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# Spectrophotometric and Thermodynamic Studies of Complexation between Catechin and Some of Transition Metals (II)

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**Abstract:** ***Cadimum and Nickel are toxic heavy metal when presented in a high level over it allowable limit. To detoxify this heavy metal a chelators were used as in a chelation therapy. This work studies the complexation of some chelator (Catechin) with Cd II, Ni II ions. A spectrophotometric technique was applied in water solvent in PH=7-7.5, at four different temperatures. No shift in it $\lambda_{max}$ but wrer increases in absorbance indicating the complex formation. The stoichiometry of these complexes were determined by a method of the continuous variation (Job's) method, it was found that Catechin-Cd, Catechin-Ni were (1:1). These chelators have a high tendency to complex with Ni II ion which was reflected by its high values of their equilibrium constants. Thermodynamic parameters indicate a spontaneous interaction (negative free energy change ΔG), and the enthalpy changer for Catechin-Cd complex were positive and Catechin-Ni have negative ΔH which depends on type of the interaction and the structures of the complexes.***

**Keywords:** chelating agents, Catechin, , thermodynamic parameters and Catechincomplexation

## 1. Introduction

Chelation characterize a private roud that ions and molecules join metal ions, chelation include the structure or subsistence of two or more divided coordinate bands between a polydentate ligand and a single central atom. Usually these ligands are organic compounds Called chelators[1]. A medical steps that share the management of chelators to take off heavy metals from the body called chelation therapy. Detoxification of heavy metal by the management of chelators forms a stable complex and stop the toxic heavy metal kind from hitting the biological targets[2].

Many epidemiological studies mention a defensive service of dietary flavonoids versus psychical ischemic disease. Flavonoids hold large assortment of potential cerebroprotectivebeneficial effects like antioxidant, antiinflammatory, anti-platelet aggregatory activities and theycan also restore endothelial function, prevent neutrophil accumulation and LDL oxidation. Many of them confirm to be antithrombogenic. They also have been shown regulatory activity on proven Hormones and enzymes [3]

Flavonoids (*flavus*– yellow), are a ubiquitous group of polyphenolic items which are existent in generality plants, concentrated in the seeds, fruit skin or husk, bark and flowers. over than 4000 various flavonoids have be known to date, making them the huge group of plant chemicals. Many fruits and vegetables, mostly buckwheat, apple and onion, are several of these sources. drinks fitted from plant extracts (beer, tea, wine, fruit juice) are the major source of dietary flavonoid assimilation[4].catechin is organ of the denomination of flavonoids invite as flavanonols. They are to a large degree share in the plant kingdom. Catechin(Fig. 1) is among the most widely consumed flavonoids, which exists in many fruits[5] in green tea, black grapes, Blackberries, apples, citrus fruits, parsley, apples, and garlic[6], and catechin-type flavonoids present in many common foods[7] existent seek work is accomplished to extend and confirm a simple UV spectroscopy based methods emploing simultaneous equation for rapid.

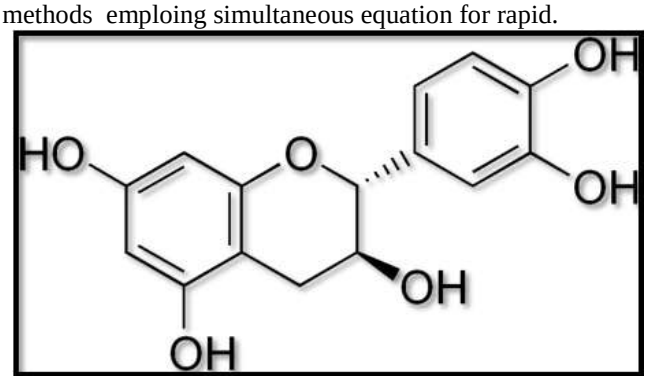


**Figure 1:** Chemical structures of the Catechin

## 2. Methods and Materials

### 2.1 Chemicals

(+)-Catechin with the purity over 99.0% was purchased from the National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). BSA was purchased from Sigma Chemical Co. (St. Louis, MO, USA). $3CdSO_4.8H_2O$ and $Ni(NO_3)_2$ were Sinopharm Chemical Reagent Co. Ltd., China. Water used in all experiments was doubly distilled water.

### 2.2 Apparatus

nm. The UV spectra were obtained on a Perkin-Elmer Lambda 17 UV spectrophotometer with the wavelength range of 200–450 nm (Perkin Elmer Corp., Edison, NJ, USA). The weight measurements were performed on an AY-120 electronic analytic weighing scale with a resolution of 0.1 mg (Shimadzu, Japan).

