

Extraction of mercuric ions Hg(II) from aqueous solutions by using

2-[4-carboxy methyl phenyl azo]-4,5-diphenyl imidazole

استخلاص الزئبق (II) من المحاليل المائية باستخدام الكاشف ٢-[٤-كاربوكسي مثيل فنيل آزو]-٤,٥-ثنائي فنيل إيميدازول

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Abstract:

The extraction of mercuric ions Hg^{2+} from aqueous media with ligand 2-[4-carboxy methyl phenyl azo]-4,5-diphenyl imidazole (4-CMePADI) dissolved in benzene studied. This study showed that the was optimum pH_{ex} of Hg^{2+} was (6) and the optimum quantity of Hg^{2+} ions in aqueous phase was 30 μg and the best shaking time needed to extraction was 15 minutes. The stoichiometric studies showed that by using slope analysis method, mole ratio method and continuous variation method, the structure of ion pair complex extracted was a sandwich structure (Metal : Ligand) (M : L) 1 : 2 $[Hg(4-CMePADI)_2]^{2+}(NO_3^-)_2$. There is no any linear relation for dielectric constant of organic solvent with distribution ratio. There is an effect for Solvent structure on the extraction method as well as salting out effect on the extraction by use lithium chloride, synergistic effect appear there is a participate of one molecule of tributyl phosphate (TBP) in ion pair complex extracted with structure $[Hg(4-CMePADI)_2(TBP)]^{2+}(NO_3^-)_2$, as well as the extraction method was exothermic reaction.

الخلاصة

استخلاص ايونات الزئبق Hg^{2+} من الأوساط المائية بواسطة الكاشف (4-CMePADI) المذاب في البنزين أظهرت أن القيمة المثلى للدالة الحامضية للاستخلاص pH_{ex} لاستخلاص أيونات الزئبق Hg^{2+} كانت (6) وأن قيمة التركيز الأمثل لأيونات الزئبق Hg^{2+} في الطور المائي كان 30 μg (2.99 $\times 10^{-5}$ M) وقد بينت الدراسة أيضاً أن الزمن الأمثل لرج الطورين المائي الحاوي على أيونات الزئبق Hg^{2+} والعضوي الحاوي على الكاشف (4-CMePADI) كان (15 دقيقة). وفي مجال دراسة التركيب المحتمل لمعقد الترابط الأيوني المستخلص إلى الطور العضوي فقد أظهرت أن لمعقد الترابط الأيوني المستخلص لأيونات الزئبق Hg^{2+} مع الكاشف (4-CMePADI) كان له تركيب ساندويج (metal: ligand) (1: 2) حسب الصيغة

$[Hg(4-CMePADI)_2]^{2+}(NO_3^-)_2$ ، أما في مجال دراسة تأثير المذيب العضوي على عملية الاستخلاص فقد أظهرت الدراسة بأنه لا توجد علاقة خطية بين ثابت العزل الكهربائي للمذيب العضوي وقيم نسب التوزيع لعمليات الاستخلاص في المذيبات المختلفة ذلك يعني عدم وجود تأثير لقطبية المذيب العضوي على عمليات الاستخلاص إلا أن الدراسة قد أشارت إلى وجود تأثير ملحوظ لتركيب المذيب العضوي على عمليات الاستخلاص مما أعطى نتائج متميزة بالاستخلاص مع مذيب الكلوروفورم $CHCl_3$ كما أن دراسة Synergism أشارت إلى مشاركة جزيئة واحدة من (TBP) في معقد الترابط الأيوني المستخلص $[Hg(4-CMePADI)_2(TBP)]^{2+}(NO_3^-)_2$ كما أشارت الدراسة الترموديناميكية بان التفاعل للتعقيد كان باعث للحرارة Exothermic.

1. Introduction:

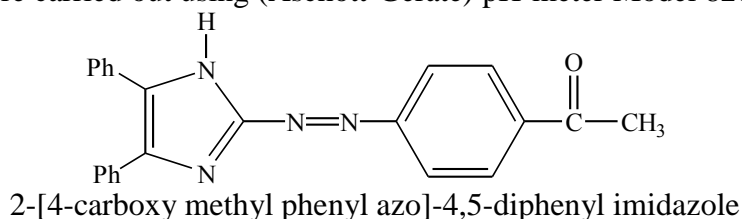
In recent years chemists have shown a growing concern in studying the complexes formed by imidazole and other related ligands as these are common components of some important biological molecules [1, 2, 3].

