from aqueous solutions. A substantial focus of these investigations lies in elucidating extraction mechanisms and ultimately developing a standardized model for extraction systems. Current reports encompass the following topics: (A) the physico-chemical properties of BTMPPA/Cyanex 272, (B) the application of Cyanex 272 as an extractant for various metal ions, and (C) the solvent extraction chemistry concerning Mn(II) and Ni(II) using different extractants.

### 1.4. The physico-chemical properties of Cyanex 272

As noted in the introduction, Cyanex 272's active ingredient, BTMPPA, typically exists in organic diluents with low polarity or those that don't strongly hydrogen bond with it, forming dimers akin to D2EHPA. Phase distribution data of BTMPPA can reveal its dimerization ( $K_2$ ), distribution ( $K_d$ ), partition ( $p$ ), and acid dissociation ( $K_a$ ) constants, illustrating its states in organic and aqueous phases. Generally, analyzing BTMPPA content in the aqueous phase provides distribution data. Like D2EHPA, studies indicate [54-59] that the anion in the aqueous phase and the organic diluent used, along with the measurement technique, influence  $K_2$ ,  $K_d$ , and  $K_a$  values. Consequently, for BTMPPA, these values are contingent on aqueous conditions and the organic diluent. Literature on  $K_2$ ,  $K_d$ , and  $K_a$  values for BTMPPA is scarce. Ke-an *et al.* [60] have reported the equilibrium constants of organophosphorous extractants including BTMPPA (Cyanex 272) by inductively coupled plasma-atomic emission spectroscopy (ICP-AAS). The 213.618 nm first order atomic emission line of phosphorous has been monitored to determine the equilibrium constants. For sulfate-acetate / chloroform-BTMPPA system at 298 K, they have reported the values of  $K_d$ ,  $K_2$  and  $K_a$  as  $43.8 \pm 1.8$ ,  $184.3 \pm 16.1 \text{ dm}^3/\text{mol}$  and  $(6.6 \pm 0.7) \times 10^{-4} \text{ mol/dm}^3$  ( $\text{p}K_a = 3.18$ ), respectively.

The equilibrium extraction reactions in low concentration regions of extractant are suggested as  $\text{M(II)} + \text{H}_2\text{A}_{2(\text{o})} \rightleftharpoons [\text{MA}_2]_{(\text{o})} + 2\text{H}^+$ ; but disolvated and monosolvated species are extracted in the cases of Ni(II) and Zn(II), respectively, at high concentration regions of Cyanex 272 ( $\text{H}_2\text{A}_2$ ). The extraction processes are found to be endothermic. The maximum loading capacities of the extractant are found to be 9.52 g Mn(II), 21.28 g Ni(II) per 100 g extractant. The extracted species are strippable by dilute  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and HCl solutions [302, 301].

The dissociation equilibria of BTMPPA and three other phosphorous acids were studied in ethanol-water mixtures at 25°C using potentiometric titration [61]. Data were analyzed graphically and numerically with LETAGROP-ZETA.  $\text{p}K_a$  values for BTMPPA were determined as 5.42,  $5.44 \pm 0.02$ , 3.38, and  $3.51 \pm 0.05$  using various methods. Biswas *et al.* [62] reported a digestion technique for BTMPPA using a mixture of 70%  $\text{HNO}_3$  – 70%  $\text{HClO}_4$  (2:1), followed by quantification of orthophosphate using molybdenum blue colorimetric method at 830 nm. Purified BTMPPA had estimated values of  $K_2$ ,  $K_d$ , and  $K_a$  as 190, 53, and  $5.52 \times 10^{-4}$ , respectively. Paatero et al. [63] found the mean self-association number of BTMPPA in chloroform at 25°C to be approximately 2.1 using Vapor Pressure Osmometry (VPO). It's recognized that hydrometallurgical liquid-liquid extraction reagents exhibit surface-active properties due to their amphipathic nature, with hydrophobic and hydrophilic groups in the same molecule. The hydrophobicity is contributed by the hydrocarbon radicals, which may be straight or branched alkyl chains, or alkylaryl groups involving benzene or naphthalene rings.

