Extraction and spectrophotometric determination of Zn(II) by Use of Ligand 2-[4-Carboxy methyl phenyl azo]-4,5-diphenyl imidazole

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Abstract:

Extraction experiments for Zn^{2+} ions from aqueous phase by using 2-[4-Carboxy methyl phenyl azo]-4,5-diphenyl imidazole (4-CMePADI) shows the optimum pH value for extraction Zn ion from aqueous phase as ion pair association complex was (pH = 9) which is giving higher distribution ratio for extraction, as well as extraction experiment for different concentrations of Zn^{2+} ions from aqueous phase by use of (4-CMePADI) dissolved in chloroform elucidate preferability 90 μg Zn^{2+} (2.75×10^{-4} M) to giving higher distribution ratio. From other hand extraction experiment about the effect of shaking time for two layers shows (15 min.) was the suitable time for shaking to reach the equilibrium of extraction and giving higher distribution ratio.

Stoichiometry for ion pair association complex extracted by using three methods showed the complex extracted have a structure of 1 : 2 which is know sandwich structure complex $[Zn(4\text{-}CMePADI)_2]^{2+}$ anion. The study about the effect of organic solvents on the extraction of Zn^{2+} ions showed preference of chloroform organic solvent for the extraction which is giving higher distribution ratio and this result shows the effect of organic solvent structure on the extraction of ion pair complex extracted, as well as thermodynamic study about the extraction of Zn^{2+}

ions shows the complexation reaction between Zn^{2+} ions and (4-CMEPADI) was indothermic behavior reaction.

1. Introduction:

The extra ordinary widespread applications of azo compounds and their derivatives as dyes, acid – base redox, metallochrome indicators from other hand behavior as ligand for complexation reaction studied and their selectivity and sensitivity, these properties help the chemists for more applications about spectrophotometric determination of many elements [1 – 4].

As well as many chemists using these compounds for extraction of some transition metal elements according to solvent extraction method, (4-CMePADI) used for extraction of Cu and Ag ions according to solvent extraction method [5]. 2-[4-Chloro-2-methoxy phenyl azo]-4,5-diphenyl imidazole (4-ClMePADI) for extraction of Zn, Cd, Hg as ion association complex according to solvent extraction method [6]. 2(α-Naphthyl azo)-4,5-diphenyl imidazole (α-NADI) used for extraction of Cu and Ag ions [7]. [8] used 2-(2-Thiazolylazo)-5-dimethylaminophenol as a functional group synthesis and sorption behavior for some trace metal ions including Zr(IV), Hf(IV), and U(VI) has been investigated by batch and column methods. [9] used 2-[2-benzothiazolylazo]-p-cresol (BTAC) as a modified for polyurethane column which is used for determination of lead in wine samples. (1-octylimidazole) and (1-octyl-2-methyl imidazole) used for the comparison of the extraction process of Zn(II) and Ni(II) [10].

2. Experimental:

All reagents and solvents were obtained from commercial sources and used as received. The ligand (4-CMePADI) synthesis as in the thesis [5]. For absorption measurements using single beam (UV – Vis.) spectrophotometer, Shimadzu (UV –

100 – 02) and double beam UV – 1700 (UV – Vis.) spectrophotometer, Shimadzu.

2.1. General Procedure:

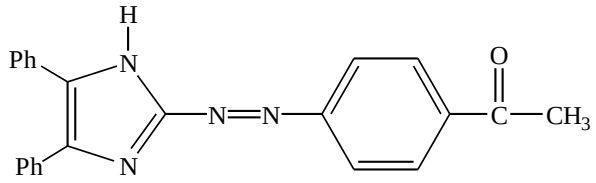
For extraction experiments have to take (5 ml) of aqueous phase contain exact quantity of Zn^{2+} ions at optimum pH, and then adding (5 ml) of organic phase contain exact concentration of ligand in organic solvent, afterward shaken the two phases at optimum time, after complete the shaken time separate the two layers and determine the Zn^{2+} ions remainder in aqueous phase by spectrophotometric method [11], for (5 ml) aqueous phase add (2 ml) of buffer solution and (2 ml) of thiosulphate solution and shaken 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 shaken with 5 ml of dilute ammonia solution (2 drops of concentrated ammonia solution in 25 distilled water) to separated unreacted dithizone, after that determine the absorption of solution at λ_{max} = 538 nm by use CCl_4 as blank, from absorbance and calibration curve Fig. (I) can be determine the quantity of Zn^{2+} reminder in aqueous phase.