However, one of the major interesting application is their possible use as metal extracting

agents. In this regard, Argoud *et al* (1979) [4] used 2-aminobenzimidazole and other derivatives as complexing agents in the purification of water from heavy metals. Lenarcik *et al* (1990) used benzimidazole, 2-aminobenzimidazole and 2-methylbenzimidazole for study the stability and extractability of Co(II), Ni(II), and Cu(II) ions [5]. Garnovskii *et al* (1999) [6] studied complexes of transition metal with substituted 2-aminobenzimidazole derivatives. Mohamed *et al* (2001) [7] studied the complexes of Zn(II) and Cd(II) ions with 2-(2-benzimidazolyl azo)-4-acetamidophenol. Xuezhony *et al* (1998) [8] synthesized 2-[2-(5-methyl benzoThiazolyl)azo]-5-demethyl aminobenzoic acid and studied its application for spectrophotometric determination of nickel. Beniamin *et al* (2003) [9] studied the comparison of the extraction process of Zn(II) and Ni(II) complexes by use of 1-octylimidazole and 1-octyl-2-methylimidazole. Ibtehaj (2005) [10] used 2-[4-carboxy methyl phenyl azo]-4,5-diphenyl imidazole (4-CMePADI) for extraction of Cu(II) and Ag(I) ions according to solvent extraction method. Zainab (2005) [11] used 2-[4-chloro-2-methoxy phenyl azo]-4,5-diphenyl imidazole (4-CIMePADI) for extraction of Zn(II), Cd(II), Hg(II) ions as ion association complex according to solvent extraction method. Alaa (2006) [12] used 2-(α -Naphthylazo)-4,5-diphenyl imidazole (α -NADI) for extraction of Cu(II) and Ag(I) ions.

2. Experimental:

All reagents and solvents were obtained from commercial sources and used as received. The ligand (4-CMePADI) synthesis as in the thesis [10]. Spectrophotometric measurements were made using a single beam UV-Visible spectrophotometer (Shimadzu UV-100-02) and double beam UV-1700 UV-Visible spectrophotometer Shimadzu. pH measurements were carried out using (Aschott-Gerate) pH-meter Model 820.



2.1. Preparation of solution:

The stock solution of Hg^{2+} ions (1 mg/ml) prepared by dissolved 1.3 gm of mercuric nitrate $Hg(NO_3)_2$ in distilled water contain 1 ml of concentration nitric acid HNO_3 and diluted this solution to 1 Liter in volumetric flask by distilled water. A working standard solutions prepared by dilution with distilled water, needful prepared 10% acetic acid for determination of Hg^{2+} ions by dissolved 10 ml of acetic acid in distilled water by using 100 ml volumetric flask, as well as prepared 2 M Hydrochloric acid HCl for determination of Hg^{2+} ions. Dithizone standard solution (1×10^{-2} M) prepared by dissolved (0.05232 gm) in 10 ml CCl_4 , and working solution (1×10^{-4} M) prepared by dilution with CCl_4 solvent. For extraction experiments prepared stock solution of ligand (4-CMePADI) (1×10^{-2} M) by dissolved (0.3885 gm) from this ligand in (100 ml) of benzene, but another concentration of ligand solutions prepared by dilution with benzene.

2.2. General Procedure:

for extraction experiments have to take (5 ml) of aqueous phase contain exact quantity of Hg^{2+} ions at optimum pH, and then adding (5 ml) of organic phase contain exact concentration of ligand in organic solvent, afterward shaking the two phases at optimum time, after complete the shaking time separate the two layers and determine the Hg^{2+} ions remainder in aqueous phase by spectrophotometric method [13], for (5 ml) aqueous phase

add (0.2 ml) of 2 M HCl and then shaking with five portions of (1×10^{-4} M) dithizone solution every portion equal to (1 ml) until the last portion do not change their green color, afterward collect the portions in (5 ml) volumetric flask and then shaking with (5 ml) of dilute ammonia solution (2 drops of concentrated ammonia solution in 25 ml distilled water) to separated unreacted dithizone, and then shaking the solution with 10% acetic acid, after that determine the absorption of solution at $\lambda = 485$ nm. by use CCl_4 as blank, from absorbance and calibration curve Figure (1) can be determine the quantity of Hg^{2+} ions remainder in aqueous phase, but for determination the quantity of Hg^{2+} ions in organic phase as a complex with the ligand (4-CMePADI), by stripping method which is include shaking the organic phase three times with nearly concentrated hydrochloric acid HCl for dissociation the Hg – complex and transfer the Hg^{2+} ions to the aqueous phase and then determine the quantity of Hg^{2+} ions by spectrophotometric method, previous method, afterward divide the quantity of Hg^{2+} ions in organic phase on the quantity of Hg^{2+} ions in aqueous phase to determined distribution ratio (D). But when determine Hg^{2+} ions in aqueous phase and calculate the difference between overall quantity of Hg^{2+} ions in aqueous phase and the remainder Hg^{2+} ions to determine the quantity of Hg^{2+} ions in organic phase was found equal to quantity determined by stripping method.

3. Results and Discussion:

Study the optimum conditions for the complexation reaction. The reaction between the ligand (4-CMePADI) and Hg^{2+} ions to produce the ion pair complex $[\text{Hg}(4\text{-CMePADI})_n]^{2+}(\text{NO}_3^-)_2$ have to extracted to the organic phase, this complexation reaction of necessity behave among many optimum conditions to reach equilibria and giving stable ion pair complex.