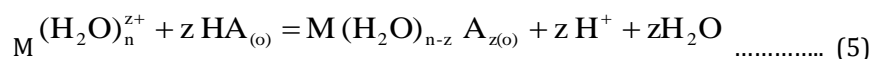
**Table 4** Summarizing the Polar Functional Groups and their Corresponding Compounds

Functional Group	Example Compound	Common Cation
Carboxylic acids; $\begin{array}{c} \text{—C=O} \\   \\ \text{OH} \end{array}$	Acetic acid (CH <sub>3</sub> COOH)	Hydrogen ion (H <sup>+</sup> )
Derivatives of Phosphoric, Phosphonic, and Phosphinic acids; $\begin{array}{c} >\text{P=O} \\   \\ \text{OH} \end{array}$	Phosphoric acid (H <sub>3</sub> PO <sub>4</sub> )	Hydrogen ion (H <sup>+</sup> )
Sulfonic acid; -SO <sub>2</sub> -OH	Sulfamic acid (H <sub>3</sub> NSO <sub>3</sub> )	Hydrogen ion (H <sup>+</sup> )
Hydroxyoximes; $\begin{array}{c} \text{—CH—C—} \\   \quad    \\ \text{OH} \quad \text{N—OH} \end{array}$	Acetoxime (CH <sub>3</sub> CONOH <sub>2</sub> )	Hydrogen ion (H <sup>+</sup> )
Oximes; =NOH	Benzaldoxime (C <sub>6</sub> H <sub>5</sub> CH=NOH)	Hydrogen ion (H <sup>+</sup> )
Amines; (1°, 2°, and 3°); -NH <sub>2</sub> , >NH and ≡ N	Aniline (C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> ), Dimethylamine ((CH <sub>3</sub> ) <sub>2</sub> NH), Trimethylamine ((CH <sub>3</sub> ) <sub>3</sub> N)	Protonated amine (R-NH <sub>3</sub> <sup>+</sup> , R <sub>2</sub> NH <sub>2</sub> <sup>+</sup> , R <sub>3</sub> NH <sup>+</sup> )
Quaternary ammonium salts; ≡ NR <sup>+</sup> X <sup>-</sup>	Tetraethylammonium ion ([Et <sub>4</sub> N] <sup>+</sup> )	Tetraalkylammonium ion (R <sub>4</sub> N <sup>+</sup> )

The table 4 provides a distinct overview of the polar functional groups, their example compounds, and the most common cations associated with each. All these groups are responsible for the hydrophilic nature. The amphipathic characteristic is necessitated by the fact that an extractant must be able to interact with aqueous phase species while still maintaining preferential organic phase solubility. The hydrophilic groups provide the functional groups, which form the metal-ligand bonds while the organic radicals ensure the desired organic phase solubility.

In spite of the growing recognition of the surfactant properties of solvent extraction reagents, it cannot be said that there is complete agreement concerning the significance of interfacial phenomena in extraction processes. In a plenary lecture presented during ISEC'80, Freiser [64] was insisted on that interfacial effects were of little importance in metal extraction. On the other hand, in another plenary lecture at the same conference, Hanson [65] has suggested that reaction occurs in "a narrow zone in the aqueous phase immediately adjacent to the interfaces but with a significant (and possibly sometimes dominating) diffusional resistance in a zone (likely to be of greater thickness) on the organic side of the interface.

Liquid-liquid extraction involves ligand exchange processes whereby metal-organic ligand bonds substitute for the metal-oxygen bonds present in the hydrated aqueous species:



In general, extractant molecules possess extremely low aqueous solubilities. For example, according to Foakes et al. [66], the aqueous solubility of commercial hydroxyoxime copper extractants can be as low as 10<sup>-6</sup> mol/dm<sup>3</sup>. Thus, it is not unreasonable to expect the locale of the extraction reaction to be near the two phase boundary. However, the tendency in the literature to appeal to indirect evidence (e.g., mathematical models of metal extraction rates, measurements of bulk phase metal distribution) as support for the significance or insignificance of interfacial phenomena in metal extraction processes is clearly unacceptable. More direct experimental evidences derived from the interfacial and the bulk phase physico-chemical investigations are needed.

In 1967, two pioneering studies appeared in which interfacial tension measurements were used to elucidate metal extraction mechanisms: one by McDowell and Coleman [67] on the uranium-amine sulfate system and other by Scibona *et al.* [68] on the kinetics of the reaction of tetraheptylammonium chloride with bromide ions. However, since then, with the exception of a few investigators such as Danesi et al. [69-71], Van Dalen et al. [72,73], Flett et al. [74,75], Yagodin et al. [76, 77] and Osseo-Asare et al. [78-80], there is little attempt to undertake systematic and extensive investigations

focusing on the interfacial region. The BTMPPA-extraction systems have not yet been investigated focusing on the interfacial region excepting the work of Singha [81-82].

Although there are some investigations on the interaction of D2EHPA-diluent in binary or ternary mixtures [83, 84], the interaction of BTMPPA- diluent has not been investigated excepting the work of Biswas and Singha [85].