### 2.3 Preparation of solutions

**Prepare (Catechin):** The stock solution of Catechin ($10^{-2}$M) was prepared by dissolving (0.29027g) in 100mL volumetric flask using distilled water as a solvent.

**Cd (II) solution:** The stock solution of Cadimum (II) ($10^{-2}$M) was prepared by dissolving (0.7699g) of Cadmium sulfate octahydrate ($3CdSO_4.8H_2O$) in (100 mL) volumetric flask using water as a solvent.

**Cd (II) solution:** The stock solution of Nickel (II) ($10^{-2}$M) was prepared by dissolving (0.2908g) of Nickel Nitrate ($Ni(NO_3)_2$) in (100 mL) volumetric flask using water as a solvent.

**Stoichiometry analysis:** The stoichiometry of the complexes ligand (Catechin) with Cadimum (II) and Nickel (II) ions were determined by continuous variation method (Jobs method)[8]equimolar concentrations ($10^{-4}$M) of a ligand and Cd,Ni (II) ions were prepared, and Job's method was applied by placing 1 to 9 mL of ($10^{-4}$M) ligands solution into a series of 10mL volumetric flask, this was followed by placing 9 to 1 mL of($10^{-4}$M) Cd,Ni (II) ions solution, and the absorbance were measured at the maximum wave length.

## 3. Results and Discussion

**Absorption spectroscopy**: The optimized solvent (water) obtained by measuring the Uv-Vis absorption spectra of Catechin. **Fig 2** show spectrum in $\lambda_{max}$ =278nm.

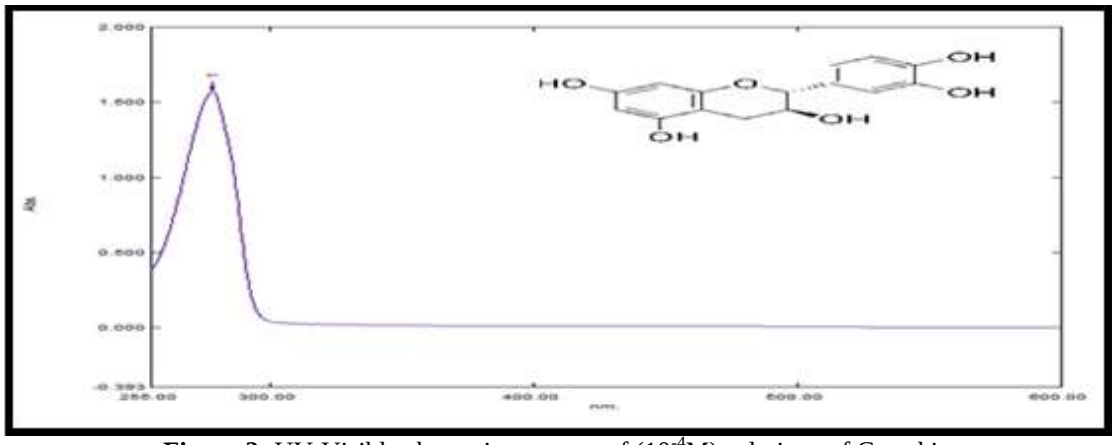


**Figure 2:** UV-Visible absorption spectra of ($10^{-4}$M) solutions of Catechin

Upon addition of Cd,Ni(II) solution to ($10^{-4}$M) chelating agent's solutions, significant changes were observed in the electronic spectra, as shown in **Table 1**. This table shows that the electronic spectra no shifts $\lambda_{max}$ to a longer wave length (bathochromic shift) upon addition of Cd (II) ion and a increase in absorbance, these evidence indicate a complex formation between the studied chelators and Cd (II) ion.

**Table 1:** Electronic spectral data of ($10^{-4}$M) Cd (II) with the Catechin

| Compound | $\lambda_{max}$ | Abs |
|---|---|---|
| **Catechin** | 278 | 0.371 |
| **Catechin-Cd** | 278 | 0.788 |
| **Catechin-Ni** | 278 | 0.823 |

**Stoichiometry of the formed complexes**

The stoichiometric ratio of Cd,Ni (II) to chelating agents (Catechin) in the complexes was determined by Jobs method of equimolar solutions. The curve displayed maxima absorbance at mole fraction $X_{max}$, which indicates the formation of complexes with metal ion to ligands ratio, Fig3