3.1. Effect of pH:

Extracted 30 μg Hg^{2+} (9.99×10^{-5} M) in 5 ml aqueous phase with 5 ml of (1×10^{-4} M) ligand solution (4-CMePADI) dissolved in benzene at different pH of aqueous phase (5 – 10) and shaken the two phases for (10 minutes) after that separate the two phases and determination of distribution ratio (D) as in the previous method, as well as the percentage of extraction (E). the results in Table (1) and the Figure (2) demonstrate that the optimum pH for extraction was (pH = 6). In acidic media the ligand molecule protonated and then can not extracte the metal ion from aqueous solution. In basic solution given ion pair complexes contain (OH) as anion and this ion pair complex is more soluble in water and then dominate the dissociation on the extraction method.

Table (1): The effect of pH on the extraction of Hg^{2+} ions

pH	5	6	7	8	9	10
D	7.6	13.3	11.22	8.4	2.2	1.5
E	88.3%	93%	91.8%	89%	68.3%	61.2%

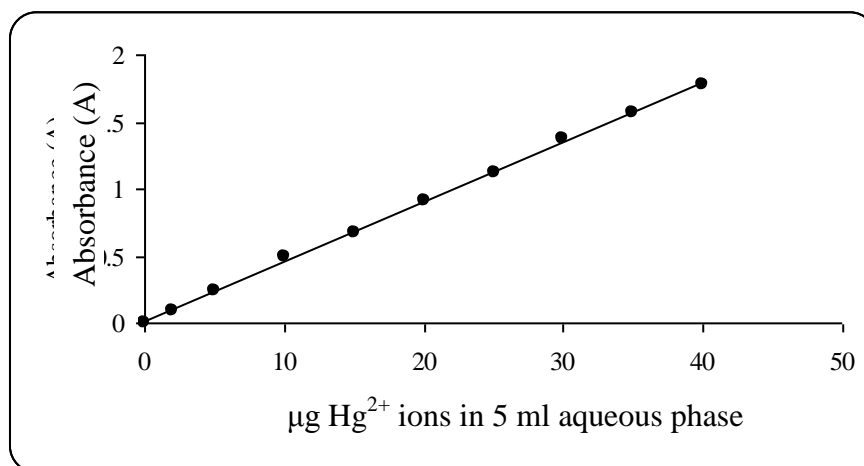


Figure (1): Calibration Curve for Hg²⁺ ions

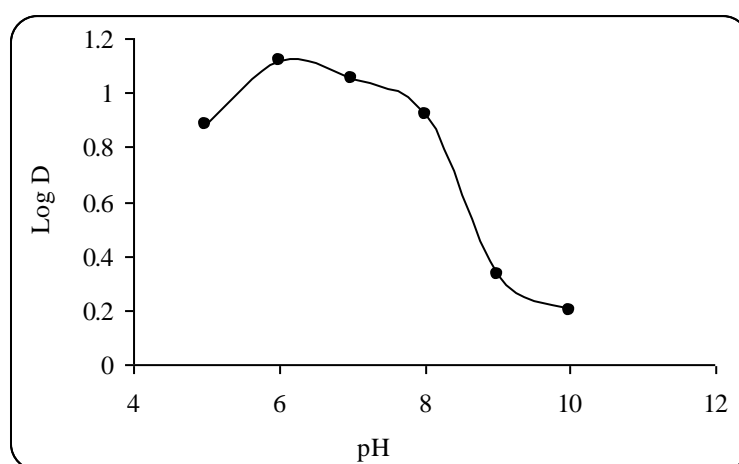


Figure (2): pH effect on the extraction of Hg²⁺ ions

3.2. Effect of Metal Ion concentration:

Extracted Hg²⁺ ions from 5 ml aqueous phase contain different quantity of Hg²⁺ ions (10 – 80 µg) by using 5 ml (1×10⁻⁴ M) of ligand (4-CMePADI) dissolved in benzene after shaking for (10 min.), and after separated the two layers determined distribution ratio (D) for each solution as in the pervious method, and the percentage of extraction (E). The results in Table (2) and Figure (3) demonstrate the effect of metal ion concentration on the extraction method and distribution ratio (D), the optimum concentration of metal ion was 30 µg (2.99×10⁻⁵ M) give higher distribution ratio, the concentration less than optimum concentration don't give complete equilibria for extraction and at this case favorite the dissociation equilibria as well as metal ion concentration more than optimum concentration according to the equilibria of extraction.

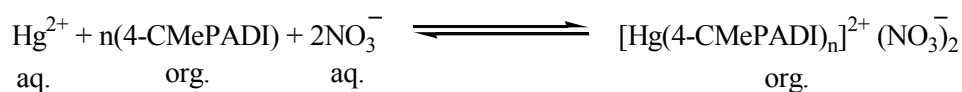


Table (2): Effect of Hg^{2+} ions concentration on the extraction method

$\mu g Hg^{2+}$	10	20	30	40	50	60	80
$[Hg^{2+}]$	0.997×10^{-5}	1.99×10^{-5}	2.99×10^{-5}	3.99×10^{-5}	4.99×10^{-5}	5.99×10^{-4}	7.99×10^{-4}
D	0.39	2.39	13.29	10	5.33	2.10	1.58
E	27.4%	61.4%	93%	90.9%	84.2%	67.7%	61.2%