### 1.5. Using Cyanex 272 with various metal ions

Since the incipency of Cyanex 272 Extractant by Cyanamide Corporation (USA and Canada) at the beginning of the eighties of the last century, it has been widely used for the separation of cobalt (II) from nickel (II). The solvent extraction characteristics of cobalt and nickel by phosphoric, phosphonic and phosphinic acid derivatives have been reported from nitrate media [86] and from sulfate media [87]. In each case, cobalt is extracted at lower pH values than nickel; under comparable conditions, the cobalt-nickel separations increases in the order di-2-ethylhexylphosphoric acid (D2EHPA) < 2-ethylhexylphosphonic acid mono 2-ethylhexyl ester (EHEHPA) < di-2,4,4-trimethylpentylphosphinic acid (Cyanex 272). Danesi et al. [88] have reported the separation of cobalt and nickel by liquid-liquid extraction and supported membranes with bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272).

The equilibrium and mass transfer (as determined by the Lewis cell) for the extraction of nickel and cobalt from sulfate solutions into BTMPPA (Cyanex 272) have been reported by Fu and Golding [87]. The concentration of nickel in the aqueous phase is shown to have little effect on cobalt extraction; nevertheless, cobalt in the aqueous phase prevents nickel extraction from occurring. It is discovered that the separation factor depends on the cobalt loading. Chou and Beckstead [89] have received a patent for their method of solvent extraction employing Cyanex 272 Extractant to separate nickel and cobalt from sulfate solution. Zinc, cobalt, and nickel have been separated using a solvent extraction process utilizing a variety of extractants, including Cyanex 272, according to Cho and Dai [90]. The cobalt(II) separation from nickel(II) in the laboratory scale has also been investigated by a number of other workers [91-97]. There are also few reports on the cobalt-nickel separation on commercial plants [98-100].

There are considerable reports on the use of Cyanex 272 as extractant for the extractive separations of Co(II) from Cu(II) [101, 102], Cu(II) from Zn(II) [103], Sc(III) from Fe(III) [104] and Th(IV) [105], Zn(II) from Cd(II) [106], from Ca(II) [107] and Fe(II) [108], Al(III) from Ni(II) [109] and from Co(II), Ni(II) and Mg(II) [110], Mn(II) from Co(II) [111] and from Zn(II) [112-115], Ti(IV) from Fe(III) [116], Co(II) from Li(I) [117] and also on the mutual separations of Cu(II)-Ni(II)-Zn(II) [118], Cu(II)-Zn(II)-Co(II)-Ni(II) [119], Fe(III)-Cu(II)-Zn(II)-Ni(II) [120, 121], Fe(II)-Cd(II)-Ni(II) [122], Co(II)-Li(I)-Ni(II) [123], Co(II)-Ni(II)-Cd(II) [124-126], Co(II)-Ni(II)-Mg(II)-Ca(II) [127], Al(III)-Ni(II) from fluoride medium [128], etc.

Moreover, there are also some mechanistic (equilibrium) studies on some individual metal ions by Cyanex 272. Among them, the extractions of Ln(III) [129-131], Mo(VI) [132, 133], Zn(II) [134-136], Th(IV) [137], V(IV) [138, 139], Ag(I) [140], Al(III) [141, 142], Co(II) [143], Zr(IV) [144], Fe(III) [145-147], Cu(II) [148, 149], Cd(II) [150], Mn(II) [151], Pb(II) [152], Ni(II) [153], Na(I) [154] etc. Cyanex 272 systems are mentionable.

The method of solvent extraction has also been applied in the study of hydrolysis of the metal ion and in the determination of the stability constant of various species present in the system. Cyanex 272 demonstrated its efficacy in the selective extraction of rare earth elements, gold, and cobalt and nickel from sulfate and chloride environments [155-157]. Zinc extraction and other heavy metal extraction, including platinum group metal extraction, are potential uses for Cyanex 301, whose primary component is bis(2,4,4-trimethylpentyl) dithiophosphinic acid [155, 158, 159]. While Cyanex 272 finds it challenging to separate them, Cyanex 302 is able to extract Co(II) over Mn(II) preferentially [159]. Hydrophobicity is attributed to hydrocarbon radicals, while polar functional groups enhance solubility.

### 1.6. Solvent extraction chemistry of Mn(II), and Ni(II) by different extractants

The characteristics of extractants like D2EHPA, Cyanex 272, TOPO, and TBP provide essential guidance for researchers exploring the solvent extraction chemistry of Mn(II) and Ni(II). These details enable informed decisions in extractant selection based on properties such as purity, solubility, density, and boiling points. For instance, the high purity and low water solubility of TBP make it suitable for precise phase separations, while D2EHPA's properties suggest its potential for robust extraction under varied conditions. Understanding these attributes helps optimize extraction processes, compare extractant efficiencies, and consider environmental impacts and safety concerns associated with their use. This knowledge is crucial for advancing efficient and sustainable metal ion separation techniques in hydrometallurgy. The following paragraphs provide a brief overview of research on the extraction of Mn(II) and Ni(II) using various extractants reported to date.



