

Extraction And Thermodynamic Study Of Cobalt From Aqueous Solutions By Using Of New Organic Reagent 5-[(3,4,5-Trimethoxyphenyl) Methyl]Pyrimidine-2,4-Diamineazo]-1-N-(4-Hydroxyphenyl) Acetamide

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Abstract

The extraction of Co²⁺ ions from the aqueous phase by new laboratory prepared azo derivation as complex agent accordingly, 5-[(3,4,5-trimethoxyphenyl)methyl]pyrimidine-2,4-diamineazo]-1-N-(4-hydroxyphenyl)acetamide reagent (L) has displayed adequate conditions for this extracting process under pH=9, and shaking time of 10 minutes and 30 µg concentration of Co²⁺ ion. The investigation of organic solvent's influence has shown no linear relation between the distribution ratio for the extraction of Co²⁺ ion and dielectric constant (ε) of most used organic solvents. Nevertheless, there was an influence on the organic solvent structure in extracting Co²⁺ ion and distribution ratio (D) values. Stoichiometric studies have clarified the most potential structure of the ion-pair complex extracted for Co²⁺ with a 1:1 ratio. The complexation reaction and the extraction thermodynamic both were in the exothermic phase. Using the electrolyte was given a perfect enhancement in extraction efficiency with higher extraction efficiency charge as a function of the ionic diameter of electrolyte cation for the smallest ionic diameter. Based on the study of the interference effect, all cations have shown an apparent interference with Co²⁺. Still, in different levels of affinity, with the organic reagent L solvent extraction as a sensitive and selective method was used for spectrophotometric determination of Co²⁺ in miscellaneous samples. The digestion of the samples was based on the dry digestion method. The prepared calibration curve at λ_{max}= 523 nm has been used for determining the concentrations of Co²⁺ in different samples.

Keywords: Cobalt(II), Solvent extraction, concentration, organic solvent's, distribution ratio

1. Introduction

In the previous studies, azo compounds and its derivatives have been extensively used as extracting agents of transition elements with the spectrophotometric determination of the same (1). The hydrometallurgical extraction of Co^{+2} from wastewater can be achieved with the application of an acidic extractant (Cyanex272) with two ionic liquids (Cyphos IL 101 or 104) (2). The separation of Co^{+2} is carried out from synthetic aqueous solutions of Cl^{-1} and SO_4^{-2} , and a real wastewater sample of SO_4 solution, including Ni^{2+} (3,4). The extractants (Cu^{+2} and Hg^{+2}) were investigated both as synergic mixtures and as single carriers with no positive synergistic effect (5-11). The novelty of this work is the styling of hydrometallurgical extraction of Co^{+2} from real SO_4 wastewater in the existence of Ni^{+2} , which permits the sustainable processing of wastewater, the recovery of the critical Ni^{2+} element, and the regeneration of the organic chemicals consumed during the extraction process (12). The solvent extraction of Co^{+2} from an SO_4^{2-} medium with N-(2-hydroxy-benzylidene)aniline is associated with two synergistic agents, Agent 1-octanol and Agent methyl isobutyl ketone. Antagonistic with the synergistic effects, it was observed that for the target metal in a mixture of 1-octanol with chloroform and methyl isobutyl ketone (MIBK) at elevated and low concentration ratios of the synergistic agents.

The synergistic extraction of Co^{+2} with the mixtures was compatible with slope analysis (13-16). The new ligand 1-2-pyridylazo 2-naphthol was used as a tricky agent for the extraction and the spectrophotometric determination of the metals in the samples, including soil, plants, human blood serum, and water (17-23). Firstly, effecting factors (pH_{ex} , the concentration of the Cu^{2+} and the mixing time) on extraction, and the results were inspected under $\text{pH}_{\text{ex}} = 9$, the concentration of the Cu^{2+} was $8 \mu\text{g/mL}$, and the mixing time was 15 minutes (24).

The stoichiometry study (Slope analysis method, Mole ratio method, Continuous Variation Method) demonstrated that the complex structure was with [1:1] [Cu^{2+} : BTADPI]. The organic solvent effect has shown no linear relation between (ϵ) for the used organic solvent (D). Thermodynamically, that indicated the reaction was endothermic, with $\Delta G_{\text{ex}} = -54.20 \text{ KJ} \cdot \text{mole}^{-1}$, $\Delta H_{\text{ex}} = 0.0131 \text{ KJ} \cdot \text{mole}^{-1}$, $\Delta S_{\text{ex}} = 167.84 \text{ J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$ (20).

