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Original Research

Role of Diluent in Nickel(II) Ion Extraction by Di(2-ethylhexyl) Phosphoric Acid

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Abstract

This work investigates the ability of di(2-ethylhexyl) phosphoric acid (*HL*) to extract Ni(II) ions from a sulfate solution and the effects of diluents on the extraction process. Striking contrasts are observed between solvents, with 1-octanol and toluene achieving extraction efficiencies of >98.65% and <6.12%, respectively. pH, extractant concentration, and diluent type strongly influence extraction performance. NiL_2 complexes are formed in 1-octanol and methyl isobutyl ketone, whereas $NiL_2 \cdot 2HL$ complexes are formed in toluene, dichloromethane, chloroform, carbon-tetrachloride, and cyclohexane. The calculated extraction constants contribute to the development of more effective extraction strategies supporting a stable and sustainable nickel supply for advanced technology sectors.

Keywords: Di(2-ethylhexyl) phosphoric acid; nickel (II) ions; liquid-liquid extraction; sulfate medium; pH; extractant concentration; diluent choice

1. Introduction

Solvent extraction plays a central role in the nickel processing industry, offering an advanced approach for isolating and refining nickel from its raw materials. The need for highly pure nickel continues to rise, particularly due to its essential use in high-performance alloys, modern battery technologies, and a wide range of other technological applications. As industries pursue higher efficiency and more sustainable practices, improving nickel extraction methods has become increasingly important.

Beyond achieving high purity, solvent extraction also supports environmental sustainability. Conventional techniques for obtaining nickel frequently rely on strong chemicals and generate considerable amounts of waste, leading to ecological concerns [1,2,3,4].

Di(2-ethylhexyl) phosphoric acid is a key extractant widely recognized for its strong performance in solvent extraction systems. Within the two-phase extraction environment, its distinctive chemical behavior allows it to selectively bind and separate Ni(II) ions from sulfate solutions. This selectivity arises from controlled differences in solubility, where the distribution of nickel between phases is intentionally adjusted to achieve high purity. Because Di(2-ethylhexyl) phosphoric acid can accurately recognize and extract nickel ions, the resulting product can meet the rigorous quality standards demanded by today's industrial applications [5,6,7,8,9,10].

Diluents play an essential role in shaping the physicochemical conditions surrounding the extractant, which in turn affects both the efficiency and selectivity of the extraction system [8,11,12]. Choosing an appropriate diluent can markedly influence the performance of the process, helping to optimize extraction yields while also reducing the overall consumption of chemical reagents [13,14,15,16].

The outcomes of this study hold significance well beyond controlled experimental settings. They provide valuable insights for improving nickel extraction strategies, helping the industry satisfy rising global demand for this critical metal while maintaining commitments to sustainability and operational efficiency. As modern technologies increasingly depend on high-purity nickel, the role of solvent extraction as a dependable and advanced processing method becomes even more vital [9,17,18,19,20].

In this work, we investigated the main parameters that determine the performance of liquid–liquid extraction. A central part of the study involved assessing how solvent selection specifically a solvent that does not mix with the feed phase and exhibits strong affinity for the desired solute can greatly improve extraction outcomes. We also examined the effects of pH and reagent concentration. Through evaluating these factors, our goal was to establish the conditions that deliver the highest efficiency and product purity within a liquid–liquid extraction system.

2. Experimental Section

2.1 Products and Solutions

Di(2-ethylhexyl) phosphoric acid of analytical grade was obtained from Fluka (Buchs, Switzerland) and used without further purification. Organic diluents, 1-octanol and chloroform, were supplied by Sigma-Aldrich (St. Louis, MO, USA). The nickel feed solution was prepared using nickel sulfate ($NiSO_4 \cdot 6H_2O$) and sodium sulfate (Na_2SO_4), both obtained from Fluka (Buchs, Switzerland). both obtained from Fluka, which provided the required ionic environment.

2.2 Techniques and Equipment

The nickel content in the aqueous phase was measured using a PYE UNICAM SP6-350 visible spectrophotometer (Pye Unicam Ltd., Cambridge, UK). Changes in pH were tracked using a NAHITA 903 pH meter (Auxilab S.L., Navarra, Spain) fitted with a glass electrode.

2.3 Analytical Procedure for Extraction

Extraction to rigorously quantify the reliability of the calculated extraction parameters, standard uncertainties were evaluated for all fundamental physical measurements. The thermostatic control apparatus maintained the extraction temperature at 25.0 ± 0.1 °C. The initial nickel concentration, prepared via class-A volumetric standards, was determined to be $(1.70 \pm 0.03) \times 10^{-3}$ M. Through the mathematical propagation of instrumental photometric errors (estimated at ±0.002 absorbance units at 720 nm), the calculated relative uncertainties for the distribution coefficients (D) and overall extraction efficiencies ($\%E$) were established to range between 3% and 6%. All subsequent data evaluation and stoichiometric modeling incorporate these statistical uncertainty boundaries to ensure empirical robustness.

After completing a mixing period of 30 minutes, the two-phase system was considered to have effectively reached a state of extraction equilibrium, ensuring that no significant changes in metal distribution would occur with further agitation. At this stage, carefully measured aliquots of the aqueous phase were withdrawn in order to evaluate the distribution coefficient of Ni(II) at the predetermined pH conditions. These samples allowed for an accurate assessment of the amount of nickel that remained in the aqueous medium after equilibrium had been established.

To quantify the concentration of Ni(II) transferred to the organic phase, the initial nickel concentration in the aqueous solution was compared with the concentration measured after extraction. The difference between these two values was used to calculate the amount of nickel loaded into the organic phase, thereby enabling determination of the extraction efficiency. This indirect method is commonly employed in solvent-extraction studies, as it provides reliable information on metal partitioning without the need to directly analyze the organic phase, which can sometimes be challenging due to matrix effects [12].

For spectrophotometric measurements, it is important to note that nickel ions display their highest absorbance at a wavelength of approximately 720 nm. This characteristic absorbance peak serves as a basis for quantitative analysis, allowing the use of UV–Vis spectrophotometry to determine Ni(II) concentrations with good precision and reproducibility.

2.4 Software

Data analysis and graphical representations were performed using OriginPro 8.5 (OriginLab Corporation, Northampton, MA, USA). Chemical structures were drawn using ChemDraw Ultra 6.0 (CambridgeSoft, Cambridge, MA, USA).

3. Results and Discussion

3.1 Effects of pH and Concentration on the Extraction of Nickel (II)

The extraction of Ni^{2+} ions from sulfate-based aqueous solutions using D2EHPA dissolved in low-polarity organic solvents such as toluene, benzene, chloroform, kerosene, or other hydrocarbon diluents is controlled by a well-defined chemical equilibrium that characterizes this extraction system. Within these nonpolar environments, molecules of Di(2-ethylhexyl) phosphoric acid tend to associate through hydrogen bonding, forming stable dimeric structures represented as $(HL)_2$ [21]. These dimers act as the active extraction species responsible for transferring nickel ions from the aqueous phase into the organic phase.

When the aqueous and organic phases are shaken or otherwise brought into intimate contact, Ni^{2+} ions encounter the dimeric extractant species residing in the organic layer. The interaction between the nickel ions and the Di(2-ethylhexyl) phosphoric acid dimers leads to the formation of a neutral metal–extractant complex, which is preferentially soluble in the organic phase. This process follows an ion-exchange pathway in which the extractant donates protons to the aqueous medium while simultaneously binding the metal ion. As the neutral complex partitions into the organic phase, protons are released back into the aqueous solution, causing a shift in solution acidity. Consequently, both the direction and the extent of the extraction equilibrium are strongly dependent on several parameters, including the polarity of the organic solvent, the degree of aggregation of Di(2-ethylhexyl) phosphoric acid, and particularly the pH of the aqueous solution. Even small adjustments in pH can significantly modify the driving force of the exchange reaction, thereby altering the overall extraction efficiency.

In solvents with very low polarity, the metal-extractant complex often displays different coordination behavior from that observed in more polar diluents. The reduced dielectric constant of the medium affects not only the stability of the formed complex but also the number of extractant molecules required to surround and coordinate the Ni^{2+} ion. As a result, extraction systems using weakly polar solvents frequently exhibit complex stoichiometries, sometimes involving additional Di(2-ethylhexyl) phosphoric acid molecules to compensate for the reduced solvation capacity of the solvent. This variability in solvent environment explains why different structural forms and coordination patterns of the nickel-Di(2-ethylhexyl) phosphoric acid complex are commonly reported [22].

The extraction of Ni^{2+} ions from a sulfate-based aqueous solution by the acidic extractant Di(2-ethylhexyl) phosphoric acid, when dissolved in organic solvents of low polarity such as toluene, benzene, chloroform, or alkanes, proceeds according to a well-defined equilibrium reaction. In such diluents, molecules of Di(2-ethylhexyl) phosphoric acid predominantly exist in a dimeric, hydrogen-bonded form denoted as $(HL)_2$. These dimers act as the reactive species that participate directly in the formation of the metal–extractant complex during the extraction process.

