EXTRACTION OF CADMIUM (II), COMPLEX WITH 2-MERCAPTOBENZOTHIAZOLE AND ITS STABILITY REGARDING GAMMA RAYS AND STUDY OF BIOLOGICAL ACTIVITY OF THE COMPLEX.

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ABSTRACT

The study in volve the temperature effect on the extraction process for some chelate systems through study of extraction of Cd (II) by 2-mercaptobenzothiazole. The work include the calculations of thermodynamics parameters(ΔH_{ex}, ΔG_{ex} , ΔS_{ex}) for the extraction processes to Cd (II). The results were indicated that ΔH_{ex} has a negative value (exothermic process).

The obtained negative values of ΔG_{ex} indicated to the spontaneous extraction processes. The results were shown that D values decrease with increase of temperature while D increase with increase of ethanol concentration as catalyst. Mole ratio method was employed for expected determination of the stoichiometry of the complex. The results showed that the ratio of Cd (II) to the reagent is (1 : 2) respectively.

The study of physical properties including molar conductivity measurements, spectrophotometric investigation gives other evidence for complex formation ratio of Cd(II) with 2- mercaptobenzothiazole.

The range of radiant stability for the complex was shown in this study. The exposition of the complex to gamma rays(0.4 Mrad/ hour) enough to break metallegand bonding a fact which was proved through the study of U.V. spectroscopy.

The biological activity for the formed complex and its effects on two kinds of bacterias (Staphylocooous Aureus and Eschriachia Coli) were studied. The results proved that Cd (II) is able to obstruct the evolution of those two kinds of bacterias.

Introduction

In the last few years many of thiocompounds were used as a legand to prepare a complexes compounds with different transition metals, as the complexes prepared give good characteristics regarding to the stability constant and the important biological activities [1-4].

2- mercaptobenzothiazole (2- HMBT) is a white compound undissolved in water and dissolve in some organic solvents, its weakly soluble in cyclohexane and DMSO, Zylene [5]. It is found in tautomeric form thion and thiol as follow:

$$(-N{=}C-S-H \rightleftharpoons NH-C{=}S)$$

2- mercaptobenzothiazole (2- HMBT) used in industry [6] and medicine [7]. The agent is able to form chelate complex with a number of metals so it is used to separate the cations and precipitate Cd (II), Pd (II), TI (II),Cu (II) [8].

The agent was used in potentiometric titration for the determination of Pd (II) and Cd (II)[9]. Rahman and Mailik[10] have used 2-mercaptobenzothiazole for the preparation of a complexes with lanthanides salts. Brodie and Michael[11] prepared some complexes by using 2-HMBT with Osemium and Rothenium in basic media. Werfali and Mcuauliff[12] have been prepared a complexes between 2-HMBT and Mo(IV) containing N,S. Shevadove[13] was used 2-HMBT as reagent in the extraction of Ir(II). Diamonotots[14] studied the extraction and separation of Pt and Au by using 2-HMBT Turel and Itawi[15,16] have been studied the extraction of Se(IV),Tl (I) using 2-HMBT as a legand.

The work deals with using 2-HMBT in the extraction of Cd(II),Pd(II) and study of different characteristics of complexes formed and including the study of stabilities and biological activities of the complexes.

Experimental

A. **Instruments** : The instruments used for the measurements are:

1- U.V. and VIS. Spectrophotometer (Shimadzu 160-japane)
2- PH-meters (PW-9421,Philips,England).
3- Electric Shaker (W. Germany).
4- Electrical conductivity instrument(CD 810 Tacussel, Holland).

B. **Chemicals[17]:**

1. Preparation of Cd (II).standard solution (8.89 * 10^{-3}M). The preparation was carried out by dissolving (0.1 gm) of Cd (II) in 2ml of concentrated (HNO_3) and then completed the volume to (100ml).
2. Solution of 2- mercaptobenzothiazole was prepared by dissolving (I gm) of the compound in (100ml) of methyl iso-butyl ketone.
3. The preparation of deionized solution was carried out by

dissolving (0.002 gm) of the compound in (10 ml) of CCl_4 as solvent and then diluted to (100ml) with same CCl_4.

4. Solution of Hydroxylamine hydrochloride was prepared by dissolving (0.002 gm) of the compound in (10 ml) of CCl_4 as solvent and then diluted to (100ml) with same CCl_4.
5. Two solution of sodium hydroxide were prepared by dissolving (20 gm) of sodium hydroxide in (100 ml) of deionized water for each other.