2. Materials and Methods

2.1. Apparatus

A Shimadzu double beam UV-Vis Spectrophotometer 1800 was employed at the range of wavelength from 250 to 1100 nm. The melting point was determined with a Stuart Scientific COLTD, FT-IR 8400 Shimadzu.

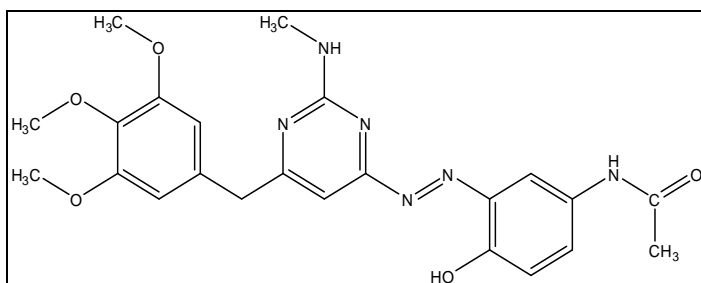
2.2. Reagents

All chemical reagents were taken from commercial sources with analytical grade. A stock solution of Co^{2+} 1 mg/mL was prepared by the dissolution of 0.4780 g of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ in 98 mL of distilled water and 2 mL of 1 M H_2SO_4 . A solution of $1 \cdot 10^{-2}$ M of 5-[(3,4,5-trimethoxy phenyl) methyl] pyrimidine-2,4-diamineazo]-1-N-(4-hydroxy phenyl) acetamide was prepared by dissolved 0.466 g in chloroform, and a 0.5% solution of 1-Nitroso-2-Naphthol was with glacial acetic acid (25).

2.3. Synthesis of the organic reagents

The organic reagents were primed based on the reported procedure (26-29) by dissolving (2.9 g, 0.01 mole) of 5-[(3,4,5-trimethoxyphenyl)methyl]pyrimidine-2,4-diamine in a solution of 4 mL of 37% HCl and 25 mL reagent water type IV. About 0.7 g of sodium nitrite was dissolved in 10 mL of reagent water type IV. The sodium nitrite was added to the above mixture while keeping the temperature at 0 °C.

The mixture was set aside for 15 minutes for a full diazotization reaction. A diazonium solution was added, drop by drop, into a 1.54g (0.01 mole) solution of N-(4-hydroxyphenyl)acetamide, and 1.2 g of sodium hydroxide was dissolved in 150 mL ethyl alcohol; the temperature was kept constant at 0 °C. After, the content remained undisturbed for 2 hours. Then, 150 mL of cooled reagent water type IV was added, the pH of the solution adjusted to 6 with an HCl solution. The reaction product was a brown powder that was formed after leaving it to rest for 24 hours. The brown precipitate was filtered, washed with cold reagent water type IV, doubly crystallized from absolute hot ethanol, and dried over CaCl₂. The synthesized azo reagent was analyzed by UV–Vis and FTIR. Table 1 exhibits the structure of the prepared azo ligand.



Scheme 1: structure of organic reagent 5-[(3,4,5-trimethoxyphenyl)methyl]pyrimidine-2,4-diamineazo-1-N-(4-hydroxy phenyl) acetamide [L].

Table 1. Spectral data of the organic reagent

a\ UV-Visible spectral peaks (nm)	
peaks(nm)	Assignments
246	π - π^* very small sensitive absorption.
296	π - π^* middle sensitive absorption.
426	n - π^* visible region high sensitive absorption
b\ FT.IR spectral bands (cm ⁻¹)	
Bands (cm ⁻¹)	Assignments
3398 -808	phenolic OH stretching and bending
3015	aromatic CH stretching
1483.12	for -N=N-

699.5	for rings of naphthol
1525	C=C stretching

2.4. Spectrophotometric determination of Co^{2+} extraction

About 5 mL aqueous solution contained a fixed quantity of Co^{2+} ions at the optimum condition, pH=9, shaking time=10 min, and concentration of metal $30\mu\text{g/mL}$. Then, it was added to 5 mL of the organic phase 5-[(3,4,5-trimethoxyphenyl)methyl]pyrimidine-2,4-diamine_azo]-1-N-(4-hydroxyphenyl)acetamide. At 1.10^{-2} M, mix the dual layers for the time 10 min. Afterward, the aqueous phase was separate from the organic phase, and the remaining amount of Co^{2+} ions in the aqueous phase was determined by the spectrophotometric method based on 1-Nitroso-2-Naphthol (Marezeko, 1974). After that, the quantity of Co^{2+} ions were calculated that transferred from the aqueous solution to the organic phase to form ion-pair association complex and calculate distribution ratio by application of Equation 1.

$$D = \frac{[A]_{\text{org}}}{[A]_{\text{aq}}} \quad (\text{Eq.1})$$

$[A]_{\text{org}}$ = Concentration of the species A in the organic phase, $[A]_{\text{aq}}$ = Concentration of the species A in the aqueous phase.