The overall extraction reaction can be represented as follows:

$$\mathrm{Ni}^{2+} + (\frac{2+p}{2})\,\overline{(HL)_2} \overset{K_{ex1}}{\rightleftharpoons} \overline{(NiL_2p(HL))} + 2H^+ \quad (1)$$

The molecules of the dimeric extractant form a neutral organometallic complex that is soluble in the organic phase. At the same time, two protons are released back into the aqueous phase, making the extraction highly sensitive to the solution's acidity (pH). The parameter p reflects the number of additional extractant molecules that participate in stabilizing the metal complex, which often increases in less polar solvents due to reduced solvation forces.

As the total concentration of nickel(II) is at a trace level as employed in this study, it is reasonable to assume that no polynuclear complexes are formed [6,23].

The extraction constant K_{ex1} corresponding to this equilibrium is defined as:

The constant of the extraction:

$$K_{ex1} = \frac{\left[\left(\overline{NiL_2p(HL)}\right)\right]\left[H^+\right]^2}{\left[Ni^{+2}\right]\left[\overline{(HL)_2}\right]^{(2+p)/2}} \quad (2)$$

This expression quantitatively describes how the equilibrium position depends on the concentration of nickel in the aqueous phase, the amount of dimeric Di(2-ethylhexyl) phosphoric acid available in the organic phase, and the concentration of hydrogen ions produced during extraction. A larger value of K_{ex1} indicates a stronger tendency for nickel to transfer into the organic phase.

To evaluate the efficiency of extraction, the distribution coefficient D is introduced:

The distribution coefficient of metal:

$$D = \frac{\left[\overline{NiL_2p(HL)}\right]}{\left[Ni^{+2}\right]} \quad (3)$$

This coefficient represents the ratio between the concentration of nickel present in the organic phase as part of the extracted complex and that remaining unextracted in the aqueous phase. Higher D values correspond to greater extraction efficiency.

By combining the definitions of D and K_{ex1}, and reorganizing the terms through logarithmic transformation, the following linearized expression is obtained:

From this, we get the following:

$$LogD = log\,K_{ex1} + (2+p)/2\,Log\left[\left(\overline{HL}\right)_2\right] + 2pH \quad (4)$$

In polar solvents such as Decanol and 1-octanol, the extraction equilibrium for the divalent metal is described by:

$$(Ni)^{2+} + (2+p)\,(\overline{HL}) \overset{K_{ex2}}{\rightleftharpoons} \overline{NiL_2p(HL)} + 2H^+ \quad (5)$$

$$K_{ex2} = \frac{\left[\overline{NiL_2p(HL)}\right]\left[H^+\right]^2}{\left[Ni^{+2}\right]\left[\overline{HL}\right]^{(2+p)}} \quad (6)$$

The logarithmic expression of the distribution coefficient:

$$LogD = LogK_{ex2} + (2+p)\log\left[\overline{HL}\right] + 2pH \quad (7)$$

The percentage extractions (% E) of Nickel (II) can be calculated by:

$$E\% = 100\frac{D}{D+1} \quad (8)$$

To determine the stoichiometric coefficients of the organometallic species formed in the organic phase during nickel extraction, the classical slope analysis method was applied. This analytical approach is widely used in solvent-extraction studies because it provides a direct and reliable means of identifying the number of extractant molecules coordinated to the metal ion, as well as the number of protons displaced during the formation of the metal-extractant complex.

The method involves constructing two separate plots that relate measurable experimental quantities to the theoretical extraction equation. In the first plot, the logarithm of the metal distribution coefficient (Log D) is plotted as a function of the pH of the aqueous phase, and the slope of this linear regression corresponds to the number of hydrogen ions released during the extraction process, since the extraction equilibrium predicts that the distribution coefficient increases proportionally with the extent of proton displacement.

In the second plot, Log D is plotted against the logarithm of the concentration of the extractant $(HL)_2$ in the organic phase. According to the extraction equilibrium model, the slope of this relationship reflects the number of extractant dimers participating in the formation of the organometallic complex. Because the aggregation state and coordination behavior of Di(2-ethylhexyl) phosphoric acid depend strongly on solvent polarity, the slope obtained from this plot offers valuable information about how many extractant molecules are required to stabilize the nickel complex under the specific conditions employed.

By analyzing the slopes of these two linear plots together, it becomes possible to deduce the full stoichiometric form of the extracted species. This dual-slope approach provides a clear and systematic way to interpret the extraction mechanism, enabling researchers to identify the composition of the metal–extractant complex present in the organic phase without requiring direct structural characterization techniques. As a result, the slope method remains one of the most effective and practical tools for elucidating stoichiometry in solvent-extraction systems.

3.1.1 Effect of pH

A comprehensive series of solvent-extraction experiments was conducted to evaluate how the logarithm of the metal distribution coefficient (Log D) varies with changes in the pH of the aqueous phase while maintaining a constant concentration of the extractant. These experiments were performed using a diverse set of organic diluents chloroform, toluene, dichloromethane, carbon-tetrachloride, cyclohexane, 1-octanol, and methyl isobutyl ketone in order to assess how the nature of the solvent influences the extraction behavior of Ni(II). Each solvent represents a different polarity class and hydrogen-bonding capacity, allowing the role of solvent environment on Di(2-ethylhexyl) phosphoric acid aggregation and metal-complex formation to be systematically explored.

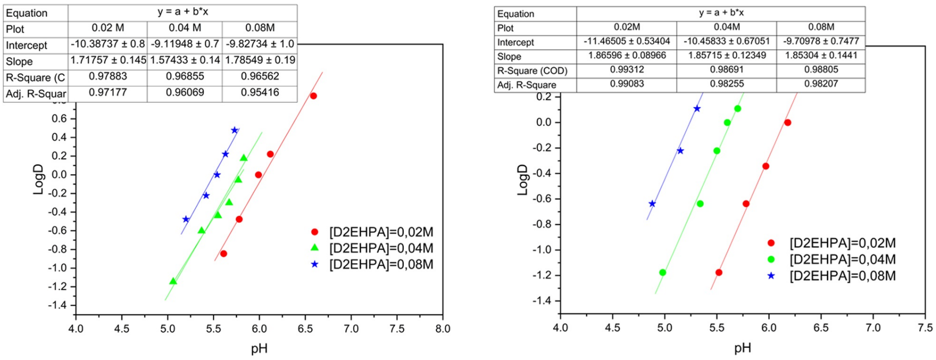
The extraction profiles obtained from these experiments are illustrated in Fig. 1, which shows the dependence of Log D on pH at 25 °C for the extraction of Ni(II) from a sulfate medium possessing an ionic strength of 1. For each organic solvent, measurements were carried out at multiple concentrations of Di(2-ethylhexyl) phosphoric acid to capture the effect of extractant availability on nickel uptake. The graphical trends reveal that the distribution coefficient increases progressively with increasing pH, consistent with the proton-release mechanism associated with Di(2-ethylhexyl) phosphoric acid -based extraction systems. At lower pH values, protonation of the extractant suppresses complex formation, whereas higher pH values favor deprotonation and facilitate the transfer of Ni(II) into the organic phase.

Across all diluents, a clear enhancement in the extraction of nickel(II) was observed as the concentration of Di(2-ethylhexyl) phosphoric acid in the organic phase was increased. This response confirms the critical role of extractant concentration in governing the equilibrium position of the extraction reaction. The greater availability of Di(2-ethylhexyl) phosphoric acid molecules particularly in their dimeric form promotes the formation of the nickel–extractant complex, thereby shifting the equilibrium toward the organic phase and elevating Log D. Although the magnitude of this effect varies among solvents due to differences in polarity and solvation properties, the overall trend underscores the strong dependence of extraction efficiency on extractant concentration, irrespective of the diluent employed.

Fig. 1 presents the extraction profiles of nickel in the presence of Di(2-ethylhexyl) phosphoric acid across a range of organic solvents, showing how strongly pH and solvent characteristics dictate the overall extraction performance. By maintaining a fixed concentration of Di(2-ethylhexyl) phosphoric acid throughout the experiments, the influence of pH and solvent effects could be evaluated more accurately. The results reveal that even small adjustments in these parameters can produce noticeable differences in extraction behavior, emphasizing the importance of carefully controlling experimental conditions to ensure consistent and reproducible extraction efficiencies.

A key pattern emerging from the data is the clear linear increase of the distribution coefficient (Log D) with rising pH. As the pH becomes more alkaline, Log D consistently rises, indicating more efficient transfer of nickel ions into the organic phase. This behavior can be attributed to the greater deprotonation of the acidic extractant, Di(2-ethylhexyl) phosphoric acid, at higher pH values. When deprotonated, Di(2-ethylhexyl) phosphoric acid exhibits a stronger affinity for Ni^{2+} ions, facilitating the formation of stable nickel–extractant complexes. As a result, the extraction process becomes progressively more effective as the pH increases.