C. Procedure of Extraction:

The extraction of Cd (II) by using (2-HMBT) was carried out by the following procedure :

- Mixing (10ml) of Cd (II) solution with equivalent volume of (2-HMBT) solution dissolved in methyl isobutyl ketone in separating funnel. The mixture was shaking for (1min) and then separating the organic layer from aqueous layer. The calculation of the Cd (II) concentration residue in aqueous phase were carried out by taken (2ml) of the phase and determined by diathiozon.

Results and Discussion

Table(l): show the values of D% of Cd (II) extraction at different temperature. The values proved that the extraction of Cd (II) is exothermic.

Table(l): Values of distribution ratio for Cd (II) extraction at different temperatures.

Aqueous phase: 10ml from($1.78 * 10^{-4}$M) Cd (II) at PH=7.

Organic phase: 10ml from ($6.04 * 10^{-3}$M) of 2-HMBT solution in methyl isobutyl ketone.

Equilibrium time: one min.

T (K°)	$1/T * 10^{-3} (K^{-1})$	D	Log D
298	3.35	32.00	1.505
303	3.30	22.80	1.357
308	3.24	11.20	1.049
313	3.19	8.00	0.903
318	3.14	6.24	0.795

The values of ΔG_{ex}, ΔS_{ex} calculated by the equation: The thermodynamic quantities ΔG_{ex}, ΔS_{ex}, were calculated by using the equation:

$$\Delta G_{ex} = -RT \ Ln \ K_{ex} \qquad (1)$$

$$\Delta G_{ex} = \Delta H_{ex} - T \ \Delta S_{ex} \qquad (2)$$

The results reported in table(2) proved that the extraction processes is spontaneous and simple reaction.

Table(2): Valuse (K_{ex}, ΔG_{ex}., ΔH_{ex}, ΔS_{ex}) for Cd (II) extraction by 2-HMBT dissolve in methyl isobutyl ketone.

T (K°)	K_{ex}	Ln K_{ex}	ΔH_{ex} Kj.mol^{-1}	ΔG_{ex} Kj.mol^{-1}	ΔS_{ex} Kj.mol^{-1}
298	$2.97*10^7$	19.51	- 68.24	- 48.256	0.055
303	$2.21*10^7$	19.17	- 64.627	- 48.280	0.054
308	$1.04*10^7$	18.46	- 64.627	- 47.191	0.057
313	$0.74*10^7$	18.12	- 64.627	- 47.074	0.056
318	$0.58*10^7$	17.88	- 64.627	- 47.192	0.055

Effect of Concentration of Ethanol as catalyst

The effect of conc. of ethanol on the extraction process was studied and the results were represented in table (3). The values of (D) increased with increase of ethanol concentration.

Table(3): Effect of catalyst indistribution of cadmium.

Aqueous phase: l0ml from Cd (II) solution ($1.78 * 10^{-4}$M) at PH=7.

Organic phase: l0ml from 2-HMBT solution ($6.04 * 10^{-3}$M) dissolve in methyl iso-butyl ketone.

Equilibrium time: one min.

Temperature: 298 ± 2 K

ETOH (ml)	D
0	32.5
1	36.5
2	40.8
3	44.9
4	49.2

Stoichiometric Study

The stoichiometry of expected formation of the complex was proved by using the results represented in figure (I). They proved that the expected formation is 1:2 of Cd (II): reagent.

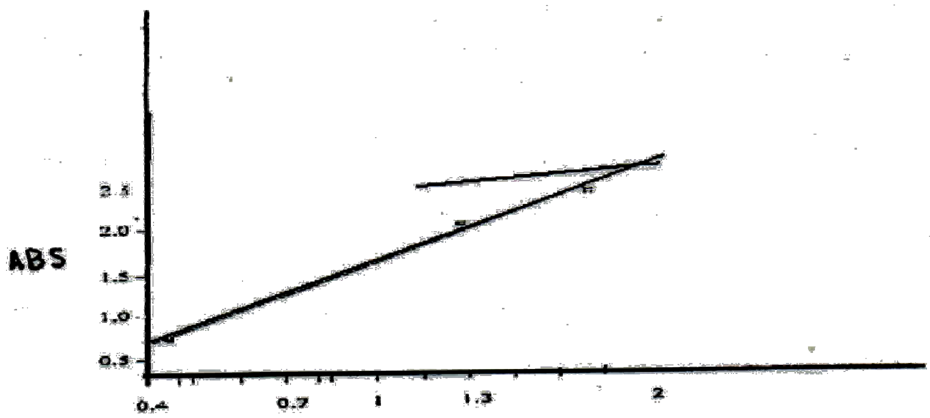


Fig (1). Mole ratio method for Cd (II): 2- HMBT.