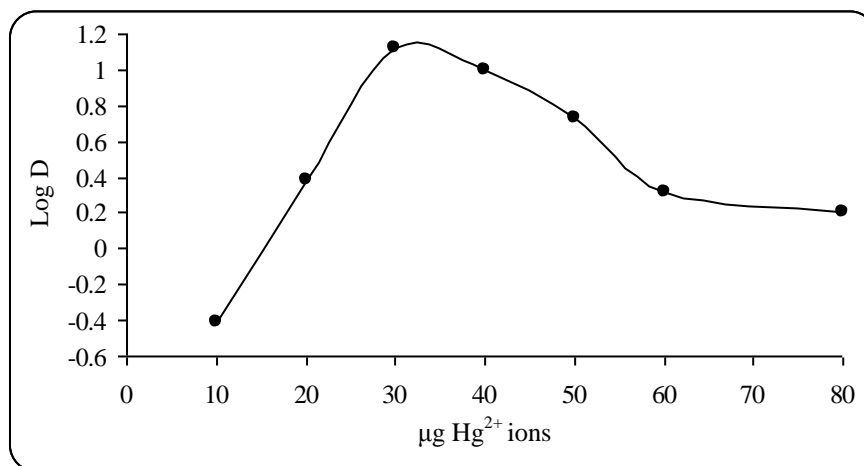


Figure (3): Effect of Hg^{2+} ions concentration on the extraction method

3.3. Effect of shaking time:

For the kinetic side of the extraction methods are carried out by studying the effect of shaking time on the extraction activity and distribution ratio values. After extracted 30 μg (2.99×10^{-5} M) Hg^{2+} ions in 5 ml aqueous phase at (ph = 6) by 5 ml of (1×10^{-4} M) ligand (4-CMePADI) dissolved in benzene by different shaking time, the results of this study in Table (3) and Figure (4) demonstrate the optimum shaking time of two layers was (15 min.) to reach the equilibria of extraction and at this time obtain the maximum distribution ratio value (D), and percentage of extraction (E), down optimum shaking time we don't reached the equilibria of extraction, and over optimum shaking time favorite the dissociation equilibria and minimize the distribution ratio (D).

Table (3): Effect Shaking time on the extraction method of Hg^{2+} ions

Time (min)	2	5	10	15	20	25
D	0.97	2.512	7.94	13.28	10	6.31
E	49.3%	71.5%	88.8%	93%	90.9%	86.3%

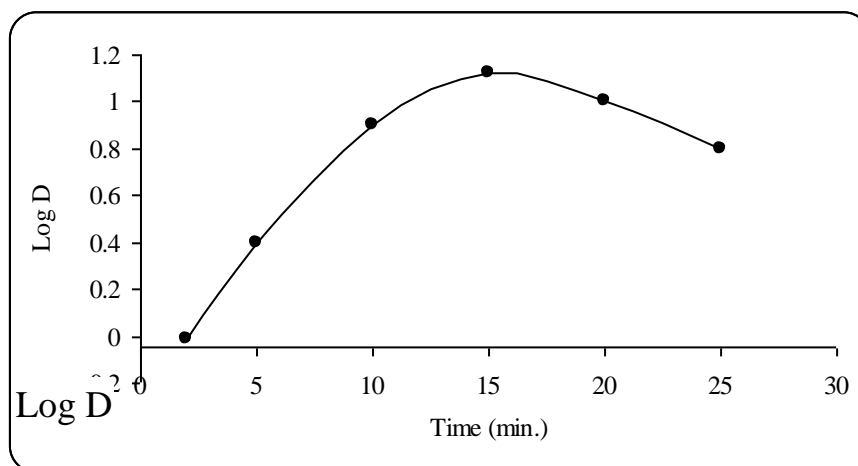


Figure (4): Effect of shaking time on the extraction method of Hg^{2+} ions

3.4. Stoichiometry:

3.4.1. Slope analysis method:

To determine the probable structure of ion pair association complex extracted, the extraction at different concentration of ligand dissolved in benzene was studied. After extracted $30 \mu g$ (2.99×10^{-5} M) Hg^{2+} ions in (5 ml) aqueous phase at (pH = 6) by (5 ml) of organic phase contain different concentrations ($1 \times 10^{-6} - 1 \times 10^{-3}$ M) of ligand (4-CMePADI) dissolved in benzene, after shaking for (15 min.) separate the phases and determined distribution ratio (D) at each concentration of ligand. The results in Table (4) and Figure (5) demonstrate the ion pair association complex having a structure of (1 : 2) (metal : ligand) $[Hg(4-CMePADI)_n]^{2+}(NO_3^-)_2$ from the slope of the straight line which is having sandwich structure.