These findings clearly demonstrate that the extraction performance of nickel is governed by a combination of chemical and physical factors that operate simultaneously within the system. The behavior of the extraction equilibrium, particularly the proton-release step inherent to Di(2-ethylhexyl) phosphoric acid-based mechanisms, plays a central role in determining the extent to which Ni(II) is transferred from the aqueous to the organic phase. At the same time, the characteristics of the solvent, including its

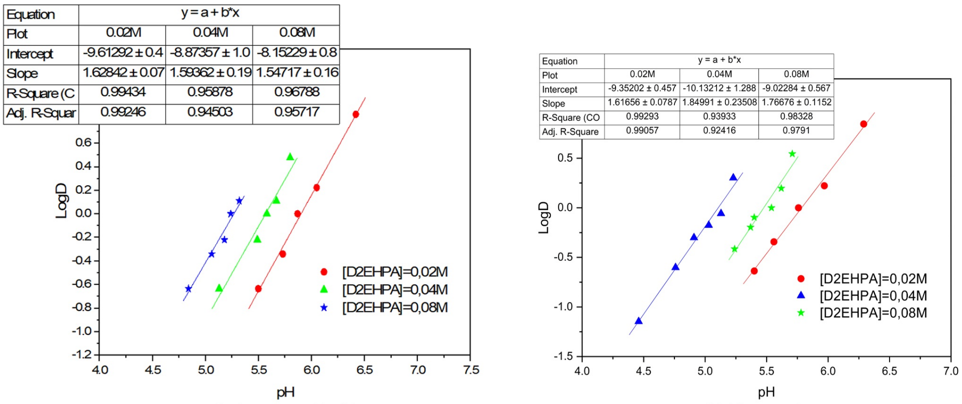


Equation	y = a + b*x		
Plot	0.02 M	0.04 M	0.08M
Intercept	-10.38737 ± 0.8	-9.11948 ± 0.7	-9.82734 ± 1.0
Slope	1.71757 ± 0.145	1.57433 ± 0.14	1.78549 ± 0.19
R-Square (C	0.97883	0.96855	0.96562
Adj. R-Squar	0.97177	0.96069	0.95416

Equation	y = a + b*x		
Plot	0.02M	0.04M	0.08M
Intercept	-11.46505 ± 0.53404	-10.45833 ± 0.67051	-9.70978 ± 0.7477
Slope	1.86596 ± 0.08966	1.85715 ± 0.12349	1.85304 ± 0.1441
R-Square (COD)	0.99312	0.98691	0.98805
Adj. R-Square	0.99083	0.98255	0.98207

Chloroform

Toluene

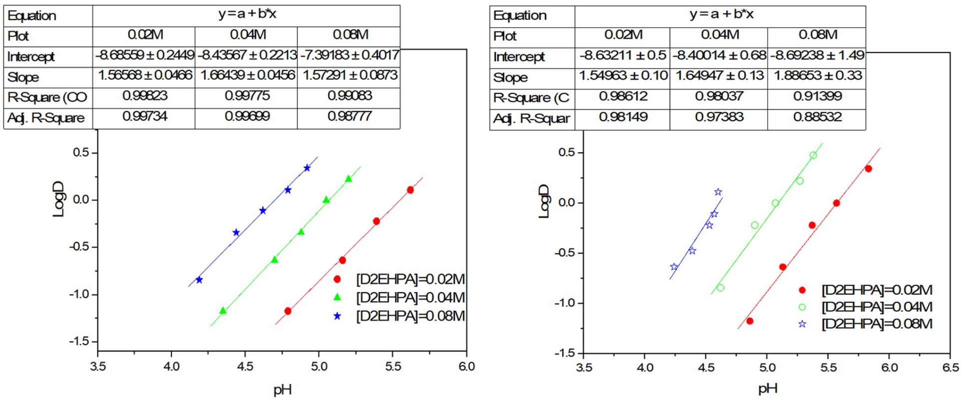


Equation	y = a + b*x		
Plot	0.02M	0.04M	0.08M
Intercept	-9.61292 ± 0.4	-8.87357 ± 1.0	-8.15229 ± 0.8
Slope	1.62842 ± 0.07	1.59362 ± 0.19	1.54717 ± 0.16
R-Square (C	0.99434	0.95878	0.96788
Adj. R-Squar	0.99246	0.94503	0.95717

Equation	y = a + b*x		
Plot	0.02M	0.04M	0.08M
Intercept	-9.35202 ± 0.457	-10.13212 ± 1.288	-9.02284 ± 0.567
Slope	1.61656 ± 0.0787	1.84991 ± 0.23508	1.76676 ± 0.1152
R-Square (CO	0.99293	0.93933	0.98328
Adj. R-Square	0.99057	0.92416	0.9791

Carbon-tetrachloride

Dichloromethane

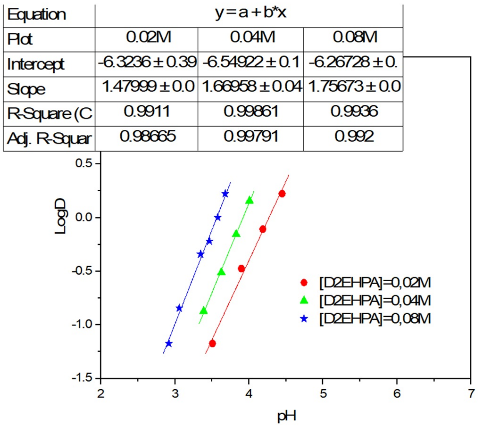


Equation	y = a + b*x		
Plot	0.02M	0.04M	0.08M
Intercept	-8.68559 ± 0.2449	-8.43567 ± 0.2213	-7.39183 ± 0.4017
Slope	1.56568 ± 0.0466	1.66439 ± 0.0456	1.57291 ± 0.0873
R-Square (CO	0.99823	0.99775	0.99083
Adj. R-Square	0.99734	0.99699	0.98777

Equation	y = a + b*x		
Plot	0.02M	0.04M	0.08M
Intercept	-8.63211 ± 0.5	-8.40014 ± 0.68	-8.69238 ± 1.49
Slope	1.54963 ± 0.10	1.64947 ± 0.13	1.88653 ± 0.33
R-Square (C	0.98612	0.98037	0.91399
Adj. R-Squar	0.98149	0.97383	0.88532

Cyclohexane

MIBK



Equation	y = a + b*x		
Plot	0.02M	0.04M	0.08M
Intercept	-6.3236 ± 0.39	-6.54922 ± 0.1	-6.26728 ± 0.
Slope	1.47999 ± 0.0	1.66958 ± 0.04	1.75673 ± 0.0
R-Square (C	0.9911	0.99861	0.9936
Adj. R-Squar	0.98665	0.99791	0.992

1-octanol

Fig. 1. Influence of pH on the distribution coefficient Organic phase: D2EHPA/diluents.

polarity, ability to stabilize extractant dimers, and interaction with the formed metal-extractant complex, significantly influence the efficiency with which the extraction reaction proceeds.

The results indicate that the recovery of nickel is not dictated solely by the available concentration of extractant, but is also highly sensitive to the exact acidity of the aqueous medium. Because the extraction mechanism involves the exchange of protons, changes in metal distribution. This sensitivity underscores the critical importance of maintaining tight pH control during experimental operations as well as during large-scale industrial extraction processes. In practical applications, insufficient regulation of pH can lead to inconsistent extraction performance, reduced metal recovery, or the formation of undesirable side products [24].

Taken together, the experimental trends reinforce the conclusion that robust and reproducible metal extraction requires both rigorous experimental control and a comprehensive understanding of the chemical equilibria governing the system. A well-defined pH environment, an appropriate choice of solvent, and an optimized extractant concentration must all be carefully coordinated to achieve high extraction efficiency and stable process performance. These considerations are essential not only for laboratory-scale investigations but also for designing industrial solvent-extraction circuits capable of delivering predictable and efficient nickel recovery.

3.1.2 Effect of Extractant Concentration

To explore the impact of Di(2-ethylhexyl) phosphoric acid concentration, we monitored the variations of Log D as a function of Log $[(\overline{HL})_2]$ and Log $[\overline{HL}]$ at constant pH for metal extraction from these solvents' sulfate medium of unit ionic strength. Figs. 2,3 illustrate the variations of Log D = f(Log. $[(\overline{HL})_2]$) and Log D = f (Log $[\overline{HL}]$), that is, Log D with the variation in the concentration of extractant in dimeric and monomeric forms at different pH values for the extraction of nickel(II) by D2EHPA. Fig. 2 shows the variations of Log D = f(Log$[(\overline{HL})_2]$) The extraction behavior of Ni(II) using D2EHPA dissolved in various organic solvents such as chloroform, toluene, dichloromethane, carbon-tetrachloride, and cyclohexane exhibits a remarkably consistent pattern regardless of the diluent employed. Despite differences in solvent polarity, dielectric constant, and solvation ability, the general shape of the extraction curves and the manner in which the distribution coefficient responds to changes in extractant concentration remain essentially the same. This uniformity suggests that the fundamental extraction mechanism is largely preserved across these media, with solvent effects influencing efficiency but not the underlying reaction pathway.