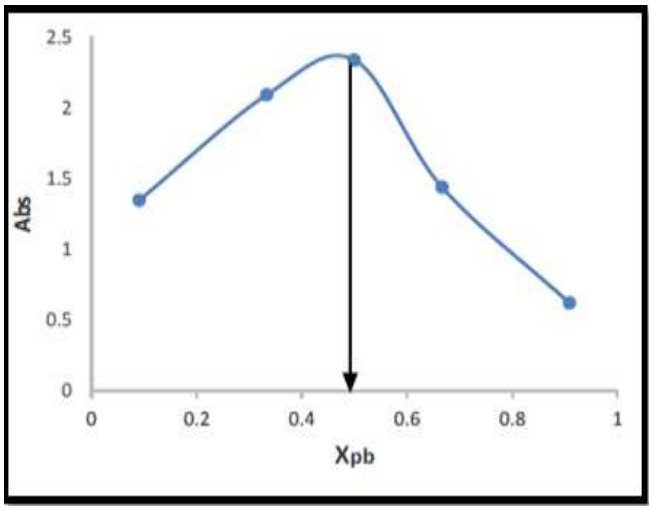


**Figure 3:** Job's plot for the composition of Cd (II) - Catechin complex at λ = 278nm.

**Stability constant (Keq):**

Equilibrium constant of stoichiometric ratio (metal: ligand) complex were evaluated by the preparation of two sets of solutions, the first one of solutions were communicated to contain stoichiometric amount of the metal ( $Cd^{+2}$) to the ligand (Catechin). The second one was formulated to contain fivefold excess of the ligand. The interaction between metal ions (M) and the ligand (L) proceeds according to the equation:

$$M + L \rightleftharpoons ML$$

α α 1-α

And $K_{eq}=[ML]/[M][L]$
Were $K_{eq}$ = stability constant.
If α is the degree of dissociation and c is the molar concentration, then the above equation (1) may be written as follows:
$K=(1-\alpha)C/(\alpha C)(\alpha C)$

$K= 1-\alpha/\alpha^2 C$ ……..(1)

$C$= concentration of the Cadimum, Nickel

Given that **α = Am - As/Am** ; where Am and As are the absorbance of the solution containing an excess and stoichiometric amount of reagent, respectively. The effect of temperature on the stability constant was studied and the results were tabulated in table2,3

**Table 2:** Stability constant of Catechin- Cd in different temperature

| | | | | **Catechin - Cd** |
|---|---|---|---|---|
| **Temp** | **$A_m$** | **$A_s$** | **α** | **$K_{eq}$** |
| **293** | 1.255 | 0.722 | 0.4247 | 7973.821584 |
| **298** | 2.416 | 1.62 | 0.3294702 | 154427.9185 |
| **303** | 2.412 | 1.59 | 0.34079602 | 141896.2118 |
| **308** | 2.355 | 1.525 | 0.35244161 | 130330.0552 |

**Table 3:** Stability constant of Catechin- Ni in different temperature

| Catechin-Ni | | | | |
|---|---|---|---|---|
| Temp | $A_m$ | $A_s$ | **α** | $K_{eq}$ |
| 293 | 1.209 | 0.811 | 0.32919768 | 15474.65657 |
| 298 | 0.797 | 0.33583333 | 0.11278403 | 14722.09052 |
| 303 | 0.788 | 0.36858974 | 0.1358584 | 11618.90359 |
| 308 | 1.212 | 0.744 | 0.38613861 | 10292.57068 |

The molar absorptivities of the complexes were calculated by recording the absorbance of a various concentration of the complexes at its stoichiometric values of each complexes and plotting of the absorbance of the complexes against concentration given a straight line with the slope equal to ($\mathcal{E}$) L . mole$^{-1}$. cm$^{-1}$ as shown in fig4

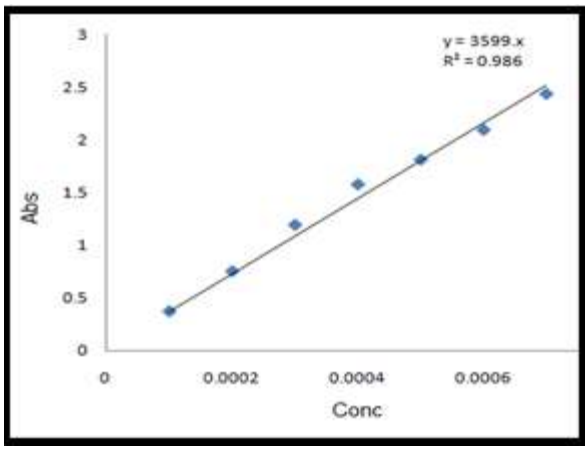


**Figure 4:** The calibration curve of Catechin

Then allows us to calculate $\Delta G^o$ at different temperatures[9].