Table (4): Slope analysis method

[4-CMePADI]	1×10^{-6}	5×10^{-6}	1×10^{-5}	5×10^{-5}	1×10^{-4}	5×10^{-4}	1×10^{-3}
D	N.E	0.126	0.398	4.17	13.28	165.9	630.9
Slope	1.61						

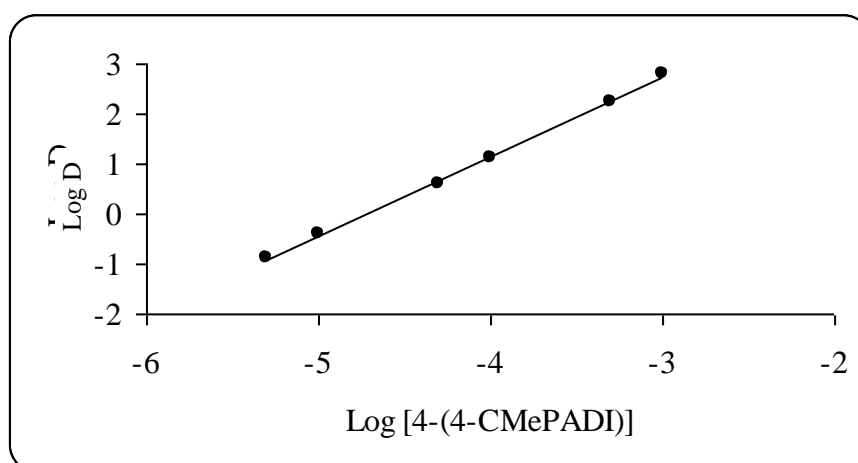


Figure (5): Slope analysis method for Hg^{2+} ion pair complex extracted

3.4.2. Mole ratio method:

Extracted $30 \mu g$ (2.99×10^{-5} M) Hg^{2+} ions in (5 ml) aqueous solution by (5 ml) different concentrations of ligand (4-CMePADI) dissolved in benzene ($1 \times 10^{-6} - 5 \times 10^{-4}$ M) at

(pH = 6) and shaking the two layers (15 min.), separate the organic phase and measurement the absorbance (A) of this layer at $\lambda = 472$ nm. By use the ligand solution as blank. The results in Table (5) and Figure (6) demonstrate the more probable structure of ion pair complex extracted was (1 : 2) (metal : ligand) $[\text{Hg}(4\text{-CMePADI})_2]^{2+}(\text{NO}_3^-)_2$ which is identify with the result in slope analysis method.

Table (5) mole ratio method

[4-CMePADI]	1×10^{-6}	5×10^{-6}	1×10^{-5}	5×10^{-5}	1×10^{-4}	2×10^{-4}	3×10^{-4}	5×10^{-4}
A	0.109	0.192	0.311	1.55	1.75	1.82	1.88	1.976
C_L/C_M	1.8							

The molar absorbtivity of complex was $5.83 \times 10^4 \text{ l.mol}^{-1} \text{ cm}^{-1}$.

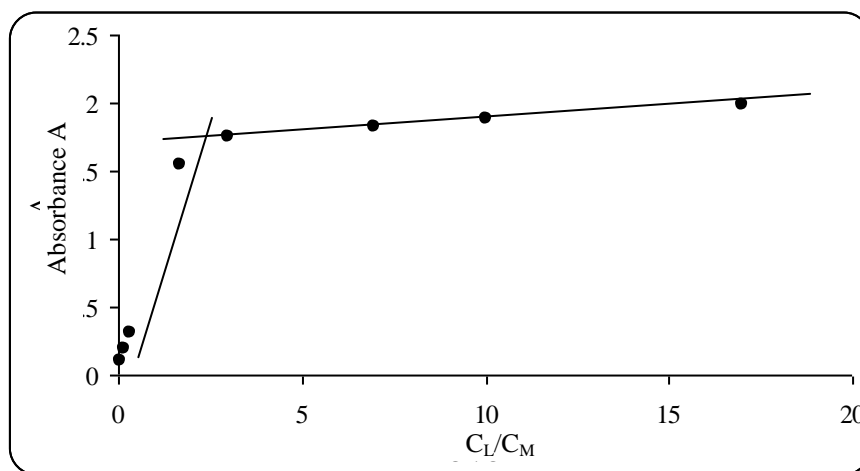


Figure (6): Mole ratio method

3.4.3. Continuous variation method:

prepare aqueous solution Hg^{2+} ions and organic solution for ligand (4-CMePADI) in benzene at the same concentration (1×10^{-3} M) and then mix different volume of the two solution to maximum volume (10 ml) at (pH = 6), after shaking the two layers (15 min.) separate the two layers and measurement the absorbance (A) of organic phase at $\lambda = 472$ nm. The results in Table (6) and Figure (7) demonstrate the more probable structure of ion pair complex extracted was (1 : 2) (metal : ligand) identify with the results of slope analysis and mole ratio for the structure which is $[\text{Hg}(4\text{-CMePADI})_2]^{2+}(\text{NO}_3^-)_2$.