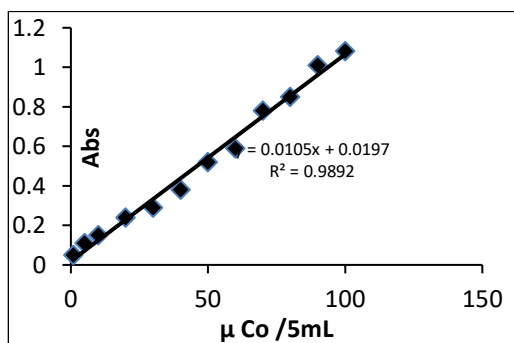


Fig. 1: Calibration curve of Co^{2+} by 1- Nitroso-2-Naphthol.

2.5. Effect of Acidic function

It was extracted $30\mu\text{g}$ of Co^{2+} in a 5 mL aqueous phase with 5 mL of 1.10^{-4} M organic reagent (5-[(3,4,5-trimethoxyphenyl) methyl] pyrimidine-2,4-diamineazo]-1-N-(4-hydroxyphenyl)acetamide. solution dissolved in chloroform under pH values from 6 to 12, of the aqueous phase (30-32). The two phases were mixed for 10 minutes and later separated. The distribution ratio (D) was computed based on the solvent extraction method and evaluated an absorbance of the organic phase depended on the contradiction of organic reagent; (32).

2.6. Effect of organic solvent

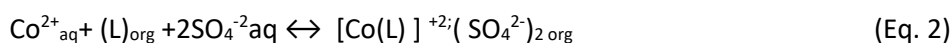
The solvent extraction method was based on the organic solvent used in the extracting method. Accordingly,

30 µg of Co²⁺ ions were extracted from 5 mL of the aqueous phase by 5 mL (1·10⁻⁴ M) organic reagent (5-[(3,4,5-trimethoxyphenyl)methyl]pyrimidine-2,4-diamine_azo]-1-N-(4-hydroxyphenyl)acetamide) dissolved in different organic solvents in dielectric constant after shaking the dual-phase for ten minutes. The organic phase was separated from the aqueous phase for determining the D-value based on the previously detailed procedure.

2.7. Effect of metal ion concentration

Co⁺² ions were extracted in various concentrations, from 1 to 60 µg/5 mL aqueous solution, then added 1.10⁻⁴ M of 5 mL from the organic reagent (5-[(3,4,5-trimethoxy phenyl) methyl]pyrimidine-2,4-diamine_azo]-1-N-(4-hydroxyphenyl)acetamide) under pH = 9. The next step was shaking the aqueous solution and organic solution for (10 min) and separating the aqueous solution and organic solution to evaluate the remainder amount of Co²⁺ ion in the aqueous phase based on the spectrophotometric determination of Co⁺² extraction.(25).

The distribution ratio (D) was computed, and the absorbance of the organic phase was determined at λ_{max}= 523 nm.



2.8. Effect of shaking time

The extraction of 30 µg of Co²⁺ ion was from the aqueous phase at pH = 9 by 5mL of (1·10⁻⁴ M) organic reagent (5-[(3,4,5-trimethoxyphenyl) methyl]pyrimidine-2,4-diamineazo]-1-N-(4-hydroxyphenyl) acetamide) by different shaking times (2-20min).