But for determination the quantity of Zn^{2+} ions in organic phase as a complex with the ligand (4-CMePADI), by stripping method which is include shaken the organic phase three times with nearly concentrated hydrochloric acid HCl for dissociation the Zn – complex and transfer the Zn^{2+} ions to the aqueous phase and then determine the quantity of Zn^{2+} ions by spectrophotonetric method, previous method, afterward divide the quantity of Zn^{2+} ions in organic phase on the quantity of Zn^{2+} ions in aqueous phase to determined distribution ratio (D).

But when determine Zn^{2+} ions in aqueous phase and calculate the difference between overall quantity of Zn^{2+} ions in aqueous phase and the remainder Zn^{2+} ions

to determine the quantity of Zn^{2+} ions in organic phase was found equal to quantity determined by stripping method.



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

2.2. Preparation of Standard Solutions:

The stock solution of Zn^{2+} ions (1 mg/ml) prepared by dissolved 1 gm of Zn metal in (15 ml) of dilute hydrochloric acid (1 : 1) and then diluted this solution to 1 liter by distilled water in volumetric flask. A working standard solutions prepared by dilution with distilled water, needful prepared buffer solution (pH = 5) for determination of Zn^{2+} by dissolved (50 gm) of unhydrous sodium acetate and (30 gm) of glacial acetic acid in 250 ml volumetric flask, as well as necessarily prepared sodium thiosulphate solution (10%) also for Zn^{2+} determination. 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 chloroform, but another concentrations of ligand solutions prepared by dilution with chloroform.

3. Results and Discussion:

Study the optimum conditions for the complexation reaction. The reaction between the ligand (4-CMePADI) and Zn^{2+} ions to produce the ion pair complex $[Zn(4\text{-}CMePADI)_n]^{2+}$ anion 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 20 μg Zn^{2+} (6.12×10^{-5} M) in 5 ml aqueous phase with 5 ml of (1×10^{-4} M) ligand solution (4-CMePADI) dissolved in chloroform at different pH of aqueous phase (4 – 10), and shaken the two phases for (10 min.) after that separate two phases and determination of distribution ratio (D) as in the previous method, the results in table (1) and Fig. (2) shows the optimum value for pH_{ex} was (pH = 9), but the other values of pH is not suitable for produce the stable ion pair complex extracted to the organic phase