Table (6): Continuous variation method

V_L ml	4	3.5	3	2.5	2	1.5	1
V_M ml	1	1.5	2	2.5	3	3.5	4
A	0.003	0.025	0.045	0.06	0.07	0.045	0.002
V_L/V_M	1.6						

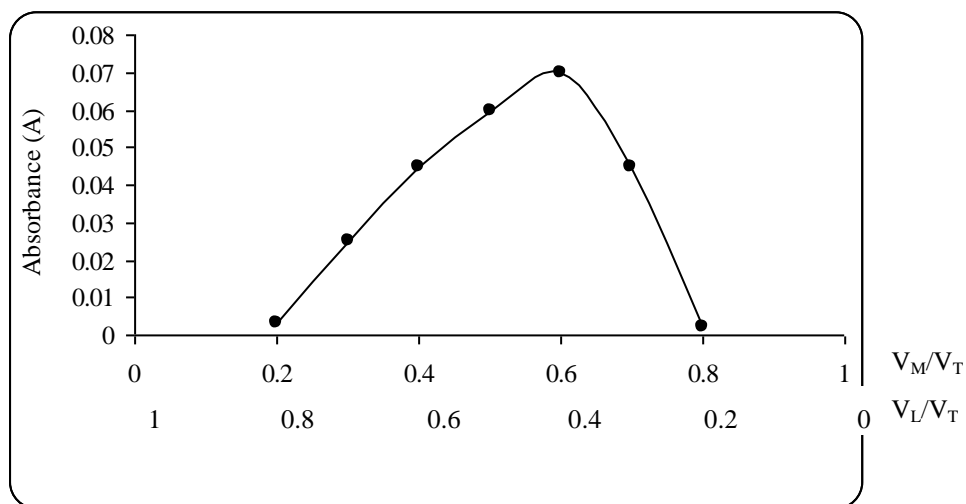
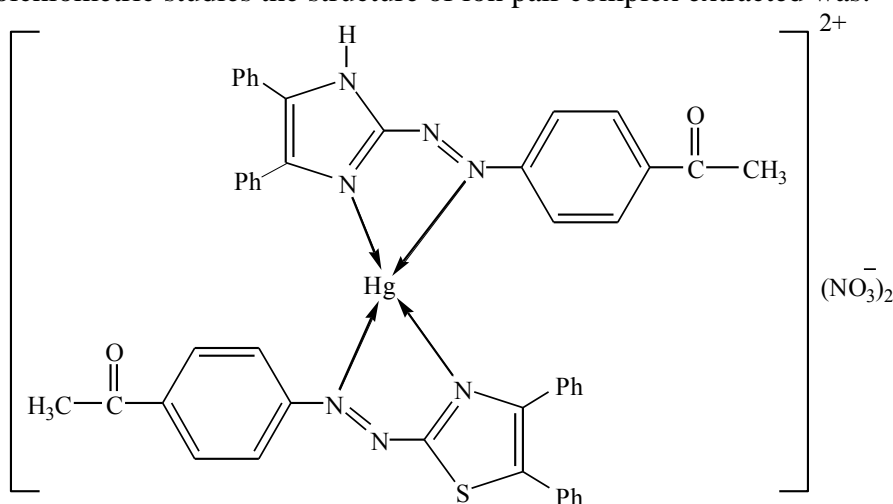


Figure (7): Continuous variation method

From the stoichiometric studies the structure of ion pair complex extracted was:



3.5. Organic solvent effect:

According to solvent extraction method which is depend on the organic solvent used in extraction method, extracted 30 μg (2.99×10^{-5} M) Hg^{2+} ions from (5 ml) aqueous phase at (pH = 6) by using (5 ml) ligand (4-CMePADI) dissolved in different organic solvents at (1×10^{-4} M), after shaking for (15 min.) separated two layers and determined distribution ratio (D) as in pervious method and percentage of extraction (E).

The results in Table (7) shows there is not any linear relation between distribution ratio (D) and dielectric constants for the organic solvents in extraction method of Hg^{2+} ions, this reflect there is not any effect for polarity of organic solvents on the extraction method but there is an effect for the structure of organic solvents on the extraction method and ion pair complex extracted, to produce ion pair (contact ion pair) or solvent separated ion pair (loose ion pair).

Table (7): Organic solvents effect on the extraction of Hg^{2+} ions

Organic solvents	ϵ	D	E
Dichloro methane	9.08	12.5	92.6%
Chloroform	5.708	17.27	94.5%
Bromo Benzene	5.4	9.16	90.16%
Benzene	2.804	13.28	93%

All thermodynamic values calculated by using the relation below:

$$\Delta G_t = \frac{Z^2}{2r} \left(\frac{1}{\epsilon_w} - \frac{1}{\epsilon_o} \right)$$

$$K_A = \frac{[\text{Hg}(4-\text{CMePADI})_2]^{2+} (\text{NO}_3^-)_{2\text{org.}}}{[\text{Hg}^{2+}]_{\text{org.}} [4-\text{CMePADI}]_{\text{org.}}}$$

$$K_{\text{ex}} = \frac{K_A D [\text{Hg}(4-\text{CMePADI})_2]^{2+} (\text{NO}_3^-)_{2\text{org.}}}{[\text{Hg}^{2+}]_{\text{aq.}} [4-\text{CMePADI}]_{\text{org.}}}$$

$$\Delta G_{\text{ex}} = -RT \ln(K_{\text{ex}})$$

Table (8): thermodynamic data values for extraction of Hg^{2+} ions by use different organic solvents ΔG_t , K_A , K_{ex} , ΔG_{ex}