2.9. Temperature effect

The extraction of 30 µg of Co²⁺ ion was from the aqueous phase at pH = 9, with 5mL of (1·10⁻⁴ M) of organic reagent (5-[(3,4,5-trimethoxy phenyl) methyl] pyrimidine-2,4-diamineazo]-1-N-(4-hydroxyphenyl) acetamide) at different temperatures 5-35 °C after shaking for 10 minutes to calculate distribution ratio D at each temperature. The extraction constant (K_{ex}) was determined by Equation 3.

$$K_{\text{ex}} = \frac{D}{[\text{Co}^{2+}]_{\text{eq}}[\text{L}]_{\text{org}}} \quad (\text{Eq. 3})$$

2.10. Stoichiometry

Two spectrophotometric methods were used to determine the appropriate structure of the extracted complex, including slope analysis (Extracted 30 µg of Co²⁺ ions from (5 mL) aqueous solution at pH = 9 by 5 mL of organic reagent (5-[(3,4,5-trimethoxyphenyl) methyl] pyrimidine-2,4-diamine_azo]-1-N-(4-hydroxyphenyl) acetamide) at different concentrations (1.10⁻⁶ M -1.10⁻² M) of organic reagent), and slope ratio(this method stipulated performed two experiments:-

The first experiment include preparing 5mL aqueous solutions for Co²⁺ in rang (5.10⁻⁶-5.10⁻⁴ M) at pH=9, and 1.10⁻⁴M for organic reagent (5-[(3,4,5-trimethoxy phenyl)methyl]pyrimidine-2,4-diamine_azo]-1-N-(4-

hydroxyphenyl)acetamide) afterward shaken for 10min and separate the two solutions by separating funnel and measure the absorbance of organic phase at $\lambda_{\max}=523\text{nm}$

The second experiment includes preparing 5mL aqueous solutions for Co^{2+} ion at 1.10^{-4}M at $\text{pH}=9$ with 5mL of organic reagent solution at different concentrations (5.10^{-6}M - 5.10^{-4}M) after shaking each solution to 10 min. a separate aqueous solution from organic solution by separating funnel and measure absorbance at $\lambda_{\max}=523\text{nm}$. After plotting the results of each experiment, which is giving a straight line and divide the slope of the second experiment on the slope of the first experiment to get slope ratio giving attention about the stricture of ion-pair complex extracted. (33-34).

2.11. Study of electrolyte salts effect

The extraction of the Co^{2+} ion from 5 mL of an aqueous solution in the presence of 0.1 M of some electrolyte was performed by 5 mL of (1.10^{-4}M) from (5-[(3,4,5-trimethoxyphenyl) methyl]pyrimidine-2,4-diamineazo]-1-N-(4-hydroxyphenyl) acetamide) dissolved in chloroform and shaking time (10min) and formerly adopted to determine the absorbance of the organic phase and the distribution ratio.

2.12. Effect of interferences

For this study, extracted Co^{2+} at the optimum conditions (30 μg of Co^{2+} ion was from the aqueous phase at $\text{pH}=9$ by 5mL of (1.10^{-4}M) organic reagent (5-[(3,4,5-trimethoxyphenyl) methyl] pyrimidine-2,4-diamineazo]-1-N-(4-hydroxyphenyl) acetamide) and shaking time (10min). In the presence of some cations (Cu^{2+} , Ni^{2+} , Mn^{2+} , and Ag^{1+}) interferences and determined the absorbance of the organic phase and the distribution ratio D.

2.13. Spectrophotometric Determination

The solvent extraction was used as a sensitive and selective method for the spectrophotometric determination of Co^{2+} in different samples (35-41). The sample was digested based on the dry digestion method. It was taken 4.0mL of sample solution and add 5mL of $1 \times 10^{-4}\text{M}$ organic reagent dissolved in chloroform at $\text{pH}=9$ condition afterward after shaking for 10 min and measure the absorbance of the organic phase at $\lambda_{\max}=523\text{nm}$ (Almi, 2020). A calibration curve was prepared at $\lambda_{\max}=523\text{nm}$, and it was employed in the determination of the concentration of Co^{2+} in different samples.

3. Results and Discussion

3.1. Absorption at the UV–Vis and FTIR spectrum

The UV–Vis spectrum absorption in Figure 4 explains the highest absorption for the extracted ion-pair complex at $\lambda_{\max}=523\text{nm}$. The UV-Vis spectra of the ion-pair complex investigated displays mainly three peaks observed in ethanol within the range of 200 to 1100 nm. The first and second peaks at 246 nm were assigned to the moderate energy ($\pi \rightarrow \pi^*$) transition of the heterogeneous aromatic ring. The other peak at 296 nm was assigned to the two benzene rings. The third broad peak belonged to the extracted ion-pair complex at 523 nm.