Molar Conductivity

The measured values of molar conductivity of the formed complex was reported in table (4). In the three different solvents the results were shown that the complex is in neutral form at room temperature and (10^{-3}) of solution.

Table (4): Molar conductivity values for 2- HMBT and Cd (II): 2- HMBT complex.

Compound	Molar conductivity (10^{-1} M) JI Scm^{-1}			
	Chloroform	Ethanol	Aceton	Mixture ethanol + acetone
$C_7 H_4 NS_2$ (L)	-	1.652	-	-
Cd $(C_7 H_4 NS_2)_2$	-	-	-	12.76

Figure (2) was shown the spectras of the reagent (2- HMBT) dissolved in methyl iso butyl ketone. The peak was represented to the electronic transition due to thioamide group (N= C=S).

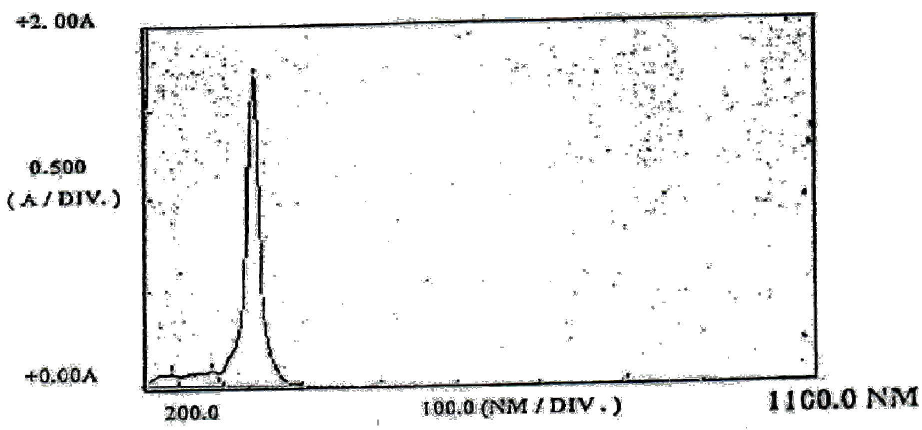
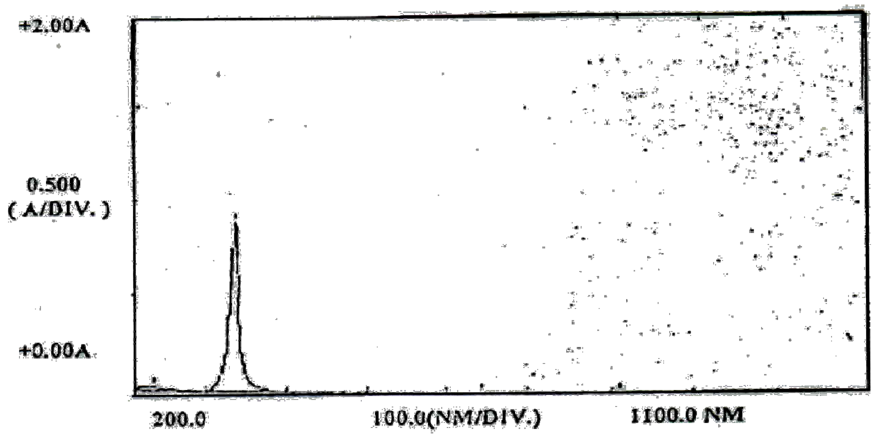


Fig (2). U.V, VIS. Spectrum for organic reagent (2- HMBT) dissolve in methyl isobutyl ketone.



Fig(3). U.V, VIS. Spectrum for Cd (II): 2- HMBT complex.

Effect of Radiation on the stability of the complex

Effect of gamma rays on the stability of the complex was stadied the rough the exposition of the complex to gamma rays in the range of (0.4 Mrad/ hour) for 6 hours. The results reported figure (4) give one peak (339 nm). The comparison with figure (3) give an clear disappearance of the other peaks before radiation . This may be interpreted by the break of metal-reagent bonding by this range of gamma rays.