### 1.6.1. Solvent extraction of Mn(II)

The behavior of manganese extraction differs according to its oxidation states (+2 to +7). Ion pair extraction happens with higher valency levels (+6 and +7), whereas chelate complex extraction is more typical for lower oxidation states. During extraction, redox reactions may take place, which might occasionally result in unreported oxidation states. The research conducted on Mn(II) solvent extraction utilizing different extractants from an equilibrium perspective are summarized below.

i) Tributyl phosphate, TBP [160-164], ii) Salicylic acid in TBP [165], iii) Thenoyltrifluoroacetone, TTA, with acetone, pyridine, bromate and its derivatives [166-168], iv) Diethyldithiocarbamate and its derivatives [169-171], v) Oxine in chloroform [172], vi) 2-methyl oxine [173], vii) Benzoylacetone in benzene and with dibenzoylmethane in benzene [174], viii) p-methoxybenzothiohydroxamic acid [175], ix) Diphenylcarbazone [176], x) Di-(2-ethylhexyl) phosphoric acid, D2EHPA [177-179], xi) Acetylacetone in chloroform or benzene [180], xii) Methyl-iso-butyl ketone, MIBK [181], xiii) Dithizone [182], xiv) 1-phenyl-3-methyl-4-capryl-(or-4-benzoyl)-5-pyrazolone [183], xv) Aminophosphonic acids [184], xvi) Fatty acids [185-187], xvii) PC88A [188, 189], xviii) Tris-(2-ethyl hexyl)phosphate [190], xix) Cyanex 272 [152], xx) N,N'-bis-(2-hydroxyphenylmethyl)-N,N'-bis(2-pyridylmethyl)-1,2 ethanediamine and its derivatives [191], xxi) Trioctylphosphine oxide, TOPO + pyrazolone [192], xxii) 5, 10, 15, 20-tetraphenyl-21H, 23H porphine [193], xxiii) LIX 1104 [194], xxiv) 4, 7-diphenyl-1, 10-phenanthroline [195], xxv) 2-propionyl-1-naphthol oxime [196], xxvi) 1-phenyl 3-methyl-4-aryl-5-pyrazolone [197], xxvii) Thenoyltrifluoroacetone (TTA) plus tribezylamine [198], xxviii) Bis-(2-hydroxy-5-octylbenzyl) amine [199], xxix) 8-mercaptoquinoline, 8-quinollinol and their derivatives [200] and xxx) 3-[(dioctylamino) methyl] alizarin [201], xxxi) Alamine 336 [202] etc.

### 1.6.2. Solvent extraction of Ni(II) with various extractants

In the divalent state nickel forms a very extensive series of compounds. This is the only oxidation state of importance in the aqueous chemistry of nickel and with the few exception of a few special complexes of nickel in other oxidation states, Ni(II) is also the only important oxidation level in its non-aqueous chemistry. The solvent extractions of Ni(II) by different extractants so far published are mentioned below:

i) Tributyl phosphate, TBP [160, 203-206], ii) Carboxylic acids [207-209], iii) Di-2-ethylhexylphosphoric acid, D2EHPA [210-213], iv) Thenoyltrifluoroacetone, TTA [214-218] v) Other Diketones: acetylactone [219, 220], isonitroacetylacetone [221], benzoylacetone [174], dibenzoylmethane [174, 220], trifluoroacetylacetone [221], vi) Dihydrogen methylene biphosphonate [222] vii) 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone [223, 224], viii)  $\beta$ -isopropyltropolone [225], ix) 8-hydroxyquinoline (oxine) and its derivatives [172, 226-231] x) Dioximes:  $\alpha$ -furdioxime [232-235],  $\alpha$ -benzyldioxime [235, 236], salicyldioxime [237], cyclopentane (or hexane) dionedioxime [232, 238-241], other dioximes [232, 235, 242-246], dimethylglyoxime [235, 247-253], xi) 1-Nitroso-2-naphthol [254] xii) Cupferon [255], xiii) Thio compounds: Thionaphthanic acid [256], Thiodibenzoylmethane [257], thio-TTA [258, 259], and thio-oxine [260], (xiv) Dithizone [261-267], xv) Dithiocarbamates [268-273], xvi) Xanthate [274] xvii) PC 88A (2-ethylhexylphosphoric acid mono-2-ethylhexyl ester) [210, 275], xviii) DP-8R and ACORGA M5640 [276], xix) 5,7-dibromo-8-hydroxyquinoline through ELM [277], xx) Cyanex 301 [278], xxi) Cyanex 272 (70% neutralized) [210], xxii) Quaternary ammonium salts [279, 280], xxiii) Various amines [281-285], xxiv) Cyanex 272 [286, 287, 288, 289, 290, 291], xxv) Aloxime [289], xxvi) LIX reagents: LIX 65N [292], LIX 87QN [293], LIX 84I [294], LIX 64N [295], LIX 84 [296], LIX 860 [297], xxvii) KELEX 100 [298], etc. While some information about the stoichiometries of the assemblies generated is available, the structures of light rare earth elements are not as well defined as those of the Ni(II) systems mentioned above. Light rare earth elements can be separated using blends of extractants such as PC 88A, Cyanex 302, and D2EHPA [299]. The solvent extractions of various metal ions studied up to 1976 have been summarized by Sekine and Hasegawa [300]. It was reported that NNPA's high extraction efficiency and selectivity for Ni(II) and Co(II) at different pH values, with  $E = 94.6\%$  and  $\beta_{Ni(II)/Co(II)} = 481$  at pH 0 for Ni(II), and  $E = 93.9\%$  and  $\beta_{Co(II)/Ni(II)} = 510.88$  at pH 6 for Co(II). Single crystal XRD analyses and DFT calculations elucidated the extraction mechanisms, confirming  $NNPANiHCl_3 > NNPA CoCl_2 > NNPANiCl_2(H_2O)_2$  as the extraction order [301].