Organic solvents	ϵ	ΔG_t kJ/mole	K_A L/mole	K_{ex}	ΔG_{ex} J/mole
CH_2Cl_2	9.08	125.8×10^{-3}	36.1×10^3	41.5×10^{12}	- 54.9
CHCl_3	5.708	209.9×10^{-3}	35.3×10^3	57.5×10^{12}	- 55.7
$\text{C}_6\text{H}_5\text{Br}$	5.4	222.8×10^{-3}	37.17×10^3	30.53×10^{12}	- 54.11
C_6H_6	2.804	444×10^{-3}	35.97×10^3	44.27×10^{12}	- 51.7

The results in Table (8) demonstrate there is not any linear relation with dielectric constant of organic solvent and appear the effect of organic solvent structure on the extraction method and may be participate the organic solvent to give contact ion pair (tight ion pair) or solvent separated ion pair (loose ion pair), this result proof the important of nature and structure of organic solvent on the extraction method as well as structure and stability of ion pair complex extracted.

3.6. Effect of salting – out agent:

Various salting – out agents such as lithium chloride, barium nitrate, potassium nitrate, sodium nitrate and ammonium nitrate are considered to enhance the method complex extraction into the organic, this study has shown lithium chloride is best electrolyte for enhanced extraction of Hg^{2+} complex into organic solvent and 0.5 M solution was suitable concentration of this electrolyte [14, 15]. By using high concentration of these electrolyte solutions which is effect to withdraw the water molecule from the hydration shell of Hg^{2+} ions to give free Hg^{2+} ions which is more suitable for complexation reaction with ligand (4-CMePADI) but these different electrolyte solution differ in the efficiency to do that, but lithium chloride give the higher efficiency by reason of small volume of lithium ions which is have large hydration shell and withdraw high quantity of water molecules from the hydration shell of Hg^{2+} ions to give free ions and good complexation reaction.

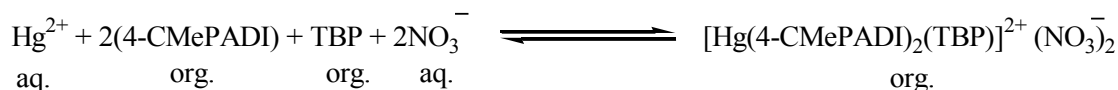
3.7. Synergistic Extraction of Hg^{2+} by 4-CMePADI and TBP:

Extraction experiments of Hg^{2+} ions by use (4-CMePADI) at concentration 1×10^{-4} M and variable concentrations of Tributyl phosphate (TBP) in benzene reveal that the efficiency of extraction of Hg^{2+} ions by (4-CMePADI) enhance and increase by use (TBP). Results in Table (9) and Figure (8) demonstrate the synergistic effect is expected to be caused by formation of more soluble complex in the organic phase than the simple complex $[\text{Hg}(4\text{CMePADI})_2]^{2+} (\text{NO}_3^-)_2$ so the determination of composition of the adduct complex is

necessary in order to elucidate the synergistic mechanism.

It was found that on keeping (4-CMePADI) Concentration, distribution ratio of Hg^{2+} complex increase with concentration (TBP) increased and after plotting log D against log [TBP] produced straight line of slope one that means one molecule of (TBP) participated in adduct formation [16].

From the above results we assume the reaction goes according to the following equation.



According to this equilibria the (TBP) molecules replace water molecules bonded in the shell of complex ions and then by addition of (TBP) molecules increase the solubility of metal complex into organic phase. This results reflect that the coordination shell of metal is not saturated by ligand (4-CMePADI).