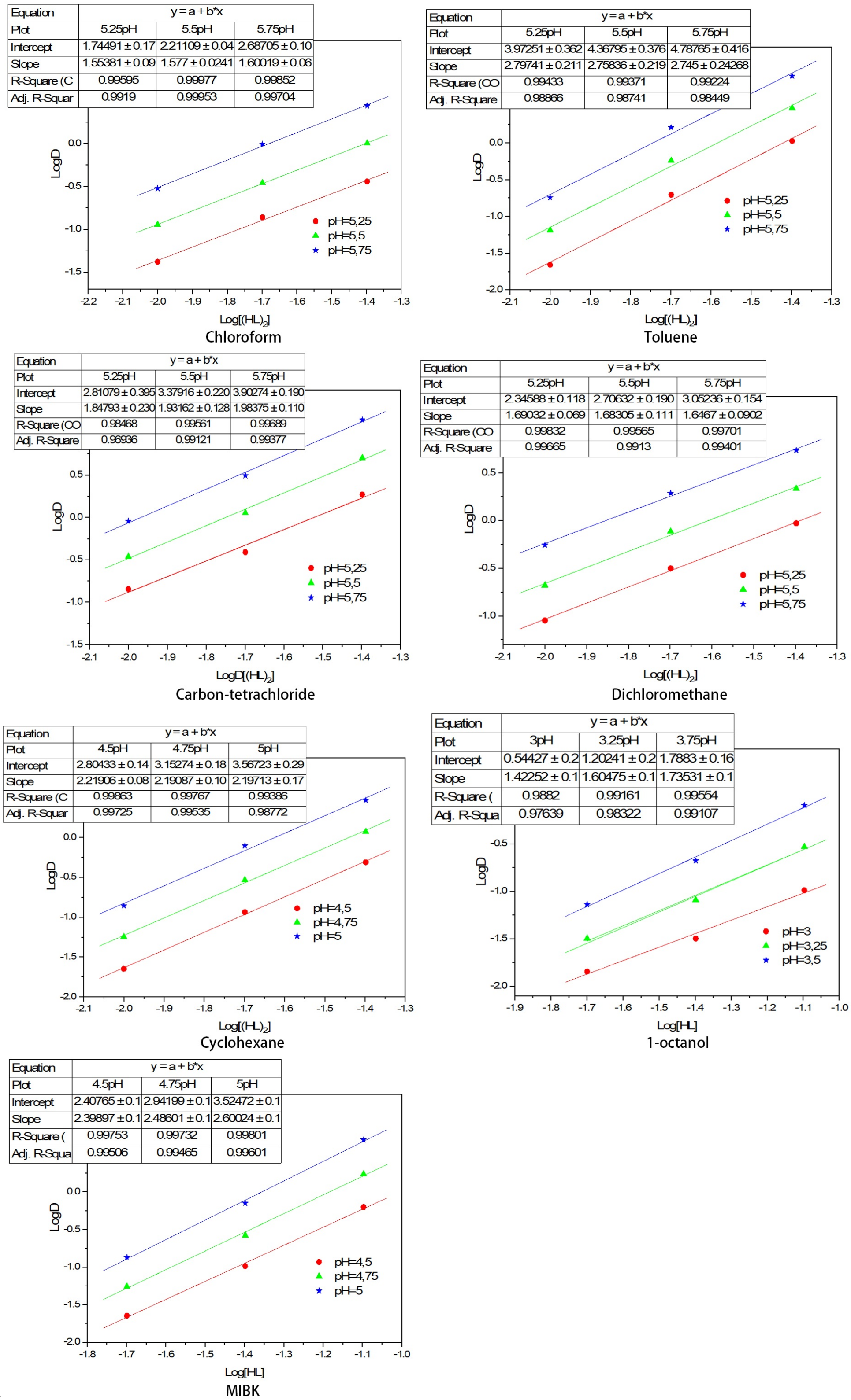
Analysis of the slopes obtained from the logarithmic extraction plots provides deeper mechanistic insight. In all examined solvents, the slopes converge to values very close to 2, indicating a second-order dependence of the extraction equilibrium on the concentration of Di(2-ethylhexyl) phosphoric acid. In the context of the extraction model, such a slope signifies that the rate-determining step or the equilibrium-determining step involves two molecules of the extractant acting together typically in their dimeric form to coordinate with a single Ni(II) ion.

This observation directly supports a stoichiometric formulation in which two units of D2EHPA are involved in forming the neutral nickel-extractant complex that partitions into the organic phase. In other words, the complexation reaction proceeds according to a 1:2 metal-to-extractant ratio, consistent with the well-established ion-exchange mechanism of acidic organophosphorus extractants. The agreement of this stoichiometry across several chemically diverse solvents further confirms that the participation of two extractant molecules is an intrinsic requirement of the nickel extraction process, rather than an artifact of any particular organic medium.

Accordingly, the stoichiometric formulation of the nickel species stabilized in the organic phase can be expressed as $\mathrm{NiL_2 \cdot 2HL}$, where Ni corresponds to the divalent nickel ion, L represents the deprotonated form of the extractant Di(2-ethylhexyl) phosphoric acid, and HL denotes the neutral, protonated extractant molecule. This structural representation illustrates that the extracted complex is not composed solely of deprotonated ligands, but rather incorporates both protonated and deprotonated extractant species, each contributing to the organization and stabilization of the nickel center within the hydrophobic environment of the organic phase.

The involvement of two L units reflects the primary coordination interaction responsible for binding and neutralizing the charge of the Ni(II) ion during transfer from the aqueous phase. Meanwhile, the participation of two additional protonated molecules, HL, suggests their auxiliary role in enhancing the solubility of the complex, reinforcing hydrogen-bonded networks, or stabilizing the overall molecular assembly via secondary interactions. Such mixed-ligand structures are characteristic of extraction systems involving acidic organophosphorus extractants, where aggregation and hydrogen bonding in the organic phase strongly influence the final configuration of the extracted species.

Collectively, these observations provide compelling support for a coherent mechanistic framework that governs the extraction process. The experimentally derived stoichiometry aligns well with the expected behavior of Di(2-ethylhexyl) phosphoric acid in low-polarity media and confirms that the formation of the nickel complex follows a predictable and reproducible reaction pathway. The consistency of this stoichiometric pattern across different solvents strengthens the conclusion that the extraction mechanism is well-defined, chemically robust, and governed by fundamental interactions intrinsic to acidic organophosphorus extractants.



Chloroform

Equation	y = a + b*x		
Plot	5.25pH	5.5pH	5.75pH
Intercept	1.74491 ± 0.17	2.21109 ± 0.04	2.68705 ± 0.10
Slope	1.55381 ± 0.09	1.577 ± 0.0241	1.60019 ± 0.06
R-Square (C	0.99595	0.99977	0.99852
Adj. R-Squar	0.9919	0.99953	0.99704

Toluene

Equation	y = a + b*x		
Plot	5.25pH	5.5pH	5.75pH
Intercept	3.97251 ± 0.362	4.36795 ± 0.376	4.78765 ± 0.416
Slope	2.79741 ± 0.211	2.75836 ± 0.219	2.745 ± 0.24268
R-Square (CO	0.99433	0.99371	0.99224
Adj. R-Square	0.98866	0.98741	0.98449

Carbon-tetrachloride

Equation	y = a + b*x		
Plot	5.25pH	5.5pH	5.75pH
Intercept	2.81079 ± 0.395	3.37916 ± 0.220	3.90274 ± 0.190
Slope	1.84793 ± 0.230	1.93162 ± 0.128	1.98375 ± 0.110
R-Square (CO	0.98468	0.99561	0.99689
Adj. R-Square	0.96936	0.99121	0.99377

Dichloromethane

Equation	y = a + b*x		
Plot	5.25pH	5.5pH	5.75pH
Intercept	2.34588 ± 0.118	2.70632 ± 0.190	3.05236 ± 0.154
Slope	1.69032 ± 0.069	1.68305 ± 0.111	1.6467 ± 0.0902
R-Square (CO	0.99832	0.99565	0.99701
Adj. R-Square	0.99665	0.9913	0.99401

Cyclohexane

Equation	y = a + b*x		
Plot	4.5pH	4.75pH	5pH
Intercept	2.80433 ± 0.14	3.15274 ± 0.18	3.56723 ± 0.29
Slope	2.21906 ± 0.08	2.19087 ± 0.10	2.19713 ± 0.17
R-Square (C	0.99863	0.99767	0.99386
Adj. R-Squar	0.99725	0.99535	0.98772

1-octanol

Equation	y = a + b*x		
Plot	3pH	3.25pH	3.75pH
Intercept	0.54427 ± 0.2	1.20241 ± 0.2	1.7883 ± 0.16
Slope	1.42252 ± 0.1	1.60475 ± 0.1	1.73531 ± 0.1
R-Square (	0.9882	0.99161	0.99554
Adj. R-Squa	0.97639	0.98322	0.99107

MIBK

Equation	y = a + b*x		
Plot	4.5pH	4.75pH	5pH
Intercept	2.40765 ± 0.1	2.94199 ± 0.1	3.52472 ± 0.1
Slope	2.39897 ± 0.1	2.48601 ± 0.1	2.60024 ± 0.1
R-Square (	0.99753	0.99732	0.99801
Adj. R-Squa	0.99506	0.99465	0.99601

Fig. 2. Variation of the distribution coefficient (D) with D2EHPA concentration.

Fig. 2 displays the plots of Log *D* versus Log [HL] for the extraction of Ni(II) by Di(2-ethylhexyl) phosphoric acid in 1-octanol and methyl isobutyl ketone (MIBK).