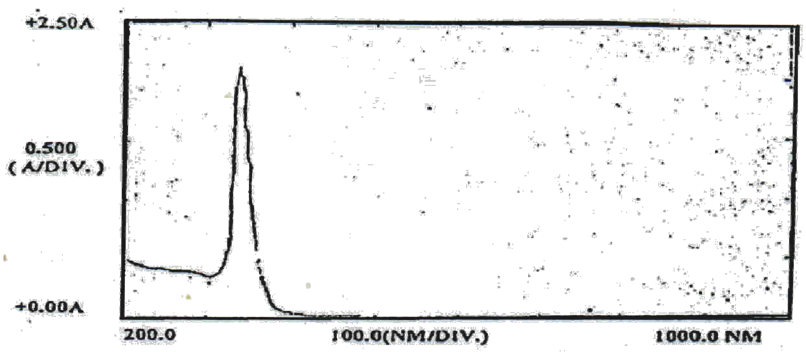


Fig (4). V.V, VIS. For Cd (II): 2- HMBT complex after radiation.

Biological Activity Study

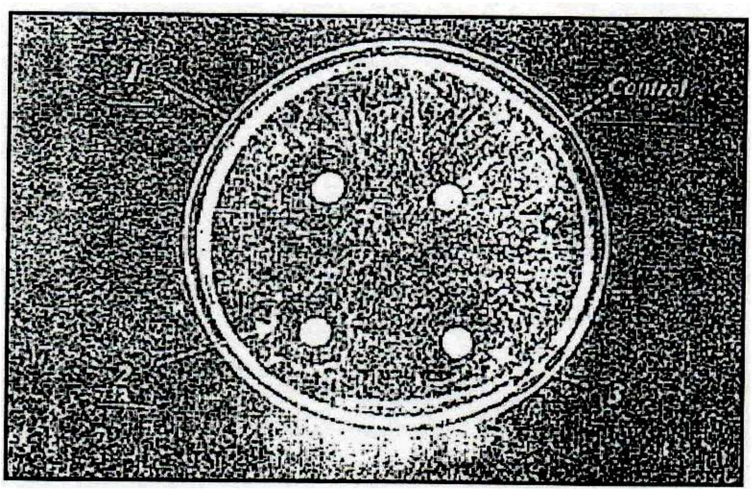
The study of biological activity of Cd (II)- reagent complex was carried out on two kinds of bacteria Staphylococcus Aureus and Eschriarchia Coli. The values reported on tables(5), (6) and the figures(5),(6), (7), proved that Cd (II)- 2- HMBT complex is able to obstruct the evolution of the two kinds of bacteria.

Table(5): Average of inhibition, zone diameter inC ern) after incubation for 24 hours for 2- HMBT and its complex against Staphylococcus Aureus bacteria.

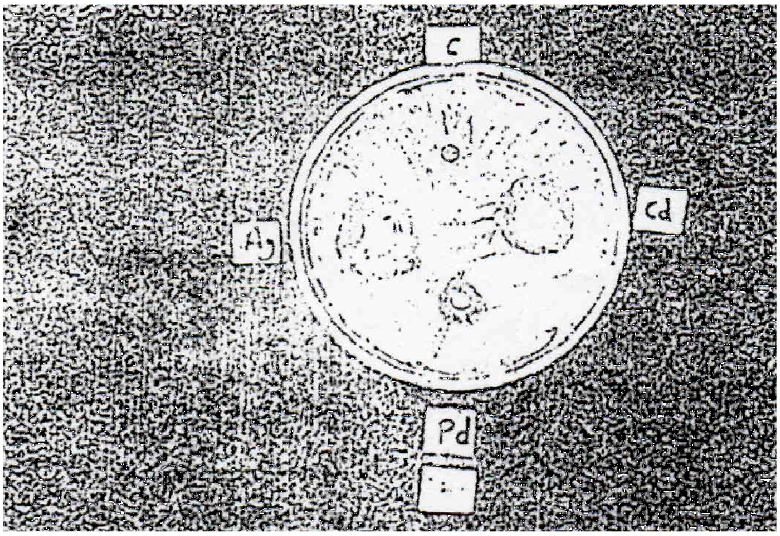
Compound	First conc.	Second conc.	Third conc.
$C_7 H_4 NS_2$ (L)	1.2	5	-
Cd $(C_7 H_4 NS_2)_2$	2.3	1.6	1.1

Table (6): Average of inhibition zone diameter in (cm) after incubation fore 24 hours) for 2- HMBT and its complex against Eschriachia Coli bacteria.