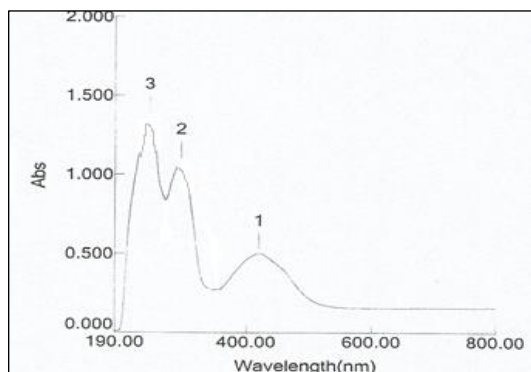


Fig.2: UV-Vis spectrum of organic reagent [L]

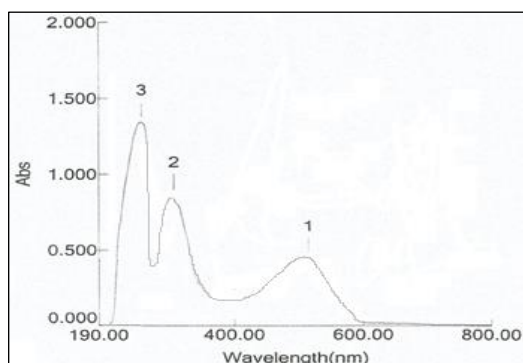


Fig.3: UV-Vis spectrum to show absorption for ion-pair complex

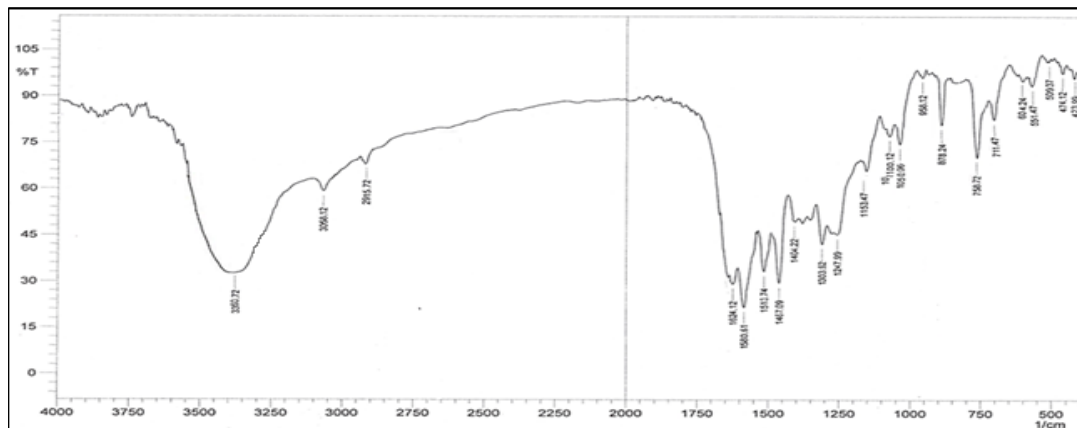


Fig. 4:FT-IR spectrum to show absorption for ion-pair complex

3.2. Effect of acidic function

The results were explained in Figures 5 and 6. The results demonstrate that optimal pH for the extraction of Co^{2+} ions was pH = 9. Efficiency at this pH and lower was appropriate for reaching favorable thermodynamic equilibrium for extracting. The decrease in the pH value contributed to a rise in the Co^{2+} hydration shell and caused the protonated agent complex to rise marginally with a decrease in the complexation value. On the other hand, when the pH value was higher than 9, which initiates a reduced extraction efficiency (34).