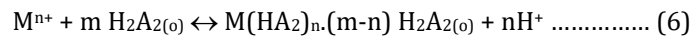
However to improve extraction procedures, provide environmentally friendly methods, and handle new issues in metal ion separation, more research is necessary.

## 1.7. Data Treatment

The way by which metal ions of both equilibrium and kinetics (forward and backward) extraction and separation have been treated in the following-

1.7.1. Equilibrium Studies [302]

Cyanex 272 is an acidic extractant. It can extract a metal ion ( $M^{n+}$ ) by chelation in combination with solvation as shown below.



The equilibrium constant or better to say extraction equilibrium constant ( $K_{ex}$ ) for Eq. (6) can be expressed as:

$$K_{ex} = \frac{C_{M(HA_2)_n(m-n)H_2A_{2(O)}} C_{H^+}^n}{C_M^{n+} C_{H_2A_2(O)}^m} \dots\dots\dots (7)$$

Defining the distribution or extraction ratio (D) as,  $\frac{C_{M(HA_2)_n(m-n)H_2A_{2(O)}}}{C_{M^{n+}}}$ , the Eq. (7) can be modified to

$$K_{ex} = D \cdot \frac{C_{H^+}^n}{C_{H_2A_2(O)}^m}$$

$$\text{or, } \log D = \log K_{ex} + n \text{ pH} + m C_{H_2A_2(O)} \dots\dots\dots (8)$$

Equation (8) represents the basic equation for a chelate forming solvent extraction system for a metal ion by an acidic extractant. It is mentionable here that the all concentration terms or pH refer to the equilibrium values of the respective species. Consequently, Eq. (8) represents that the value of log D should be independent of initial or equilibrium metal ion concentration at a constant equilibrium pH and equilibrium extractant concentration.

1.7.2. Kinetics Studies [303, 304]:

Working formula for flux calculation:

For each forward or backward extraction experiment, flux ( $F_f$  or  $F_b$ ) was calculated as follows:

$$\text{Flux } (F_f) \text{ or } (F_b) = a_M \text{ (kmol)/A (m}^2) \times t \text{ (s)} \dots\dots\dots(9)$$

where,  $a_M$  = amount of M(II) transferred =  $(x V/NM) \times 10^{-9}$  kmol

$$= \frac{\text{Conc. change in aqueous phase } (x, \text{ mg/L}) \times \text{Vol. } (v, \text{ mL}) \text{ of } N = 100 \text{ drops}}{N(100) \times \text{At. wt. of metal, M}} \times 10^{-9} \text{ kmol}$$

$$\text{as: } V/N = 4/3 \pi r^3 ; r = (3V/4\pi N)^{1/3} \text{ cm}$$

$$A = 4\pi (3V/4\pi N)^{2/3} \text{ cm}^2 = 4.83567 (V/N)^{2/3} \text{ cm}^2$$

$$A = 0.000483567 \times (V/N)^{2/3} \text{ m}^2;$$

t = drop fall time, s

Considering atomic weight of Mn, and Ni 58.70 and 65.40 respectively

$$\text{or, } (F_f) \text{ or } (F_b) = 3.76 (V/N)^{1/3} (1/t) \times 10^{-8} \text{ kmol/m}^2 \text{ s (10a) for Mn(II)}$$

$$= 3.52 (V/N)^{1/3} (1/t) \times 10^{-8} \text{ kmol/m}^2 \text{ s (10b) for Ni(II)}$$

At a constant temperature,

$$F_f = k_f [M^{2+}]^a [H^+]^b [H_2A_2]^{c(o)} [SO_4^{2-}]^d [Ac^-]^e \dots\dots\dots(11)$$