The resulting graphs exhibit slopes close to 2, corresponding to $p = 0$. This indicates that the species transferred into the organic phase has the stoichiometry NiL_2, and that no additional protonated Di(2-ethylhexyl) phosphoric acid

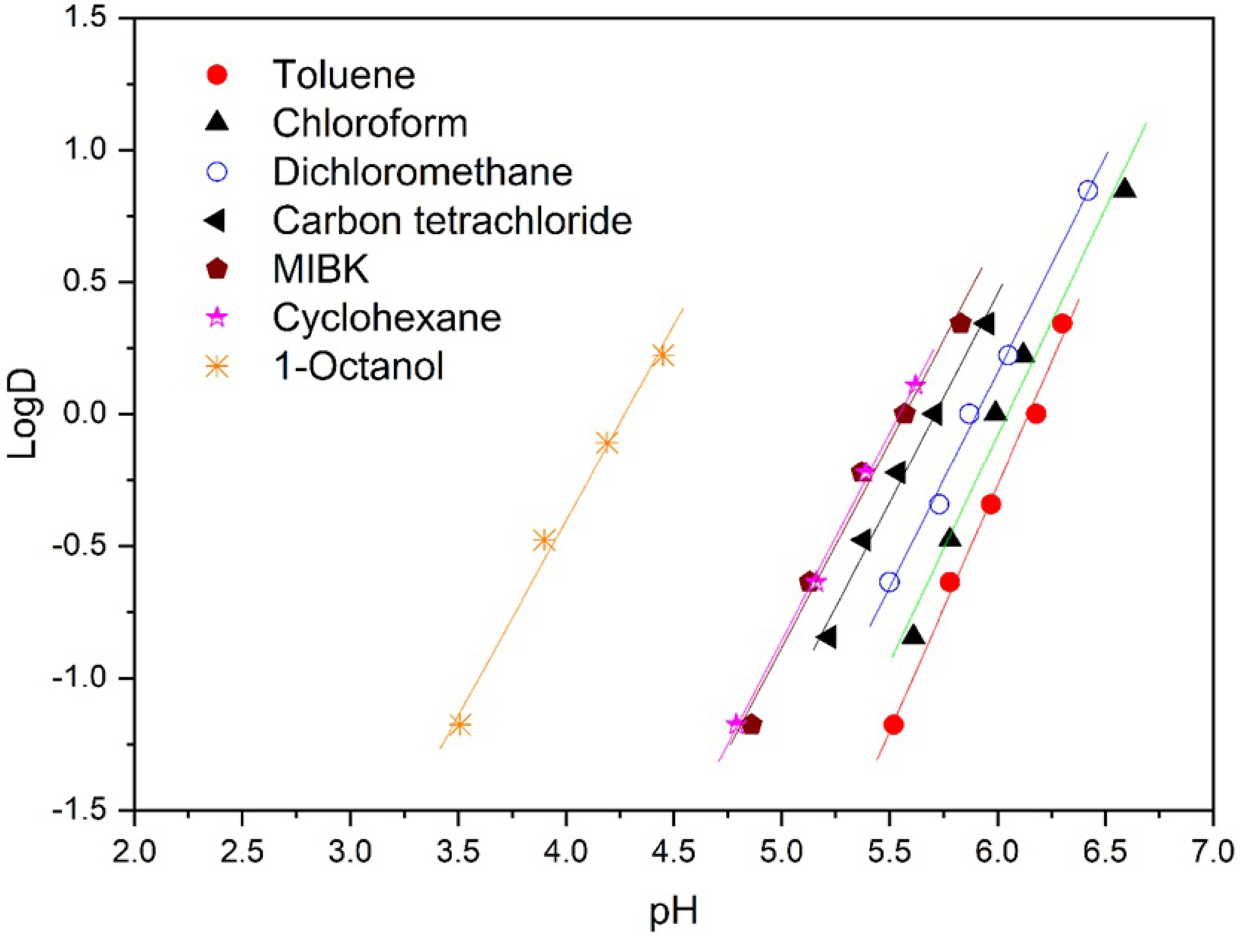


Fig. 3. Influence of aqueous phase pH on Ni(II) extraction using D2EHPA in different diluents; [Di(2-ethylhexyl) phosphoric acid] = 0.02 M.

molecules (HL) are involved in coordinating the extracted complex.

A similar conclusion was reported by Tao and Nagaosa [25] for the extraction of Ni(II) from a perchlorate medium (0.1 M $(NaH)ClO_4$) using Di(2-ethylhexyl) phosphoric acid dissolved in 1-octanol.

The plots presented in Fig. 2 provide a detailed illustration of how the concentration of Di(2-ethylhexyl) phosphoric acid affects the distribution coefficient (Log *D*) during the extraction of Ni(II) when the extractant is dissolved in different organic diluents. These graphical representations make it possible to directly compare the extraction behavior across a broad range of solvents and highlight the role of extractant concentration in governing the transfer of nickel from the aqueous to the organic phase.

Fig. 2, which corresponds to extraction systems employing chloroform, toluene, dichloromethane, carbontetrachloride, and cyclohexane as organic solvents, shows the relationship between Log *D* and Log[$(HL)_2$], where $(HL)_2$ denotes the dimeric form of Di(2-ethylhexyl) phosphoric acid that predominates in low-polarity media. For each solvent, the curves obtained at the three investigated pH values exhibit positive and nearly linear slopes. This behavior clearly indicates that increasing the concentration of the dimeric extractant leads to enhanced nickel extraction, as reflected by the rise in the distribution coefficient. The consistent upward trend observed across all diluents reinforces the conclusion that extractant availability is a critical factor controlling the extent of metal loading in these systems.

Furthermore, the differences in the slopes measured at various pH levels provide additional insight into the proton-exchange mechanism underlying the extraction reaction. Higher pH values which favor deprotonation of the extractant result in more pronounced increases in Log *D* with increasing extractant concentration. This effect confirms the strong dependence of extraction efficiency on the acidity of the aqueous phase, as even modest increases in pH significantly promote the formation of the metal–extractant complex and facilitate nickel transfer to the organic medium.

Fig. 2 presents the analogous plots of Log *D* versus Log[HL] for extraction systems using 1-octanol and MIBK as diluents. The extraction behavior in these comparatively more polar solvents is particularly notable because solvent–

Table 1. Statistical parameters of the linear regression analysis for Ni(II) extraction as a function of pH in different diluents.

Equation	y = a + b*x						
Plot	Toluene	Chloroform	Dichloromethane	Cyclohexane	Methyl isobutyl ketone	Tetrachloride	1-Octanol
Intercept	–11.46505 ± 0.53404	–10.38737 ± 0.87899	–9.61292 ± 0.41996	–9.03988 ± 0.57848	–8.63211 ± 0.5693	–8.68559 ± 0.24496	–6.3236 ± 0.3995
Slope	1.86596 ± 0.08966	1.71757 ± 0.14583	1.62842 ± 0.07091	1.58265 ± 0.10394	1.54963 ± 0.10616	1.56568 ± 0.04667	1.47999 ± 0.09919
R-Square (COD)	0.99312	0.97883	0.99434	0.98723	0.98612	0.99823	0.9911
Adj. R-Square	0.99083	0.97177	0.99246	0.98297	0.98149	0.99734	0.98665

extractant interactions differ substantially from those observed in nonpolar media. In 1-octanol and MIBK, solvation effects, hydrogen bonding, and variations in extractant aggregation can influence the stability, structure, and overall stoichiometry of the nickel-Di(2-ethylhexyl) phosphoric acid complex. The distinct trends observed in these solvents thus highlight the important role of diluent properties in determining extraction efficiency and mechanistic pathways, underscoring that solvent selection is a key factor in optimizing metal recovery processes.

3.2 Effect of the Diluent on the Extraction of Nickel (II) by D2EHPA

A comprehensive study was undertaken to explore how the nature of the organic diluent affects the extraction of Ni(II) by the acidic extractant Di(2-ethylhexyl) phosphoric acid. Because the physicochemical properties of the solvent such as polarity, dielectric constant, and ability to promote or disrupt extractant aggregation play a decisive role in determining extraction performance, a broad set of organic media was examined. The selected solvents included chloroform, toluene, dichloromethane, carbon-tetrachloride, cyclohexane, 1-octanol, and methyl isobutyl ketone (MIBK). These diluents span a wide polarity range, enabling a detailed comparison of how solvent environment influences the extractant's molecular form and, consequently, the overall extraction mechanism.

Fig. 3 illustrates the variation of the distribution coefficient (Log *D*) as a function of pH for the extraction of Ni(II) by Di(2-ethylhexyl) phosphoric acid in each of the tested solvents at a fixed extractant concentration of 0.02 M. In all systems, a clear linear relationship is observed, with Log *D* increasing steadily as the pH of the aqueous phase rises. This consistent linearity reflects the proton-exchange mechanism characteristic of Di(2-ethylhexyl) phosphoric acid -based extraction processes, in which increasing pH shifts the equilibrium toward the deprotonated extractant, thereby facilitating complex formation with Ni(II). The linear regression parameters (Slope, Intercept) and coefficient of determination (R2) for the extraction of Ni(II) versus pH in different diluents are summarized in Tables 1 and 2.

Remarkably, the slopes of the lines obtained for all diluents are clustered around a value of approximately 2. This uniformity indicates that the extraction reaction exhibits a second-order dependence on the active form of the extractant and that the stoichiometric involvement of two extractant molecules per nickel ion is maintained regardless of the solvent. The fact that such consistent behavior is observed across solvents of markedly different polarity highlights the robustness of the extraction mechanism and confirms that the fundamental coordination environment of the Ni(II)-Di(2-ethylhexyl) phosphoric acid complex remains essentially unchanged.

These findings demonstrate that, although diluents can influence extraction efficiency and complex stability to varying extents, the underlying chemical pathway governing nickel extraction by Di(2-ethylhexyl) phosphoric acid is remarkably stable. This mechanistic consistency suggests that solvent effects primarily alter equilibrium position and complex solvation rather than modifying the intrinsic stoichiometry of the extracted species.