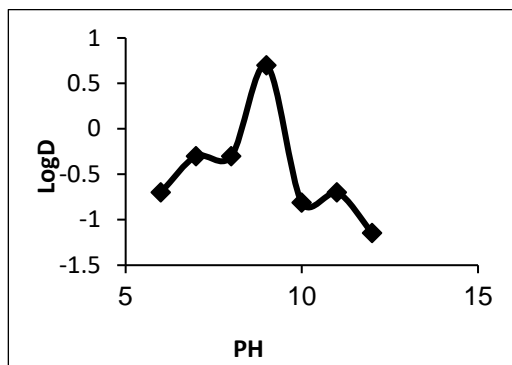


Fig. 5: $D=f(pH)$

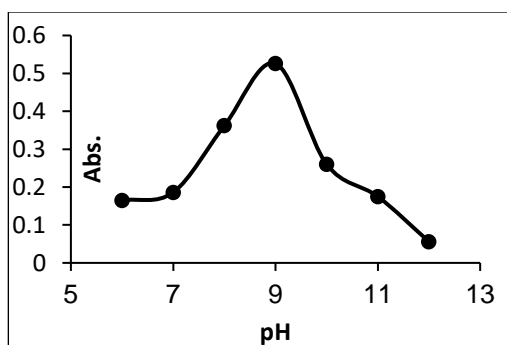


Fig. 6: Effect of pH on complex formation as extraction

3.3. Effect of metal ion concentration

The results were depicted in Figures 7 and 8, which demonstrate a linear relation between extraction efficiency with the increasing metal ion concentration because of the increased rate of forwarding direction of thermodynamic equilibrium for formed ion pair species to reach maximum rate at 30 $\mu\text{g/mL}$. Any concentration of Co^{2+} ion more than the optimum value would lead to a decrease in the extraction efficiency to increase the backward direction of thermodynamic equilibrium according to the mass-action law effect.

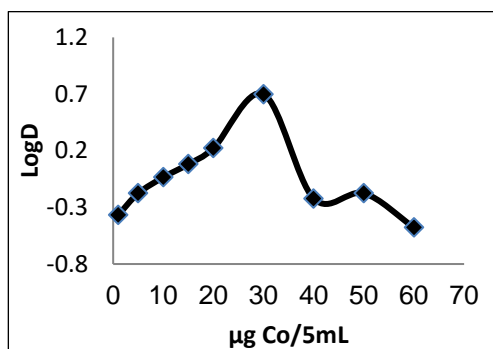


Fig. 7: The outcome of Co^{2+} concentration based on the activity of extraction and D value

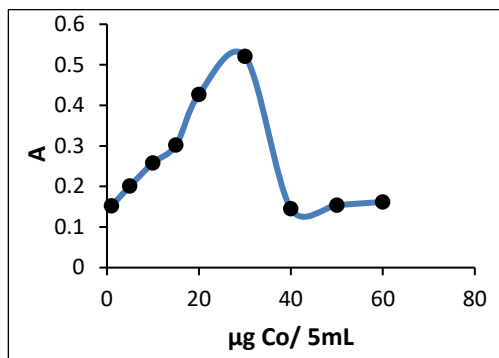


Fig. 8: The outcome of Co^{2+} concentration based on thermodynamic equilibrium designed for complex formation and extraction

3.4. Effect of shakingtime

The consequences of this investigation were depicted in Figures 9 and 10. It indicates that 10 minutes was the best shaking period for the two layers, and it achieved the extraction equilibria with the highest distribution ratio value (D).

The optimum shaking time was 10 min to reach the best thermodynamic equilibrium and higher extraction efficiency. Any shaking time less than optimum value might not be appropriate to reach the favorable thermodynamic equilibrium.

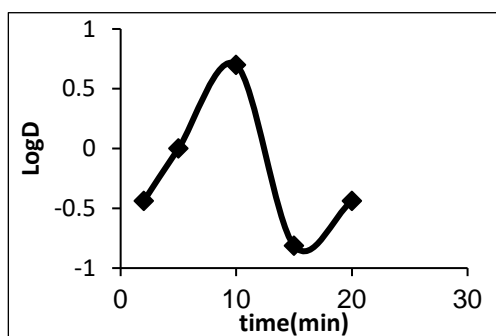


Fig. 9: $D=f(\text{shaking times})$

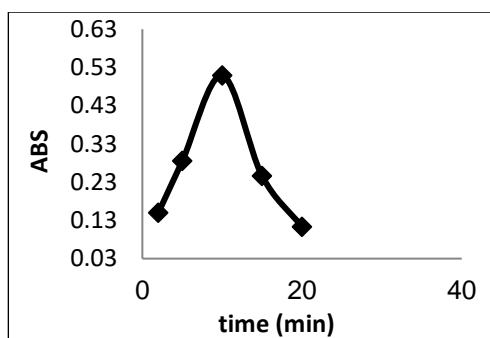


Fig.10: shaking time influence on complex formation and extraction

3.5. Effect of organic solvent

The organic solvent did not show any linear relationship between the distribution ratio and the dielectric constant of the organic solution. Namely, there was no influence on the polarity of organic solvent on extraction activity, but there was an influence on organic solvent structure. This result did reveal the participated organic solvent in complex formation. Thermodynamic parameters for extracting purposes in different organic solvents involved transfer free energy ΔG_t , association constant k_A , constant extraction k_{ex} , and free energy of extraction ΔG_{ex} based on the applied relation.