Except temperature, there are five other variables. On keeping all other variables constant except one (say, M(II) concentration), if flux values ( $F_f$ ) are measured at various concentrations of M(II) concentration, then Eq. (14) is applicable:

$$\log F_f = \log \{k_f [H^+]^b [H_2A_2]^{c(o)} [SO_4^{2-}]^d [Ac^-]^e\} + a \log [M^{2+}] \dots \dots \dots (12)$$

Equation (12) states that the plots of  $\log F_f$  vs.  $\log [M^{2+}]$  will be straight line with the slope equalling to "a", the reaction order with respect to  $[M^{2+}]$ . Whilst the intercept of the line will be equal to  $\log \{k_f \cdot [H^+]^b [H_2A_2]^{c(o)} [SO_4^{2-}]^d [Ac^-]^e\}$  from which the value of  $k_f$  can be evaluated after knowing the values of b, c, d and e.

In the similar way, the values of b, c, d and e can be evaluated as the slope of the  $\log F_f$  vs.  $\log [H^+]$ ,  $\log F_f$  vs.  $\log [H_2A_2]^{(o)}$ ,  $\log F_f$  vs.  $\log [SO_4^{2-}]$  and  $\log F_f$  vs.  $\log [Ac^-]$ ; plots, respectively. Intercepts of the plots will yield again the value of  $k_f$ .

Temperature dependence data of the rate study can be treated by the Arrhenius equation to obtain the value of activation energy ( $E_a$ ):

$$\log F_f = \log \text{constant} - E_a/2.303 RT \dots \dots \dots (13)$$

The slope of the  $\log F_f$  vs.  $1/T$  plot will be equal to  $(-E_a/2.303 R)$  from which the value of  $E_a$  can be determined. The temperature dependence rate data can also be treated by the activated complex theory as follows:

$$\log \left( \frac{k_f h}{kT} \right) = \log \left( \frac{F_f h}{kT f(R)} \right) = - \frac{\Delta H^\ddagger}{2.303RT} + \frac{\Delta S^\ddagger}{2.303R} \dots \dots \dots (14)$$

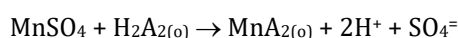
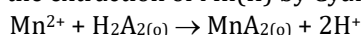
$$\text{or, } \log \frac{F_f h}{kT} = \log f(R) - \frac{\Delta H^\ddagger}{2.303RT} + \frac{\Delta S^\ddagger}{2.303R} \dots \dots \dots (15)$$

so that the plot of  $\log \left( \frac{F_f h}{kT} \right)$  vs.  $\frac{1}{T}$  will be a straight line with slope equaling to  $-\Delta H^\ddagger/2.303R$  and intercept equaling to  $\log f(R) + \Delta S^\ddagger / 2.303$ . From the experimental slope value, the value of  $\Delta H^\ddagger$ ; whilst from the experimental intercept value the value of  $\Delta S^\ddagger$  can be evaluated at calculating  $\log f(R)$  value.

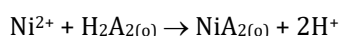
These equations serve as essential tools for researchers investigating metal ion extraction processes. They are critical for calculating flux ( $F_f$  or  $F_b$ ), which measures the rate at which metal ions transfer across interfaces over time. Equations (11) and (12) establish relationships between flux and variables such as metal ion concentration and temperature, providing valuable insights into reaction kinetics and rate constants ( $k_f$ ). Equation (13) applies the Arrhenius equation to explore temperature dependence and determine activation energy ( $E_a$ ), essential for understanding the energy requirements of extraction processes. Equations (14) and (15) utilize activated complex theory to further analyze temperature effects, aiding in the determination of activation parameters such as enthalpy ( $\Delta H^\ddagger$ ) and entropy ( $\Delta S^\ddagger$ ). Together, these equations enable researchers to comprehensively investigate extraction mechanisms and their sensitivity to experimental conditions. the variations of flux in backward extractions can be treated.

### 1.8. Mechanism of Extraction for details on the extraction equilibrium reaction for Mn(II) and Ni(II) by Cyanex 272 ( $H_2A_2$ ) [303-305]

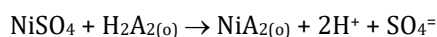
The extraction equilibrium reaction for the extraction of Mn(II) by Cyanex 272 ( $H_2A_2$ ) can be represented as



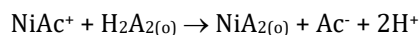
The extraction equilibrium reaction for the extraction of Ni(II) by Cyanex 272 ( $H_2A_2$ ) can be represented as -



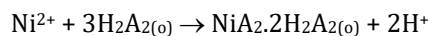
At higher sulphate ion concentration region, the equilibrium reaction would be as:



and at higher acetate ion concentration region, the equilibrium reaction would be as:



But at higher concentration regions of extractant, the disolvated species will be formed as:



During the studied with D2EHPA, Cyanex 272 and Aloxime 800,  $\text{NiL}_2$ , and  $\text{CuL}_2$  complexes were found [306]. The adsorption kinetics of Ni(II) and Mn(II) ions from aqueous solutions suggest that the process follows the pseudo second-order model, indicating predominantly physisorption and a non-specific mechanism [307, 308]. Hydrometallurgical techniques have proven effective in recovering metals like caesium, lanthanum, cobalt, iron, manganese, nickel, and zinc from waste Ni-MH cells [308]. The successful development of a new solvent extraction system using TODGA in an ionic liquid, achieving up to 99% manganese extraction in one step with high separation factors for cobalt and other metals [310]. Cyanex 272 demonstrated superior performance over DEHPA as an extractant agent, with factors such as equilibrium pH influencing Mn(II) extraction efficiency and the effectiveness of separation factors. The study revealed efficient extraction kinetics (<15 min) for both Zn(II) and Mn(II), emphasizing the environmental sustainability of the process through efficient organic solvent recovery using 1 M  $\text{H}_2\text{SO}_4$  stripping solution [311].

### 1.9. Analysis of Mn(II) and Ni(II) extraction

The analysis of Mn(II) and Ni(II) extraction encompasses detailed exploration of Cyanex 272's chemical and physical properties, emphasizing its role in solvent extraction, particularly for these metal ions. It investigates equilibrium constants ( $K_2$ ,  $K_d$ ,  $K_a$ ) critical for understanding BTMPPA's distribution behavior across aqueous and organic phases, influenced by factors like temperature and solvent type. The text underscores the amphipathic nature of Cyanex 272, pivotal for its surfactant properties and interactions with metal ions in both aqueous and organic phases. Kinetic studies are integrated to highlight the dynamic nature of extraction processes, offering insights into mechanisms driving metal ion separation. Ultimately, understanding these equilibrium and kinetic parameters is crucial for optimizing extraction in hydrometallurgy and other metal separation applications.

The investigation into manganese and nickel solvent extraction using D2EHPA, Cyanex 272, TOPO, and TBP is comprehensive, encompassing essential properties such as purity, solubility, density, and boiling points. However, specific details on extraction mechanisms for Mn(II) and Ni(II) with these agents, including equilibrium constants ( $K_{\text{ex}}$ ) and kinetic studies, are lacking. Further comparative analysis of Cyanex 272 and D2EHPA in terms of selectivity and efficiency under varying conditions, and their practical applicability in hydrometallurgical processes, would enhance the study. The study's objectives include investigating equilibrium behavior and kinetics during Mn(II) and Ni(II) extraction using Cyanex 272, aiming to develop methodologies for their extraction, separation, and purification. This involved comprehensive review of literature and research sources to inform methodology development and enhance understanding in the field.

This table provides a concise outline of various extractants used in solvent extraction processes, along with their corresponding acronyms.

Nomenclature	Acronym
Cyanex 272/ BTMPPA	bis(2,4,4-trimethyl pentyl) phosphinic acid
Cyanex 301	bis(2,4,4-trimethylpentyl) dithiophosphinic acid
$\text{H}_2\text{A}_2$	Dimer of Cyanex 272 molecule
D2EHPA	di-2-ethylhexylphosphoric acid
TODGA	N,N,N',N'-Tetraoctyl diglycolamide
EHEHPA	2-ethylhexylphosphonic acid mono 2-ethylhexyl ester