Table 3 (Ref. [21,22,23]) compiles the logarithmic values of the extraction constants K obtained for the various organic diluents investigated, allowing for a direct comparison of extraction behaviour across the different solvent systems.

In Table 3 the differences observed in the Log K_{ex} values obtained in this work, compared with those reported in previous studies, can be explained by the additional complexity introduced by the sulfate medium [6].

In The variations observed in the values of log K_{ex} obtained in this study, when compared with those reported previously in the literature, can be attributed to the additional complexity imposed by the sulfate medium, as also indicated by Tahmasebizadeh P et al. [6]. The presence of sulfate ions influences both the speciation of nickel in the aqueous phase and the degree of interaction between the metal ion and the extractant, thereby modifying the apparent extraction constant. As a result, the extraction behaviour in sulfate media cannot be directly compared with systems involving nitrate or chloride without considering these additional equilibria.

The extraction constants follow the decreasing trend:

1-octanol > cyclohexane > methyl isobutyl ketone > carbon-tetrachloride > dichloromethane > chloroform ≈ toluene.

Table 2. Linear regression equations of Log *D* versus pH for Ni(II) extraction in different diluents.

R2	Slope (a)	Linear Equation (Log *D*=a·pH+b)	Diluent
0.9931	1.87	Log *D* = 1.87 pH – 11.47	Toluene
0.9788	1.72	Log *D* = 1.72 pH – 10.39	Chloroform
0.9943	1.63	Log *D* = 1.63 pH – 9.61	Dichloromethane
0.9872	1.58	Log *D* = 1.58 pH – 9.04	Cyclohexane
0.9861	1.55	Log *D* = 1.55 pH – 8.63	MIBK
0.9982	1.57	Log *D* = 1.57 pH – 8.69	Carbon-tetrachloride
0.9911	1.48	Log *D* = 1.48 pH – 6.32	1-Octanol

Table 3. The values of the extraction constants K_{ex} of nickel(II) by D2EHPA in the different diluents.

Aqueous phase	Diluent	$LogK_{ex}$	Proposed complex	Source
0.33 M Na_2SO_4	1-octanol	4.93	NiL_2	Our work
	Cyclohexane	–6.85	$NiL_2 \cdot 2HL$	
	Methyl isobutyl ketone	–6.88	NiL_2	
	Carbon-tetrachloride	–7.12	$NiL_2 \cdot 2HL$	
	Dichloromethane	–7.42	$NiL_2 \cdot 2HL$	
	Toluene	–7.98	$NiL_2 \cdot 2HL$	
	Chloroform	–7.80	$NiL_2 \cdot 2HL$	
	Chloroform	–7.23	$NiL_2 \cdot 2HL$	(Louichaoui et al., 2024 [23])
	1-octanol	5.22	NiL_2	
0.5 M (NaH) NO_3	Toluene	–8.82	$NiL_2 \cdot 2(HL)_2$	(Juang and Chang, 1991 [21])
0.5 mol/dm^3 (NaH)NO_3	Toluene or benzene	–5.69	$NiL_2 \cdot 2(HL)_2$	(Komasawa et al., 1981 [22])
		–4.34		
	n-Heptane	–4.34		
	Toluene	–8.82	$NiL_2 \cdot 2(HL)_2$	

This sequence highlights the substantial influence of the diluent on extraction efficiency. The marked differences among solvents reflect variations in polarity, hydrogen-bonding capability, and their capacity to stabilize extractant aggregates or the resulting metal–extractant complex.

In the case of 1-octanol, Ni(II) extraction is significantly more efficient than in the other solvents examined. Although some degree of interaction between Di(2-ethylhexyl) phosphoric acid and the diluent occurs as expected for an alcohol 1-octanol provides a favorable environment for both the stabilization and solubilization of the [Ni(Di(2-ethylhexyl) phosphoric acid)2] complex. This enhanced solvation contributes to a higher effective extraction constant. The strong solvating ability of 1-octanol, combined with its intermediate polarity, likely supports the integrity of the nickel–Di(2-ethylhexyl) phosphoric acid species, thereby improving its partitioning into the organic phase and yielding superior extraction performance overall.

In contrast, solvents such as carbon-tetrachloride, chloroform, toluene, and dichloromethane yield significantly lower extraction efficiencies. This reduced performance is attributed to stronger solvation or specific interactions between the diluent and Di(2-ethylhexyl) phosphoric acid, which reduce the activity of the extractant molecules and hinder complex formation with Ni(II).

For methyl isobutyl ketone (MIBK), a more polar diluent, the extraction behavior differs markedly from that observed in 1-octanol. The extraction curve does not show the same degree of enhancement, likely because MIBK exhibits partial solubility in the aqueous phase. This favors the formation of additional complexes such as $NiSO_4(MIBK)_4$ in parallel with NiL_2, thereby reducing the overall efficiency of Di(2-ethylhexyl) phosphoric acid in this medium. Ghebghoub and Barkat [24] reported formation of $ZnSO_4(MIBK)_4$ during extraction with acidic chelating extractants.

To evaluate the performance of Di(2-ethylhexyl) phosphoric acid in these various diluents, the extraction percentage (*%E*) and distribution coefficient (D) were calculated. These values, summarized in Fig. 4 and Table 4, provide a comparative measure of the effectiveness of each solvent system.

This work investigates the performance of Di(2-ethylhexyl) phosphoric acid in extracting Ni(II) across a range of organic solvents. Consistent with earlier findings for Cu(II) and Co(II) [24], the results show that 1-octanol provides particularly favourable extraction conditions for Ni(II), even though noticeable interactions occur between the extractant and the diluent. The efficiency observed in 1-octanol highlights its ability to maintain and stabilize the nickel-Di(2-ethylhexyl) phosphoric acid complex more ef-

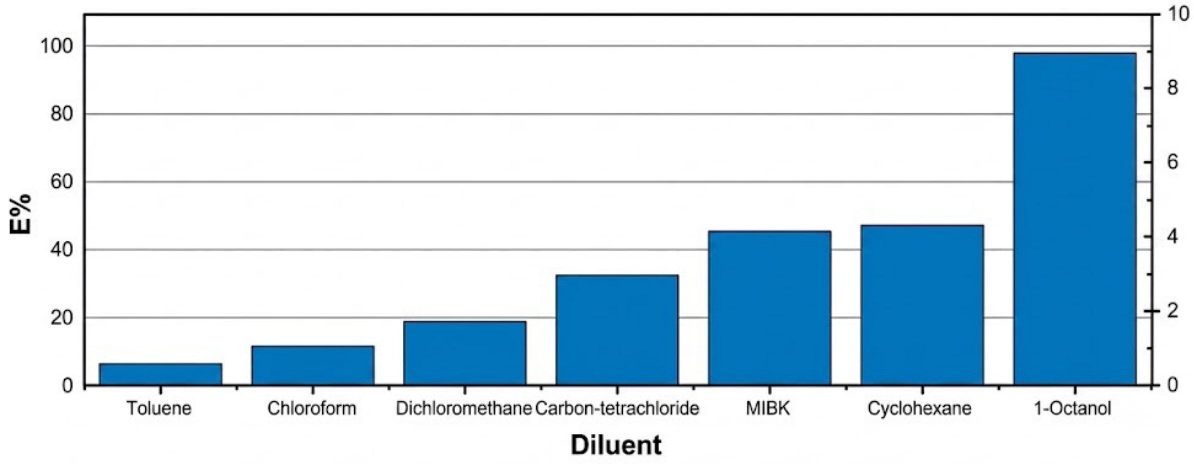


Fig. 4. Optimisation of extraction efficiency through various diluents.

Table 4. Summary of the distribution coefficients (D) and corresponding extraction percentages (*%E*) obtained for the extraction of Ni(II) using D2EHPA in different organic solvents.

Diluent	D	E (%)
Toluene	0.06528	6.12777
Chloroform	0.12371	11.00887
Dichloromethane	0.23635	19.11703
Carbon-tetrachloride	0.48197	32.52245
MIBK	0.83512	45.50775
Cyclohexane	0.88953	47.07675
1-Octanol	73.31006	98.65429

fectively than the other solvents examined.

4. Visible Spectra of the Organic Phase During Nickel(II) Extraction

Fig. 5 displays the visible-region absorption spectra recorded for the organic phase during the extraction of Ni(II) by Di(2-ethylhexyl) phosphoric acid in the different organic solvents investigated. These spectra provide insight into how the optical properties of the nickel-extractant complexes vary according to the nature of the diluent. Because each solvent offers a distinct microenvironment differing in polarity, solvating ability, and potential for hydrogen bonding the recorded spectra reveal subtle but significant shifts in absorbance intensity and wavelength maxima.

Such spectral features are closely linked to the coordination environment of the Ni(II) ion once transferred into the organic phase. Variations in band position or intensity indicate differences in complex stability, ligand interactions, and the extent of solvation provided by each diluent. Consequently, the spectral data serve as an informative tool for probing the interaction between Ni(II), the deprotonated and protonated forms of Di(2-ethylhexyl) phosphoric acid, and the surrounding organic medium. By comparing spectra across solvents, it becomes possible to identify how the nature of the diluent influences the geometry, electronic transitions, and overall structure of the extracted nickel complexes.