In Table 2, the consequences depicted free energy of transition ΔG_t for Co^{2+} ions from the aqueous phase with organic phase intensification with a dielectric constant of organic solvents lessening with the increased approach between the cation and anion association complex extraction that contacts ion pair or loses ion pair. However, k_{ex} and ΔG_{ex} were shown a vast value utilizing Chloroform organic solvent that exhibited sharing organic solvent and increased stability of the extracted ion-pair complex.

Table 2: Organic solvent effect on the extraction of Co^{2+} ions and ΔG_t , k_A , k_{ex} , ΔG_{ex}

Organic Solvents	ϵ	Abs. at $\lambda_{max}=523$	D	%E	$-\Delta G_t$	$K_A \times 10^4$	$K_{ex} \times 10^8$	$-\Delta G_{ex}$
Nitro benzene	35.740	0.164	2.000	83.000	0.025	3.502	22.72	43.880
Dichloro methane	9.0800	0.144	1.500	60.000	0.350	4.670	1.136	41.900
Chlorobenzene	5.708	0.129	0.660	40.000	0.708	5.830	0.750	41.000
Bromo benzene	5.400	0.157	0.740	43.300	0.75	5.380	0.860	41.000
Chloroform	4.806	0.520	5.000	83.330	0.326	10.800	129.619	57.830
Benzene	2.804	0.160	1.720	63.330	1.49	3.680	19.620	43.150
Carbone tetrachloride	2.380	0.422	4.000	80.000	1.7	2.910	45.450	45.050

3.6. Stoichiometry

The results were depicted in Figures 11, 12 and 13. All the applied methods in this study indicated that the more probable structure of the extracted complex was with a 1:1 ratio ($Co(II):L$).

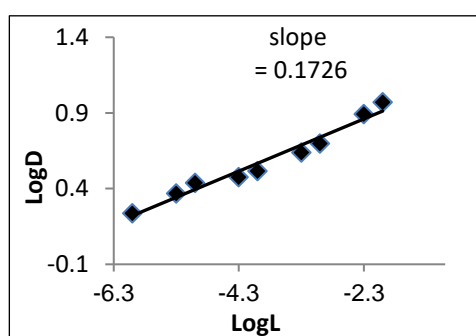


Fig.11: Slope analysis method

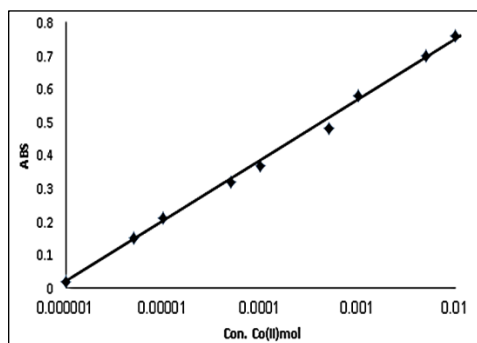


Fig.12: The slope ratio method change organic reagent concentration

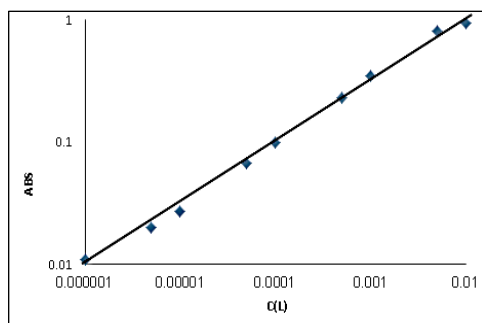


Fig.13: The slope ratio method change metal ion concentration

3.7. Temperature effect

The results regarding the investigation of the temperature effect were represented in Figures 14 and 15.

The thermodynamic data of extraction Co^{2+} ions were $\Delta H_{\text{ex}} = -0.0155 \text{ kJ.mol}^{-1}$, $\Delta G_{\text{ex}} = -43.87 \text{ kJ.mol}^{-1}$ and $\Delta S_{\text{ex}} = 116.9 \text{ J.k}^{-1}.\text{mol}^{-1}$.