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

pH	4	5	6	7	8	9	10
D	N.E	2.03	1.70	2.03	2.38	3.44	2.84
E	N.E	% 67	% 62.96	% 67	% 70.4	% 77.48	%73.96

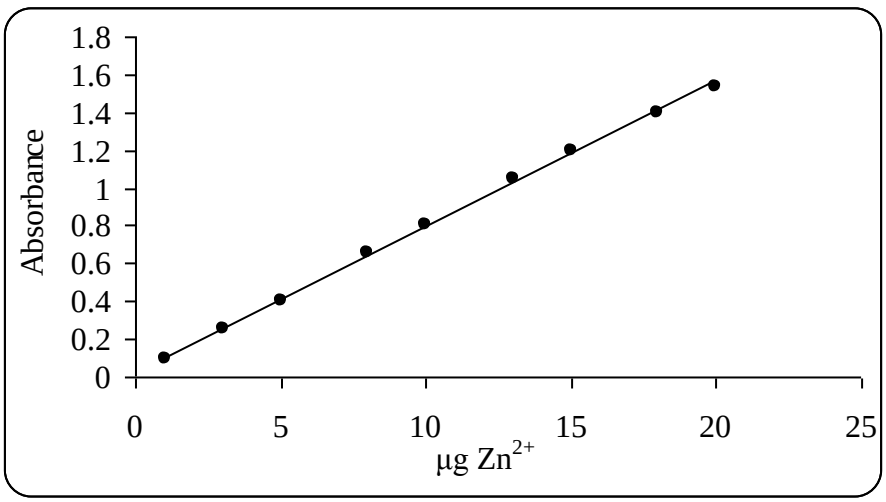


Fig. (1): Calibration curve for Zn^{2+} ions

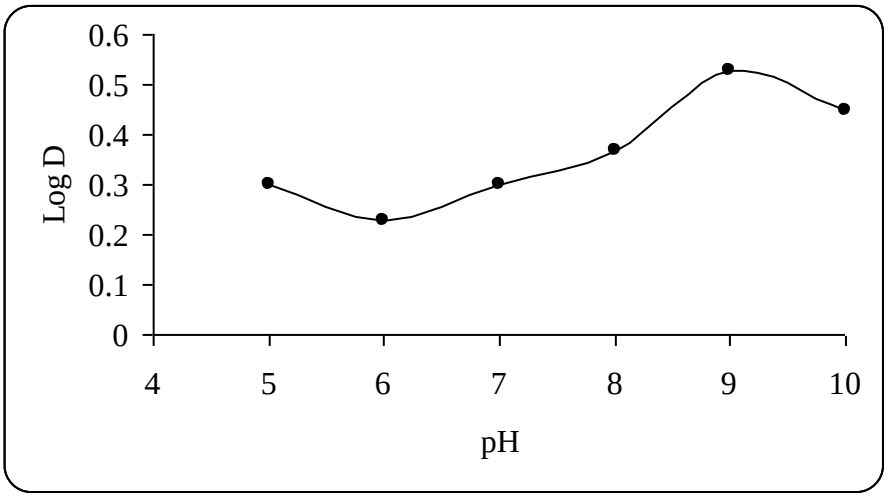


Fig. (2): Effect of pH on the extraction of Zn^{2+} ions

3.2. Effect of Zn^{2+} Ion Concentrations:

The complexation reaction between Zn^{2+} ion and ligand (4-CMePADI) behave according to the thermodynamic equilibria below:

$$Zn^{2+}_{aq.} + 4\text{-CMePADI}_{org.} + anion_{aq.} \rightleftharpoons [Zn(4\text{-CMePADI})_n]^{2+}_{Org.}\ anion$$

To clear the effect of the concentration of Zn^{2+} ions in aqueous phase on the extraction equilibria, extracted Zn^{2+} ions by using different aliquot of aqueous phase (5 ml) at (pH = 9) contain different quantity of Zn^{2+} ions (10 – 100 μg) by using (5 ml) (1×10^{-4} M) of ligand (4-CMePADI) dissolved in chloroform, after shaking for (10 min.) and separated the two layers determined distribution ratio for each solution as in the previous method. The results in Table (2) and Fig. (3) demonstrate the optimum concentration of Zn^{2+} Ions in aqueous phase suitable for extraction and extraction equilibria to shows higher distribution ratio (D) was 90 μg Zn^{2+} (2.75×10^{-4} M), and the results appear distribution ratio (D) increase with increasing Zn^{2+} ion concentration in aqueous phase until reached to the equilibrium of thermodynamic complexation reaction at optimum concentration, as well as the concentration of Zn^{2+} ions more than optimum quantity effect to deviate the equilibria in direction of dissociation and decline distribution ratio (D).

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

Zn^{2+} µg	10	20	30	40	50	60	70	80	90	100
D	2.44	3.44	9.64	12.33	15.66	18.35	22.33	25.66	36.5	33.48
E	%70.9	%77.5	%90.6	%92.5	%94	%94.8	%95.7	%96.2	%97.3	%97.1

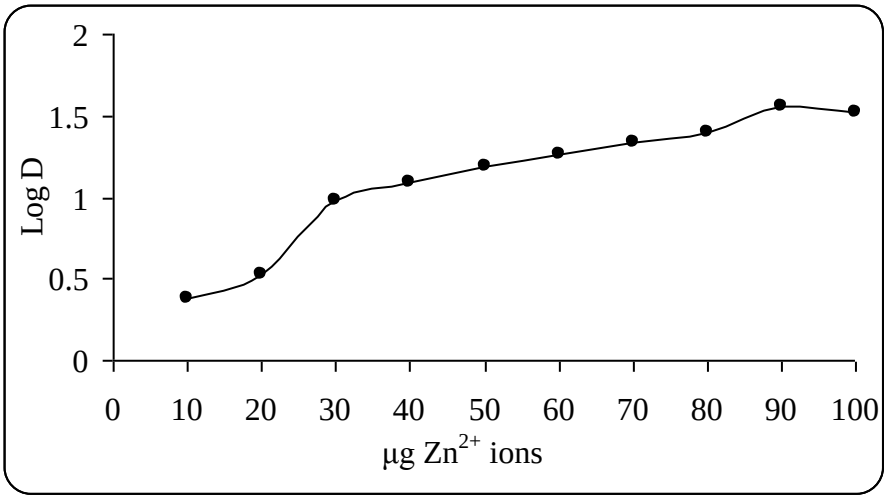


Fig. (3): Effect of Zn^{2+} ions concentration on the extraction method

3.3. Effect of Shaking Time:

After extracted 90 µg (2.75×10^{-4} M) Zn^{2+} ions in (5 ml) aqueous phase at (pH = 9) by (5 ml) of (1×10^{-4} M 4-CMePADI) dissolved in chloroform by different shaking time, the results in Table (3) and Fig. (4) shows the kinetic side of extraction equilibria need (15 min.) as optimum shaking time for two immisible layers to reach equilibrium and given higher distribution ratio (D), shaking time less than (15 min.) not enough to reach the equilibria, but the shaking at time more than (15 min.) help to deviate the equilibria in the direction of dissociation and decline distribution ratio (D).