LIX-reagents	LIX reagents, developed by General Mills Chemicals, are a series of extractants used in solvent extraction processes
DP-8R and ACORGA M5640	di-2-propylheptyl phosphoric acid & ACORGA M5640 is a mixture of di-2-ethylhexyl phosphoric acid (D2EHPA) and mono-2-ethylhexyl phosphoric acid (M2EHPA).
TBP	Tri butyl phosphate
ELM	Extractive Liquid Membrane
DFT	Density Functional Theory
NNPA	N-(naphthalen-2-yl)-N-phenylacetamide
TOPO	tris-(2, 4, 4-trimethylpentyl) phosphine oxide
Aloxime 800	An extractant used in solvent extraction processes
PC 88A	2-Ethylhexyl 2-ethylhexyphosphonic acid
Aloxime	Aloximes are chosen based on their specific chemical structure and properties like; 5-Nonylsalicylaldoxime, 8-Hydroxyquinolineoxime, Bis(2,4,4-trimethylpentyl) oxamide, 5,8-Dihydroxy-1,4-naphthoquinone-2-oxime
LIX 65N	Liquid Ion Exchange( 2-hydroxy-5-nonylacetophenone oxime 65N )
DMG	dimethylglyoxime
thio-TTA	Thenoyltrifluoroacetone (sulfur-containing group)
Oxine	8-hydroxyquinoline
Xanthate	Xanthate is a chemical compound used primarily in the mining industry as a flotation agent for recovering metals from ores
TTA	Thenoyltrifluoroacetone
LIX 1104	Liquid Ion Exchange ( 2-hydroxy-5-nonylacetophenone oxime 1104)
LIX 64N	2-hydroxy-5-nonylacetophenone oxime
LIX 65N	2-hydroxy-5-nonylacetophenone oxime
MIBK	Methyl Isobutyl Ketone
$\beta$ -diketones	Acetylacetone (2,4-pentanedione, Benzoylacetone (2,4-dioxopentane, Dibenzoylmethane, Trifluoroacetylacetone, Isonitroacetylacetone
KELEX 100	Kelating Extractant 100
Alamine 336	aliphatic amine extractant
WWII	World War II
a, b, c, d, e	Reaction orders w.r.t $[M^{2+}]$ , $[H^+]$ , $[H_2A_2]_{(o)}$ , & $[Ac^-]$ , respectively
R	Universal gas constant, $8.314 \text{ J deg}^{-1} \text{ mol}^{-1}$
RDC	rotating diffusion cell
$f_{(R)}$	Function of reactants
$E_a$	Activation energy, $\text{kJ mol}^{-1}$
$h$	Planck's constant, $6.6252 \times 10^{-37} \text{ kJ s}$
$R^2$	Correlation coefficient
$\Delta S^\ddagger$	Entropy of activation, $\text{kJ/mol K}$
$\Delta H^\ddagger$	Enthalpy of activation, $\text{kJ mol}^{-1}$

$K_2$	Dimerization constant of Cyanex 272, $\text{kmol}/\text{m}^3$
HA	Monomer of Cyanex 272 molecule
$P_{\text{HA}}$	Distribution constant/partition coefficient of HA
$K_a$	Acid dissociation constant
$F_f$	Flux of forward extraction, $\text{kmol}/\text{m}^2\text{s}$
$F_b$	Flux of backward extraction, $\text{kmol}/\text{m}^2\text{s}$
$K_{\text{ex}}$	Equilibrium constants from the rate study

## 2. Conclusion

The development of solvent extraction techniques for separating metal ions has progressed from traditional methods to modern advancements. The field has progressed beyond traditional choices like TBP and  $\beta$ -diketones due to advancements in extractant design and process improvement. Newer agents such as LIX-reagents, D2EHPA, and Cyanex-reagents have been introduced as alternatives. These advancements highlight the ongoing progress in effectively removing metal ions from complicated mixtures, hence improving the efficiency of solvent extraction methods.

Research on the extraction of Mn (II) and Ni (II) using D2EHPA, Cyanex 272, TOPO, and TBP has demonstrated their significant potential in hydrometallurgical applications. Although equilibrium constants ( $K_{\text{ex}}$ ) and kinetic studies have been useful, it is crucial to conduct more extensive research on extraction mechanisms and thoroughly evaluate the efficacy of extractants in various settings. When optimizing metal ion separation processes, factors such as purity, solubility, and environmental sustainability are important to consider. These factors are vital for tailoring the techniques to meet specific industrial requirements.

In the future, there are many opportunities to improve the sustainability, efficiency, and selectivity of metal extraction processes by making further improvements in solvent extraction techniques. This review enhances the discussion in the field of hydrometallurgy by summarizing important discoveries and outlining directions for future research. Scientists can improve the accuracy of solvent extraction chemistry by constantly exploring new methods and solvents. This will make it easier to come up with more effective and environmentally friendly ways to get metals out of things.

### *Future Directions of The Research*

To progress in the field of metal ion separation using solvent extraction, it is crucial to strategically focus on many main directions. Conducting mechanistic research is crucial for understanding the intricate interactions between metal ions and extractants in various situations. The goal is to gain deeper insights that help enhance process optimization. It is crucial to develop new extractants that prioritise improved selectivity, efficiency, and sustainability. These extractants should adhere to the principles of green chemistry in order to minimize their influence on the environment. Efforts to optimise should focus on improving the speed of extraction, the ratios of different phases involved, and the effects of temperature on the process in order to enhance overall efficiency. Prioritizing sustainable practices means reducing the use of solvents, improving energy efficiency, and developing methods for reusing extractants and solvents. Investigating the use of solvent extraction in difficult matrices, including industrial effluents and urban mining residues, will broaden its usefulness and significance. Ensuring practical viability and economic feasibility requires integrating complementary separation approaches and scaling from laboratory research to commercial applications. Prior involvement with regulatory frameworks will promote wider acceptance of solvent extraction methods, strengthening their crucial position in sustainable metal retrieval and environmental management in hydrometallurgy.

## Compliance with ethical standards

### *Disclosure of conflict of interest*

There are no conflicts of interest.

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