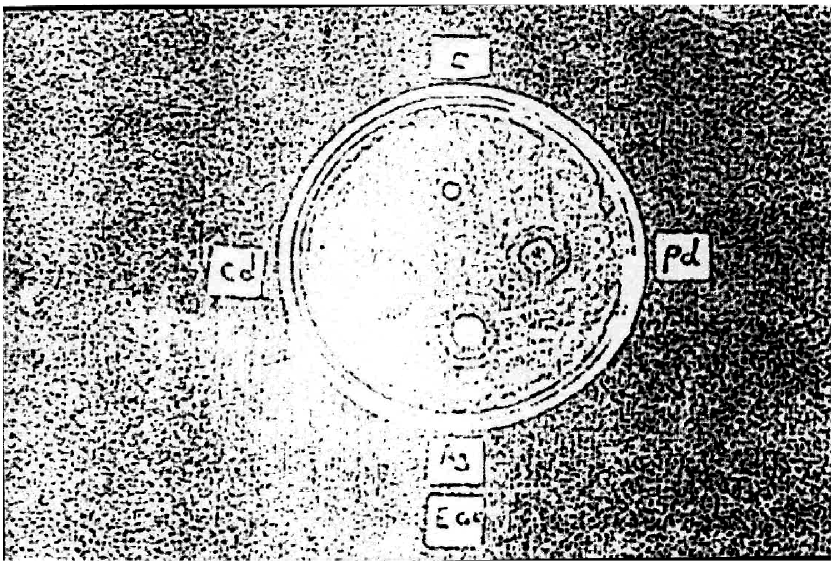
Compound	First conc.	Second conc.	Third conc.
$C_7 H_4 NS_2$ (L)	-	-	-
Cd $(C_7 H_4 NS_2)_2$	1	2	1.5



Fig(5). Inhibition diameters for three concentrations of 2- HMBT on Staphylococcus Aureus bacteria.



Fig(6). Inhibition diameters for three concentrations of Cd (II) : 2- HMBT on Staphylococcus Aureus bacteria.



Fig(7). Inhibition diameters for three concentrations of Cd (II) : 2- HMBT complex on Eschiachia Coli bacteria.

Conclusion

The extraction process of Cd (II) by using 2- mercaptobenzothiazol as reagent is exothermic. The stoichiometric study indicate that the ratio is 1: 2 of Cd (II): reagent respectively. The study of U.V. spectroscopy proved that the exposition of complex to gamma rays (0.4 Mrad/hours) is enough to break the Cd (II)- reagent bonding. The important role of Cd (II): 2- HMBT complex was proved by the obstruction of the evolution of Staphylococcus Aureus and Eschriachia Coli bacteria.

References

1- A. C. Fabretli, G. Franchini, A. Giusti, G. Tosi and P. Zannini, Transition Metal Chemistry, 10, 284, (1985).

2- Z. Travnieek. J. Walla. L. Kvitek, Z. Sindelat and M. Biler, Transition Metal Chemistry, 24, 633, (1999).

3- Serrano. I. Garcta, J. Perez, E. Perez, G. Sanchez, J. Gorcia, G. Garcia, E. Molins. Inorganic Chemica Acta. 355, 33-40, (2003).

4- S. Khan, S. A. Nami, K. S. Siddiqi. Journal of Molecular Structure, (2007).

5- Marcus and Kertes, " Ion Exchange and solvent extraction of metal complexes" Johnwiley interscience, 370, (1969).

6- A. F. Halasa and G. E. P. Smith, J. org. chern. 86, 636(1971).

7- M. Bravar. J. Jeiencic, Kaut Schuk. Gummi kunst stoff, 39(4), 3l4(1986).

8- R.Pavide, G. Aasseiti, J. F. Murray, M.E. Brokke and A. D. Gutman, J. med. chern., 13, 263(1970).

9- A. K. Majunder and M. M. Chakrra bartly, Anal. Chern. 162, 96(1958).

10- A. U. Mailik and F. R. Rahmani, J. Inorg. Nucl. Chern., 37, 1552(1975).

11- A. M. Brodie and Michael, J. chern. Soc. Dalton. Trans., 663, (1986).

12- C. A. Mcauliff and A. Werfali, Inorg. Chern. Acta., 60(87), (1982).

13- Sheradova, Zh. Anal. Khim, 34, 1554(1979).

14- A. Diamontots. Anal. Chern. Acta. 66, 147(1973).

15- R. K. Itawi and Z. R. Turel, J. Radioanal. Nucl. Chern. Letter 96, 47l(1985).

16- R. K. Itawi and Z. R. Jurel, J. Radioanal. Nucl. Chern. Letter 87, 151(1984).

17- G. H. Morrison and Henry Freiser, " solvent extraction in analytical chemistry" John Wiley and Sons Inc,654, (1957).