Each spectrum shown in the figure corresponds to a specific organic solvent, and the differences observed among these curves whether in peak positions, relative intensities, or overall spectral profiles highlight clear variations in the characteristics of the extracted nickel complexes. Such distinctions suggest that the coordination environment surrounding the Ni–Di(2-ethylhexyl) phosphoric acid species is strongly influenced by the solvent in which the extraction occurs.

Shifts in the absorption maxima provide evidence of changes in the ligand field experienced by Ni(II), implying that the geometry or the donor interactions of the extractant molecules may differ depending on the diluent. Likewise, modifications in the shapes, widths, or intensities of the absorption bands point to solvent-dependent variations in complex stability, solvation effects, and possible aggregation or reorganization of the extracted species within the organic phase.

Altogether, these spectral variations reinforce the conclusion that the solvent plays a significant role in determining the structural and electronic properties of the Ni–Di(2-ethylhexyl) phosphoric acid complexes formed during extraction. The observed differences therefore offer valuable insights into how the microenvironment of the organic phase governs the behavior and final configuration of the extracted metal species.

Such spectral distinctions provide insight into how effectively Ni(II) is transferred into each organic phase and how the solvent contributes to stabilizing the metal–extractant complex. These observations can be directly related to the differences in extraction efficiency noted across the diluents, reinforcing the role of solvent-extractant interactions in governing complex formation and stability.

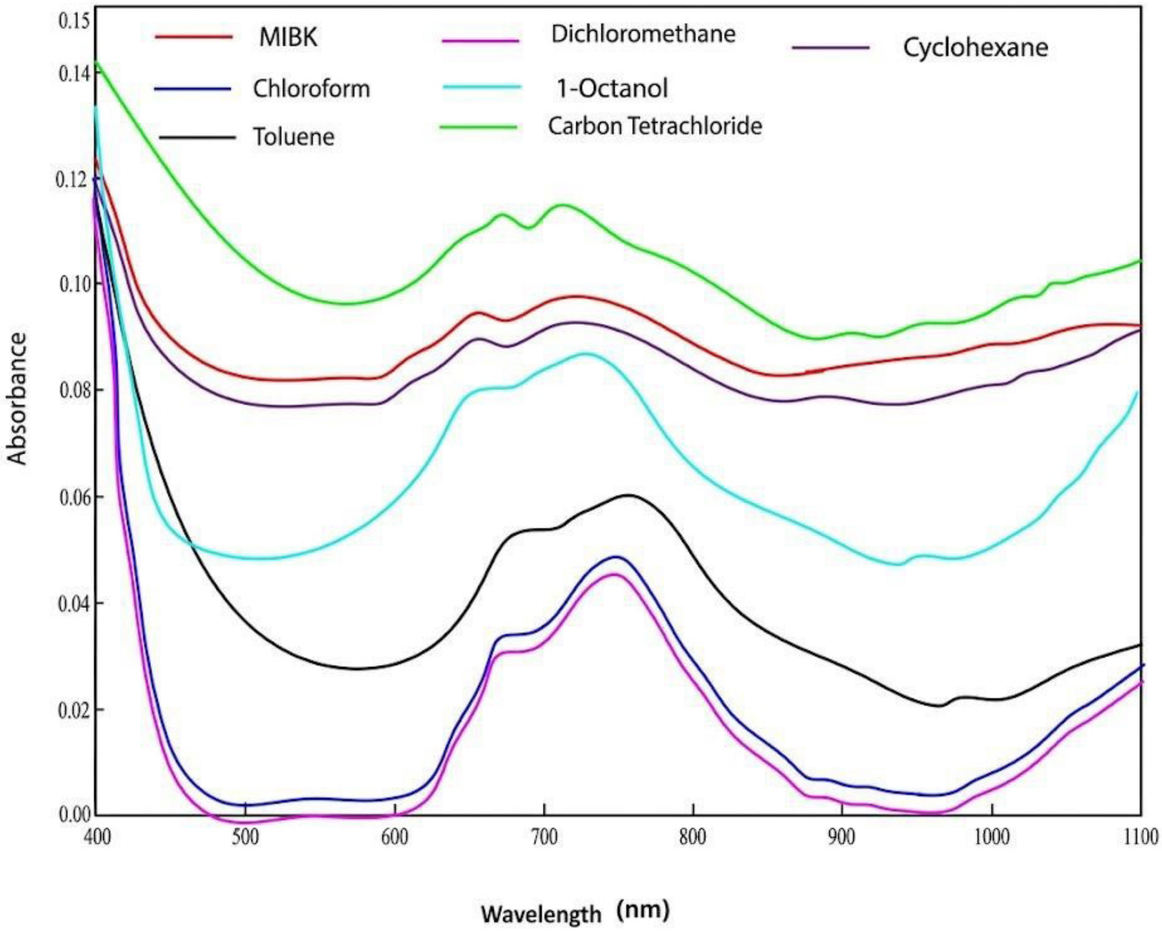


Fig. 5. Visible spectra of the organic phase during the extraction of nickel(II) by D2EHPA in different solvents.

Outlines the proposed structural framework of the extracted nickel(II) complexes, including a detailed depiction of the $NiL_2 \cdot 2HL$ species formed in the organic phase (Fig. 6).

The stoichiometry of the extracted organometallic species was further confirmed through electronic spectroscopy of the organic phase during nickel(II) extraction. Spectral measurements were carried out on the organic layers containing the Ni(II) complexes formed in various nonpolar solvents. The absorption maxima observed in these spectra provide valuable information regarding the structural arrangement of the metal complex once transferred into the organic medium.

The recorded spectra shown in Fig. 5 display features characteristic of octahedral coordination, thereby supporting the formation of octahedral Ni(II) complexes within the organic phase. Table 5 summarizes the wavelengths of the principal absorption bands for the complexes formed in the different nonpolar diluents. These values are consistent across the solvent series and align well with the octahedral geometries previously described by J. Preston and other researchers [26,27,28].

Table 5. Maximum wavelengths of nickel(II) complexes.

Solvents	Wavelength (nm)
Chloroform	750
Toluene	753
Dichloromethane	751
Carbon-tetrachloride	749
Cyclohexane	745
MIBK	743
1-octanol	745

The literature further confirms that Ni(II), with its d^8 electronic configuration, is capable of forming both octahedral and, under certain conditions, tetrahedral complexes [29,30]. The spectroscopic evidence obtained in this study strongly supports the predominance of octahedral species under the extraction conditions employed.

Furthermore, Fig. 7 illustrates the proposed structure for the nickel(II) complexes, showcased as the NiL_2 complex.

The electronic spectra recorded for the organic phase during the extraction of Ni(II) by Di(2-ethylhexyl) phosphoric acid in the relatively more polar solvents namely 1-octanol and methyl isobutyl ketone (MIBK) provide compelling and direct evidence regarding the stoichiometry of the organometallic species generated in these media. Un-

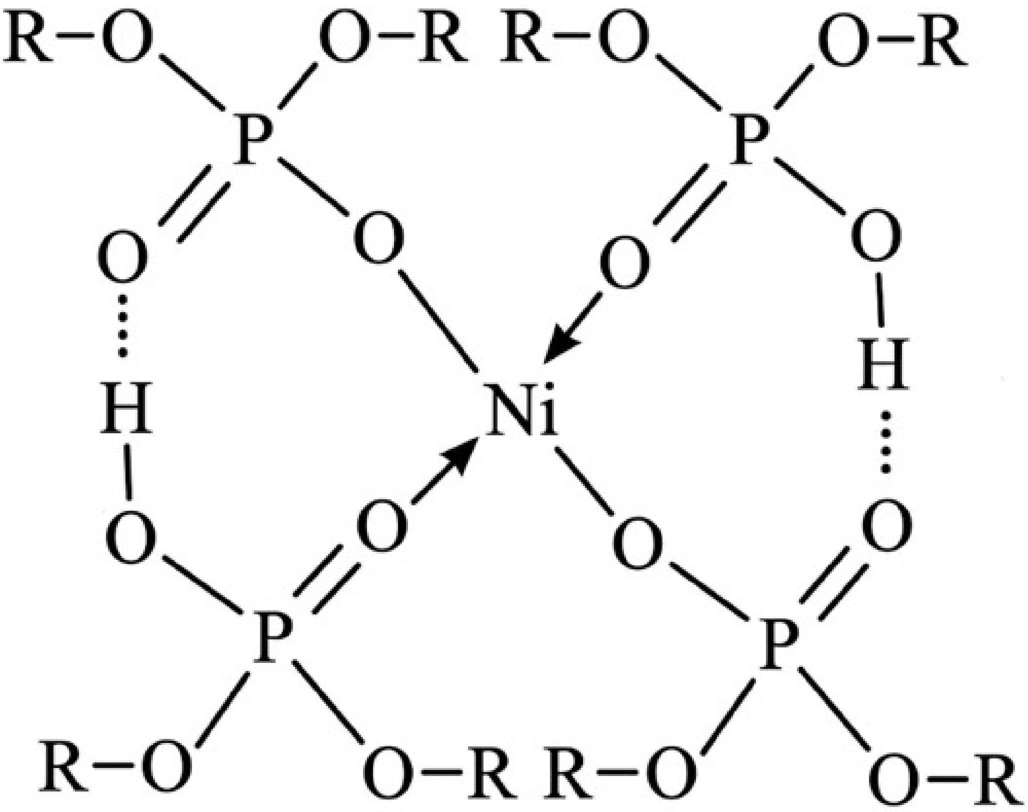


Fig. 6. Structure of the $NiL_2 \cdot 2HL$ complex (R=C8H17).