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

Time (min.)	5	10	15	20	25
D	24.7	36.5	49	35	28
E	%96.1	%97.3	%98	%97.2	%96.6

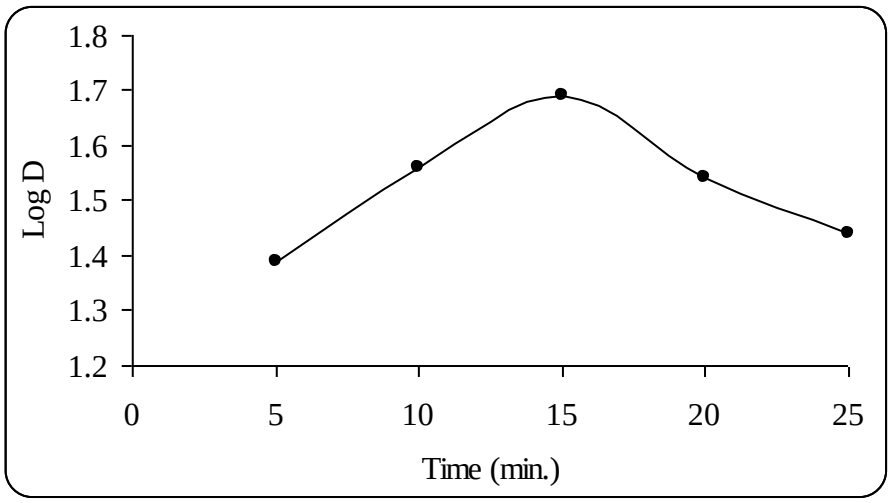


Fig. (4): Effect of shaking time on the extraction method of Zn^{2+} ions

3.4. Organic Solvent Effect:

In solvent extracted method the organic solvent effected on the efficiency of the extraction because in this method used two immisible phase to find out the effect of organic solvent on the extraction of Zn^{2+} ions, extracted 90 μg Zn^{2+} ions (2.75×10^{-4} M) in (5 ml) aqueous phase at (pH = 9) by use (5 ml) of (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 previous method. The results in table (4) shows there is not any linear relation between distribution ratio and dielectric constants for organic solvents used in the extraction, but this results showing an affinity for chloroform organic solvent in extraction method of Zn^{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 contact ion pair (tight ion pair) or solvent separated ion pair (loose ion pair). [12, 13]

Table (4): Organic solvents effect on the extraction of Zn^{2+} ions

Organic solvents	Dichloro methane	chloroform	Bromo benzene	Benzene	Toluem	CCl_4
ε	9.08	5.708	5.4	2.804	2.478	2.38
D	43.4	49	32.5	28.3	33.3	21.4
E	%97.2	%98	%97	%96.6	%97.1	%95.5

3.5. Stoichiometry:

3.5.1. Slope Analysis Method:

Extracted 90 μg Zn^{2+} ions in (5 ml) aqueous phase at (pH = 9) by (5 ml) of organic phase contain different concentration (1×10^{-6} – 1×10^{-3} M) of ligand (4-CMePADI) dissolved in chloroform, after shaking for (15 min.) separate the phases and determine distribution ratio (D) at each concentration of ligand. The results at Table (5) and Fig. (5) shows the ion pair complex extracted to the organic phase have a structure of sandwich structure 1 : 2 $[Zn(4\text{-}CMePADI)_2]^{2+}$ anion.