Table (9) Synergistic effect on the extraction of Hg^{2+} ions

[TBP]	5×10^{-6}	1×10^{-5}	5×10^{-5}	1×10^{-4}	5×10^{-4}	1×10^{-3}
D	25.1	39.8	79.8	125.89	340.5	510.18

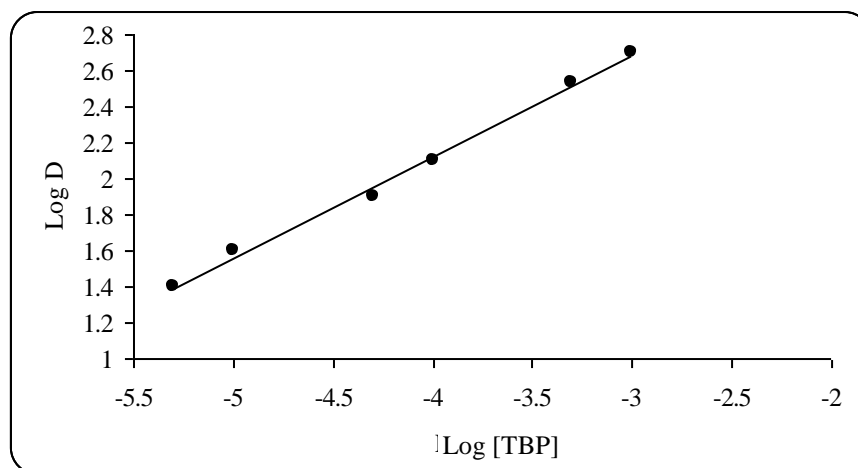


Figure (8): Synergistic effect on the extraction of Hg^{2+} ions

3.8. Temperature effect:

Extraction of Hg^{2+} ions from aqueous solution at optimum condition by (4-CMePADI) dissolved in benzene at different temperature from (5 – 40°C). The results in Figure (9) demonstrate that the reaction between Hg^{2+} ions with (4-CMePADI) was exothermic reaction that means the increase in temperature may has an effect to increase the dissociation equilibria and thermodynamic data for extraction of Hg^{2+} ions appear the exothermic behaviour of extraction reaction and the lower value of ΔH_{ex} demonstrated the dissociation of the complex as well as the large value of ΔS_{ex} appear the reaction is intropic in region and this results appear the effect of Hg^{2+} ions in aqueous phase give difficulty for extraction by (4-CMePADI) and the lower stability of Hg^{2+} - complex in benzene solvent which used for extraction. The thermodynamic data of extraction Hg^{2+} ions was $\Delta H_{ex} = -0.02183 \text{ kJ mol}^{-1}$; $\Delta G_{ex} = -48.5 \text{ kJ mol}^{-1}$ and $\Delta S_{ex} = 162.7 \text{ kJ}^{-1} \text{ mol}^{-1}$. Which is calculated by application of this relation below.

$$K_{ex} = \frac{D}{[Hg^{2+}]_{aq.} [4 - CMePAD]_{org.}}$$

After plotting log K_{ex} against $1/T$ °K and determined the slope of the straight line relation:

$$\text{slope} = \frac{-\Delta H_{ex}}{2.303R}$$

$$\Delta G_{ex} = -RT \ln(K_{ex})$$

$$\Delta G_{ex} = \Delta H_{ex} - T\Delta S_{ex}$$

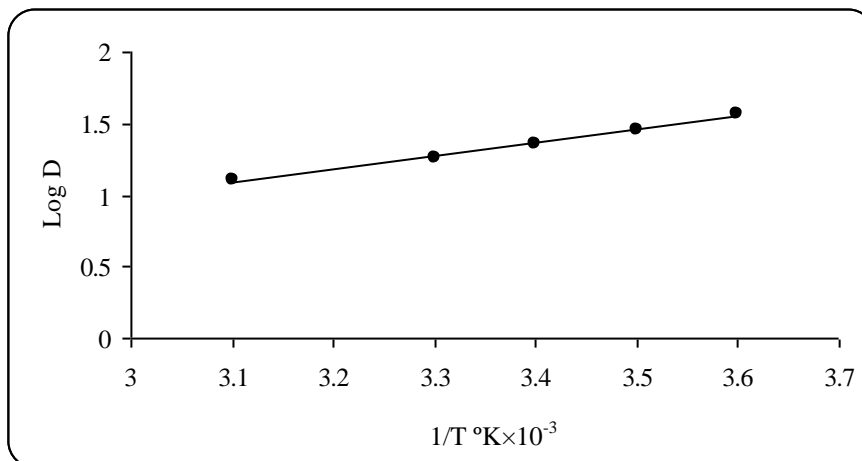


Figure (9): Temperature effect on the extraction of Hg^{2+} ions

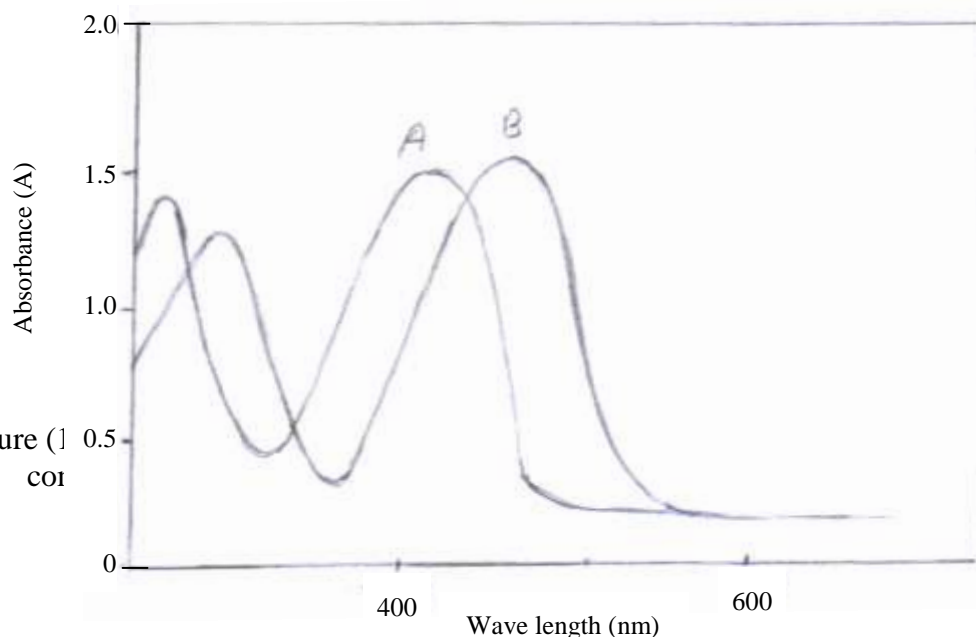


Figure (10)

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