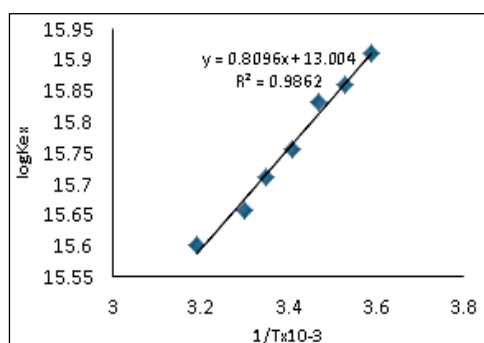


Fig. 14: K_{ex}=f(T°K)

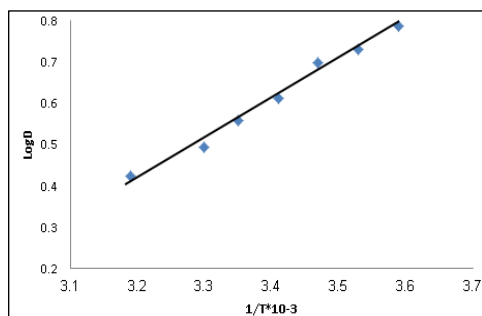


Fig.15: $D=F(T^{\circ}K)$

3.8. Study of electrolyte salts Effect

The consequences indicated that each used electrolyte was given an enhancement in extraction efficiency. It led to a rising in the extraction efficiency charge of a function for the ionic diameter of electrolyte cation for the smallest ionic diameter. The highest extraction efficiency has occurred as withdrawing more water molecules for its hydration shell and destroyed the hydration shell of Co^{2+} , where Li^{+} gave the highest rising extraction. The other larger cation was given less rising extraction. The consequences have illustrated in Table 3.

Table 3: Effect of electrolyte salts on extraction efficiency of Co^{2+}

Electrolyte Salts	Absorbance at $\lambda=523$ nm	D
LiCl	0.436	20.10 0
NaCl	0.385	19.46 0
KCl	0.321	18.50 0
NH_4Cl	0.203	10.20 0
MgCl_2	0.282	18.90 0
CaCl_2	0.276	15.60 0
SrCl_2	0.205	11.20 0

3.9. Effect of interferences

The consequences of interferences were described in Table 4. The results showed that all cations were given interference with Co^{2+} , but in different affinity levels with the organic reagent L. The presence of interferences belongs to a behavior and nature metal cation under diverse optimum conditions for complex formation (36).

Table 4: Interference effect on extraction efficiency

Interferences	D
CuCl_2	0.35
NiCl_2	2.32
MnCl_2	4.10
AgNO_3	3.00

3.10. Spectrophotometric results

The application and the accumulated quantity of Co^{2+} in different samples were depicted in Table 5.

Table 5: Accumulated quantity of Co^{2+} in different samples

The samples	ppm Co^{2+}
Chicken liver	0.520
Cow meat(Beef)	0.090
The white meat of Chicken	0.100
Tap-Water	0.796
Sea-Water	0.781

4. Conclusion

Using a new organic reagent, 5-[(3,4,5-trimethoxyphenyl)methyl]pyrimidine-2,4-diamine zo]-1-N-(4-hydroxyphenyl)acetamide in the study of extraction and thermodynamic investigation of cobalt ion from an aqueous solution has fulfilled successfully. The optimum conditions for this extraction method were obtained at pH = 9, 10 minutes of shaking time, and the concentration of Co^{2+} ion in the aqueous phase was 30 $\mu\text{g/mL}$. Stoichiometric studies demonstrated that the more probable structure of ion-pair complex extracted for Co^{2+} was with a 1:1 ratio. The results indicated no linear relation between the distribution ratio for the extraction of Co^{2+} ions and the dielectric constant for the adopted organic solvents. However, there was an influence on the organic solvent structure in extracting Co^{2+} ions and the distribution ratio value (D). The complexation reaction and the extraction thermodynamic presented an exothermic behavior. The employed electrolyte enhanced the extraction efficiency with higher extraction efficiency in charge of a function for the ionic diameter of electrolyte cation for the smallest ionic diameter. Based on the study of the interference effect, all cations interfered with the Co^{2+} , but with different levels of affinity with the organic reagent L5-[(3,4,5-trimethoxy_

phenyl)methyl]pyrimidine-2,4-diamineazo]-1-N-(4-hydroxyphenyl)acetamide.

5. Acknowledgment

I would like to state my sincere gratitude to the Department of Pharmaceutical Chemistry, College of Pharmacy, University of Kufa, and College of Science, Kufa University in Iraq for funding this work.

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