Table (5): Slope analysis method

[L]	1×10^{-6}	5×10^{-6}	1×10^{-5}	5×10^{-5}	1×10^{-4}	5×10^{-4}	1×10^{-3}
D	0.002	0.02	0.06	0.56	2.04	19.95	89.1
slope	1.55						

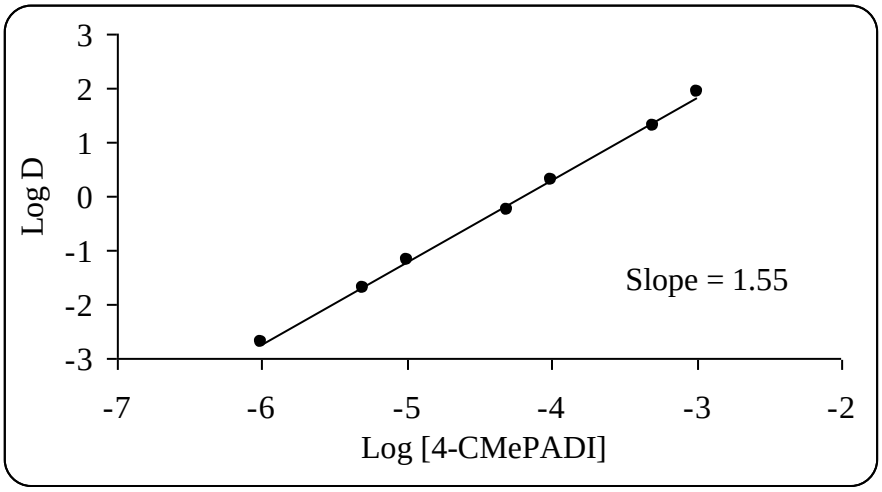


Fig. (5): Slope analysis method for Zn^{2+} ion pair complex extracted

3.5.2. Mole Ratio Method:

Extracted 90 μg Zn^{2+} (2.75×10^{-4} M) in (5 ml) aqueous phase by (5 ml) different concentration of ligand (4-CMePADI) dissolved in chloroform (1×10^{-6} – 1×10^{-3} M) at (pH = 9) and shaking the two layers (15 min.) separate the organic phase and measurement the absorbance of this layer at λ = 464 nm. by use the ligand solution as plank. The results in Table (5) and Fig. (6) demonstrate the ion pair complex extracted have a sandwich structure 1 : 2 $[Zn(4\text{-CMePADI})_2]^{2+}$ anion this result identify the result in slope analysis.

Table (5): Mole ratio method

[L]	1×10^{-6}	5×10^{-6}	1×10^{-5}	5×10^{-5}	1×10^{-4}	5×10^{-4}	1×10^{-3}
C_L/C_M	0.036	0.18	0.36	1.8	3.6	18.1	36.2
A	0.06	0.11	0.30	0.79	1.03	1.3	1.66

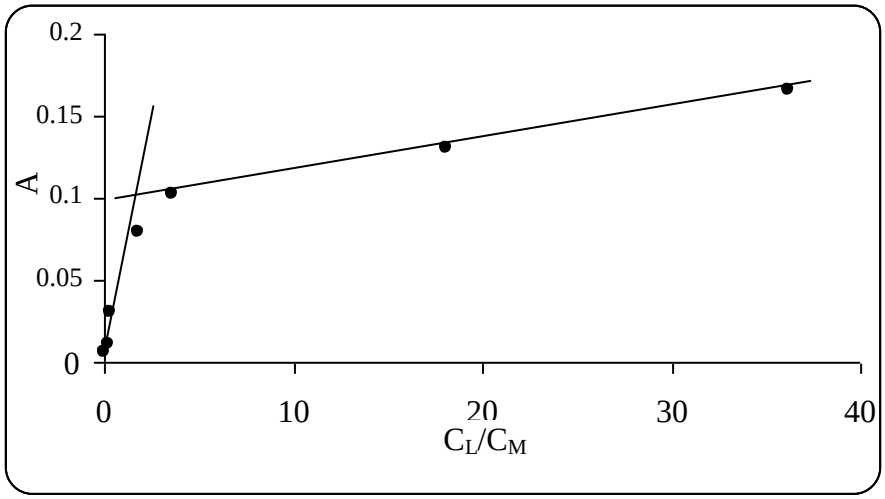


Fig. (6): Mole ratio method

3.5.3. Continuous Variation Method:

Prepare aqueous solution Zn^{2+} ions and organic solution for ligand (4-CMePADI) in chloroform at the same concentration (1×10^{-3} M) and then mix different volume of the two solutions to maximum volume 10 ml at (pH = 9), after shaking the two layers (15 min.) separate the two layers and measurement the absorbance of organic phase at λ = 464 nm. the results in Table (6) and Fig. (7) shows the ion pair complex extracted have sandwich structure 1 : 2 $[Zn(4\text{-}CMePADI)_2]^{2+}$ anion identify with the previous results.