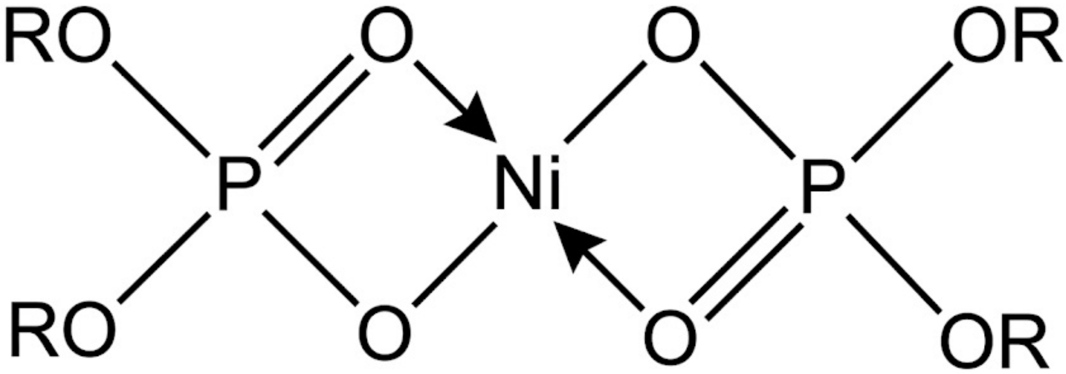


Fig. 7. Structure of the NiL_2 complex (R=C8H17).

like less polar diluents, these solvents create a distinct solvation environment that enhances the clarity and resolution of the observed spectral features, allowing for unambiguous interpretation of the complex species present.

The spectra display well-defined absorption bands whose wavelengths and relative intensities are characteristic of the ligand-field interactions surrounding the Ni(II) center. These spectral patterns, including the positions of the d–d transition bands and their intensity ratios, align with expectations for a complex containing two deprotonated extractant ligands and two neutral Di(2-ethylhexyl) phosphoric acid molecules. Consequently, the spectral signatures provide strong confirmation of the formation of the $NiL_2 \cdot 2HL$ species in the organic phase.

Furthermore, the behavior observed in 1-octanol and MIBK underscores the important role of solvent polarity in stabilizing the extracted nickel complex. The enhanced solvation afforded by these solvents likely supports the organization of the mixed-ligand cluster and helps preserve its geometry, thereby yielding well-resolved electronic transitions. The precise locations of the absorbance maxima thus serve as diagnostic markers for the coordination environment, revealing valuable information about the structure, bonding interactions, and overall electronic configuration of the Ni–D2EHPA complex under the extraction conditions employed.

Fig. 5 displays the electronic absorption spectra of the Ni(II)–Di(2-ethylhexyl) phosphoric acid complexes formed in polar solvents, showing transitions characteristic of an octahedral ligand-field environment. The assignment of an octahedral geometry is supported by both the energy and splitting patterns of the observed bands, which align with the typical spectral behaviour of d^8 ions such as Ni(II). Correspondingly, Table 5 lists the wavelengths of the dominant absorption maxima for the complexes in each solvent. These values are consistent with previously reported data [29,30], confirming that the octahedral configuration of the Ni(II)–Di(2-ethylhexyl) phosphoric acid complexes is preserved regardless of the diluent employed.

5. Limitations

Although this study successfully demonstrates the efficiency of Di(2-ethylhexyl) phosphoric acid in extracting Ni(II) using various diluents, certain limitations should be acknowledged. First, the experiments were conducted using synthetic aqueous solutions, which, while useful for establishing fundamental mechanisms, do not fully replicate the complexity of real industrial effluents that may contain competitive interfering ions. Second, the extraction process was performed in batch mode on a laboratory scale; therefore, continuous counter-current extraction tests are necessary to fully evaluate the industrial feasibility. Finally, a detailed economic analysis regarding solvent recovery and long-term reusability was outside the scope of this work and warrants future investigation.

6. Conclusion

This study provides an in-depth and systematic evaluation of the extraction behaviour of Ni(II) from a sulfate medium using Di(2-ethylhexyl) phosphoric acid as the organic extractant. Through a detailed investigation of the effects of aqueous-phase pH, extractant concentration, and the choice of diluent, the work offers a clearer understanding of the parameters that dictate both the efficiency and selectivity of the solvent-extraction process. The findings have implications not only for fundamental coordination and extraction chemistry but also for the optimization of industrial operations where reliable metal recovery is required.

Among the variables examined, the pH of the aqueous phase emerged as a particularly critical factor. As the pH increased, progressive deprotonation of Di(2-ethylhexyl) phosphoric acid occurred, enhancing its capacity to interact with and bind Ni(II) ions. This shift in acid–base equilibrium drives the formation of increasingly stable nickel–extractant complexes. The linear correlation between Log D and pH obtained in all systems reinforces the conclusion that precise control of solution acidity is indispensable for maximizing extraction efficiency. Even small deviations in pH meaningfully influence the equilibrium position and, consequently, the extent of metal transfer into the organic phase.

The concentration of Di(2-ethylhexyl) phosphoric acid in the organic phase also played a decisive role in determining the level of Ni(II) extracted. Increasing the amount of extractant expands the pool of active species available to participate in complex formation, thereby promoting higher extraction yields. This enhancement was especially noticeable under conditions where Di(2-ethylhexyl) phosphoric acid predominantly existed in its monomeric form, as monomeric species typically exhibit the greatest affinity for metal ions and therefore drive the formation of the most stable complexes. The observed dependence of extraction efficiency on extractant concentration underscores the need for appropriately selecting and optimizing extractant dosage in both laboratory studies and industrial solvent-extraction circuits.

Slope analysis clearly demonstrated that the nature and composition of the nickel species extracted into the organic phase depend strongly on the solvent employed. In relatively polar diluents such as 1-octanol and methyl isobutyl ketone (MIBK), the data indicated the formation of a simpler coordination entity with a stoichiometry corresponding to NiL_2. This structure suggests that the enhanced solvation capacity of these media stabilizes the deprotonated extractant ligands sufficiently to support the formation of a more compact complex without the need for additional protonated extractant molecules.

In contrast, extractions performed in less polar solvents such as toluene, dichloromethane, chloroform, carbon-tetrachloride, and cyclohexane resulted in the stabilization of a more aggregated species, identified as $NiL_2{\cdot}2HL$. The presence of both deprotonated (L^-) and protonated (HL) extractant molecules within this complex points to the importance of extractant aggregation and hydrogen-bonding networks under low-polarity conditions. These findings underscore the decisive role of solvent polarity in modulating Di(2-ethylhexyl) phosphoric acid association behavior and consequently dictating the structural form of the nickel complex transferred to the organic phase.

The comparative extraction efficiencies of the solvents investigated followed the decreasing sequence:

1-octanol > cyclohexane > MIBK > carbon-tetrachloride > dichloromethane > chloroform > toluene

This ordering reflects the contrasting abilities of the solvents to solvate and stabilize the Ni–Di(2-ethylhexyl) phosphoric acid species. Polar solvents such as 1-octanol exhibited superior performance due to their capacity to support the formation and solubilization of the nickel complex, leading to enhanced extraction yields. Conversely, nonpolar solvents typically displayed weaker or more fluctuating extraction efficiencies, likely due to reduced stabilization of the complex or differences in extractant aggregation.

The visible absorption spectra obtained during the extraction process further reinforced these interpretations. Solvent-dependent shifts in band positions and intensities revealed variations in ligand-field strength and electronic transitions associated with each complex. These spectral features serve as direct evidence of differences in complex geometry, stability, and coordination environment, providing strong support for the solvent-dependent structures identified through slope analysis.

The practical implications of these findings are significant. Sectors requiring high-purity nickel such as electronics, catalysis, and advanced alloy production can benefit from the optimized extraction conditions identified in this work. The extraction constants summarized in Table 3 provide a useful guide for selecting efficient and environmentally favorable solvent systems. Such optimization contributes to cleaner production pathways and supports more sustainable nickel recovery processes.

In summary, this study deepens the understanding of Ni(II) extraction using Di(2-ethylhexyl) phosphoric acid by clarifying the roles of pH, extractant concentration, solvent characteristics, and complex stoichiometry. The insights gained offer a strong foundation for developing more efficient, economical, and environmentally responsible extraction strategies for industrial applications.

Availability of Data and Materials

The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

Author Contributions

Conceptualization and methodology were designed by FG and DB; Experimental work was carried out by FG, AK and NM; Data analysis and interpretation were performed by FG and AC; The original draft was written by FG; Review and editing were conducted by DB and AC. All authors have read and agreed to the published version of the manuscript. All authors have participated sufficiently in the work and agreed to be accountable for all aspects of the work.

Ethics Approval and Consent to Participate

Not applicable.

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Conflicts of Interest

The authors declare no conflicts of interest.

Declaration of AI and AI-Assisted Technologies in the Writing Process

During the preparation of this work, the authors used Grammarly, DeepL Translator, and ChatGPT (OpenAI) to improve the readability and language quality of the manuscript. After using these tools, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

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