Table (6): Continuous variation method

Sample No.	V_L	V_M	V_M/V_L	A

1	1	9	0.9	0.001
2	2	8	0.8	0.011
3	3	7	0.7	0.017
4	4	6	0.6	0.020
5	5	5	0.5	0.022
6	6	4	0.4	0.020
7	7	3	0.3	0.0175
8	8	2	0.2	0.015
9	9	1	0.1	0.012

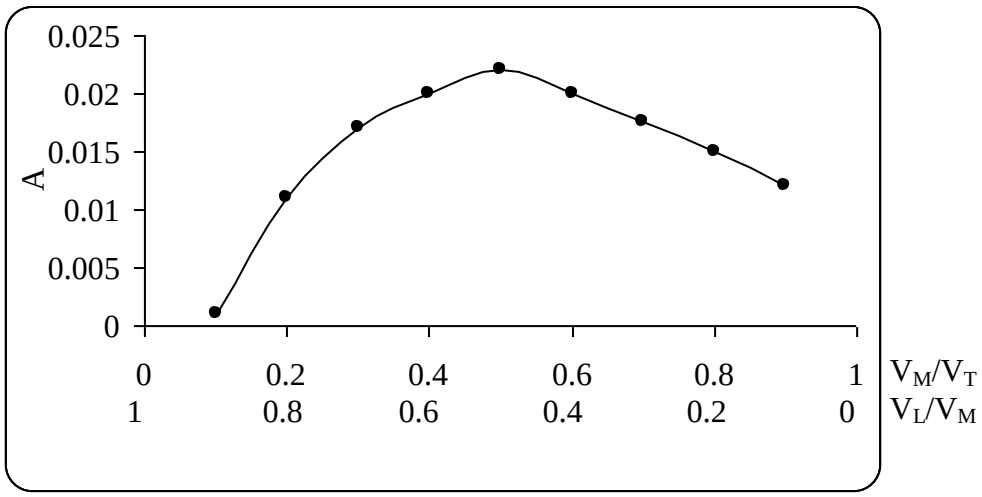
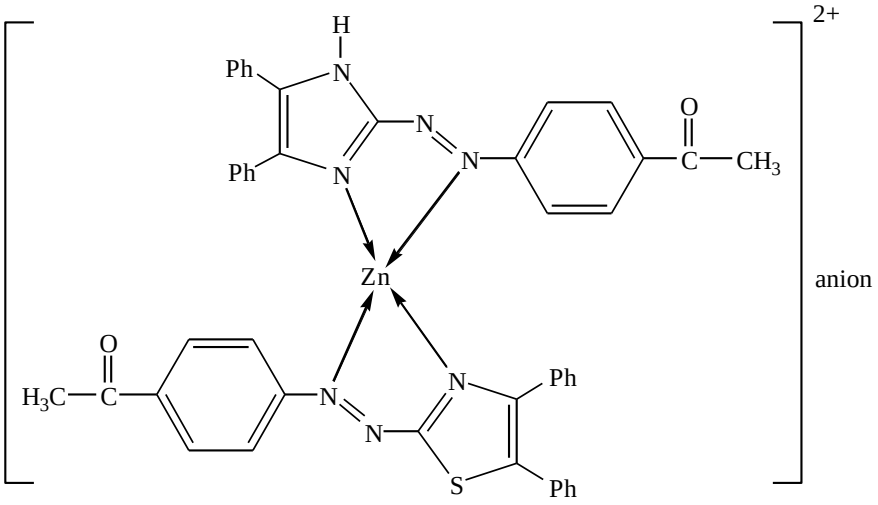


Fig. (7): Continuous variation method

3.6. Nature of Complex:

Ion pair complex extracted has a structure as clear below:



3.7. Temperature Effect:

To explain the effect of temperature on the extraction of Zn^{2+} ions by this new ligand, extracted 90 μg Zn^{2+} (2.75×10^{-4} M) in (5 ml) aqueous phase at (pH = 9) by use (5 ml) of (1×10^{-4} M) (4-CMePADI) dissolved in chloroform at different temperature (5 – 40°C), after shaking and calculate distribution ratio at each temperature, the results in Table (7) and Fig. (8) shows the complexation reaction between Zn^{2+} ions and (4-CMePADI) was indothermic reaction.

Table (7): Temperature effect on the extraction of Zn^{2+} ions

T °C	T °K	1/T °K×10^{-3}	D	K_{ex}
5	278	3.6	12.4	4.5×10^{8}
10	283	3.5	19.94	7.25×10^{8}

20	293	3.4	31.6	11.49×10^{8}
30	303	3.3	50.1	18.2×10^{8}
40	313	3.2	79.5	28.9×10^{8}

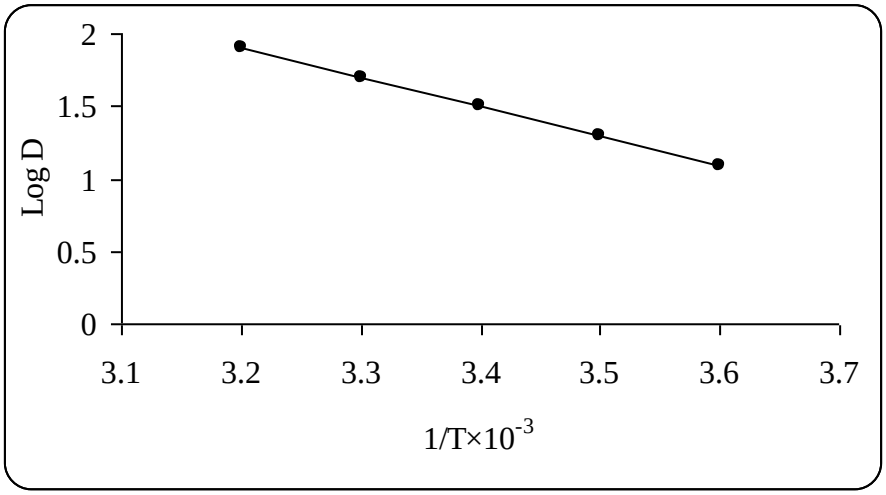


Fig. (8): Temperature effect on the extraction of Zn^{2+} ions

Calculate K_{ex} from the relation below:

$$K_{ex} = \frac{D}{[M^{n+}]_{aq.}[L]_{org.}}$$

after plot log K_{ex} vs. 1/T determine the slope of the straight line and then calculate thermodynamic data of the extraction of Zn^{2+} ions

$$slope = \frac{-\Delta H}{2.303R}$$

$\Delta G_{ex} = -RT\ln K_{ex}$, $\Delta G_{ex} = \Delta H_{ex} - T\Delta S_{ex}$ all these values in Table (8):

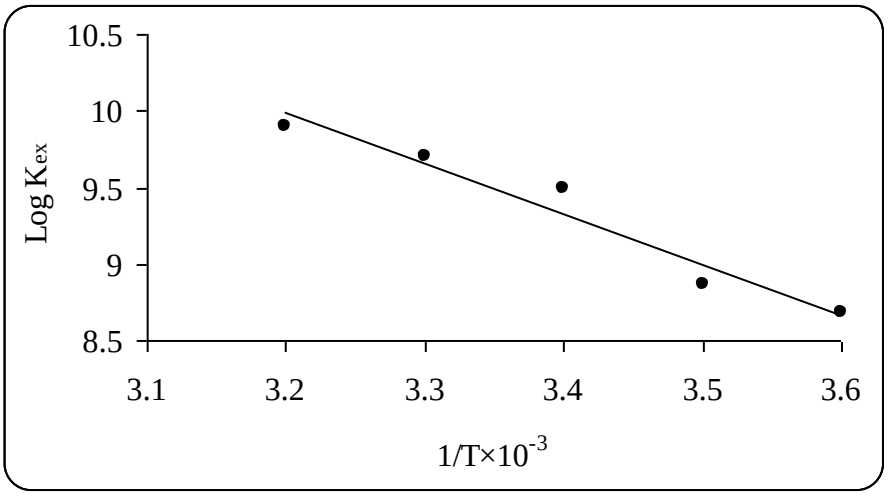


Fig. (9): Temperature effect on the extraction constant of Zn^{2+} ions

Table (8): Thermodynamic data for extraction of Zn^{2+} ions

ΔG	–56.7 kJ.mol^{-1}
ΔH	0.0388 kJ.mol^{-1}
ΔS	181.3 J.K^{-1}.mol^{-1}

Thermodynamic data in Table (8) shows from ΔH_{ex} the reaction is indothermic reaction and by increase temperature increase the connection between Zn^{2+} ions and ligand (4-CMePADI) [14, 15]. The high value of ΔS_{ex} reflect complexation reaction was intropic inregion, as well as increase temperature help to increase stability of ion pair complex extracted to the organic phase in addition of solvent effect and the kind of ligand [16].

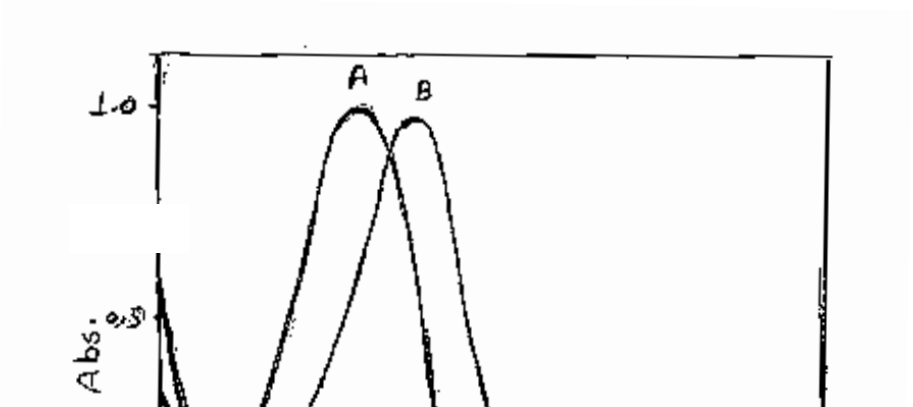


Fig. (10): Absorption spectra for 1×10^{-4} M (4-CMePADI) dissolved in chloroform and it's complex with zinc ions (Zn^{2+}) at pH = 9 (A ligand B it's complex with Zn^{2+})

استخلاص وتقدير طيفي للخارصين باستعمال الكاشف 2-[4-كاربوكسي مثيل فنيل آزو]-4،5-ثنائي فنيل اميدازول

شوكت كاظم جواد ، حيدر ناجي خضير ، فوزي يحيى وادي ، حسين عبد علي سلمان و هادي حسن هادي

كلية التربية للبنات – جامعة الكوفة

الخلاصـة:

تم استخلاص أيونات الخارصين Zn^{2+} من الطور المائي باستعمال الكاشف 2-[4-كاربوكسي مثيل فنيل آزو]-4،5-ثنائي فنيل اميدازول (4-CMePADI) وقد اظهرت القيمة المثلى للدالة الحامضية pH_{ex} لأستخلاص ايونات Zn^{2+} من الطور المائي كمعقد ترابط ايوني كان (pH = 9) الذي أعطى قيمة نسبة التوزيع (D). كذلك تجربة الاستخلاص لتراكيز مختلفة من ايونات Zn^{2+} في الطور المائي باستعمال (4-CMePADI) مذاب في الكلوروفورم أظهرت ان $90\ \mu g\ Zn^{2+}$ (2.75×10^{-4} M) يعتبر هو التركيز الامثل الذي يعطي أعلى قيمة لنسبة التوزيع (D) من جانب آخر تجربة الاستخلاص حول تأثير زمن الرج فقد أظهرت ان الرج لزمن مقداره (15 min.) كان هو الزمن الامثل الذي يعطي أعلى قيمة لنسبة التوزيع (D). اما دراسة تركيب معقد الترابط الأيوني المستخلص إلى الطور العضوي فقد تمت بإجراء ثلاثة أنواع من التجارب وهي طريقة تحليل الميل وطريقة النسب المولية وطريقة التغيرات المستمرة وقد أثبتت التجارب الثلاث بان لمعقد الترابط الأيوني المستخلص الى الطور العضوي له تركيب ساندويج بنسبة مولية (M : L) 1 : 2 anion $[Zn(4\text{-}CMePADI)_2]^{2+}$. إما دراسة تأثير المذيب العضوي على عملية الاستخلاص فقد أثبتت التجربة باستخدام عدد من المذيبات العضوية المختلفة في ثابت العزل الكهربائي لها انه ليس هناك اية علاقة خطية بين ثابت العزل الكهربائي للمذيبات العضوية المختلفة وقيم نسب التوزيع (D) في هذه المذيبات ولكن أظهر مذيب الكلوروفورم تأثير ملحوظ على عملية الاستخلاص وأعطى أعلى قيم لنسب التوزيع (D).

أشارت هذه النتائج إلى وجود تأثير لنوع وتركيب المذيب العضوي على عملية الاستخلاص في تكوين معقد الترابط الأيوني المستخلص. أما الدراسة الثرموداينامية فقد أشارت إلى أن تفاعل التعقيد بين أيونات Zn^{2+} والكاشف (4-CMePADI) هو تفاعل ماص للحرارة.

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