$\Delta G^o = -RT\, lnKeq$……..(2)

**Thermodynamic parameters: Tables 4** reported the thermodynamic parameters of the complexation of Cd (II) with Catechinchelators. The enthalpy change was calculated by substituting the values of the slope of Vant Hoff plot ($lnK_{eq}$ vs. 1/T) as in equation (7) and **Figure 5,6**

$$lnK_{eq} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \text{……..(3)}$$

Slope = - ΔH/R , R = gas constant
Entropy change for the system can then be calculated from:

$\Delta G^o = \Delta H^o - T\Delta S^o$……..(4)

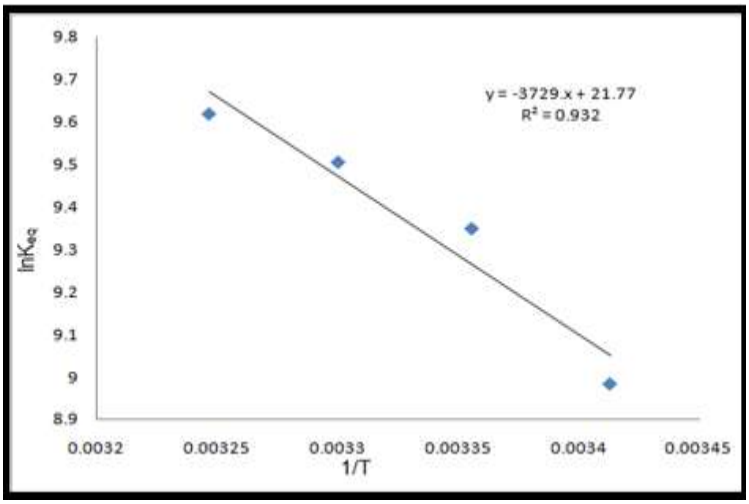


**Figure 5:** Vant Hoff plot for interaction of Catechin- Cd (II) complex at 278nm

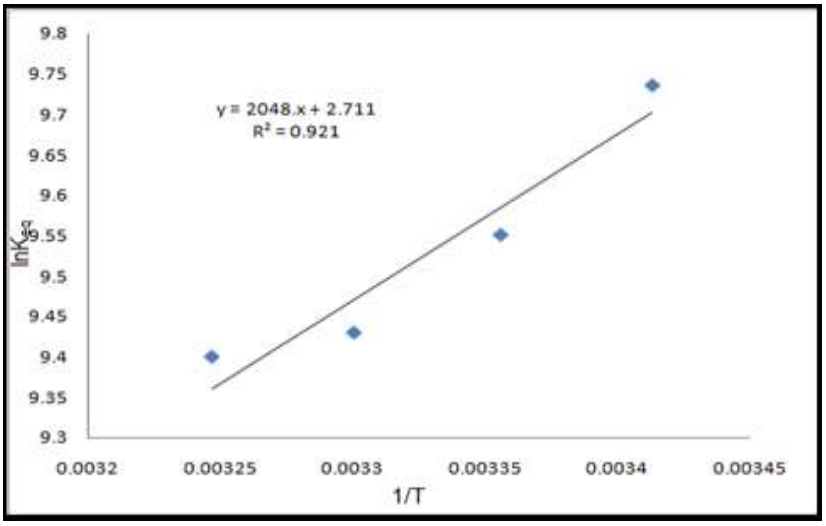


**Figure 6:** Vant Hoff plot for interaction of Catechin- Ni (II) complex at 278nm

**Table 4:** Thermodynamic parameters for Catechin- Cd (II) complex.

| Temp | $K_{eq}$ | ΔG ( J.mole$^{-1}$) | ΔH ( J.mole$^{-1}$) | ΔS (J.mole$^{-1}$.K$^{-1}$) |
|---|---|---|---|---|
| 293 | 8.983919 | -21884.8 | 31002.906 | 180.99578 |
| 298 | 9.348564 | -23161.7 | | |
| 303 | 9.504624 | -23943.5 | | |
| 308 | 9.617925 | -24628.7 | | |

**Table 4:** Thermodynamic parameters for Catechin- Ni (II) complex.

| **Temp** | **$K_{eq}$** | **ΔG ( J.mole$^{-1}$)** | **ΔH ( J.mole$^{-1}$)** | **ΔS (J.mole$^{-1}$.K$^{-1}$)** |
|---|---|---|---|---|
| **293** | 15474.65657 | -23500 | -21865.82 | **5.853056** |
| **298** | 14722.09052 | -23777.5 | | |
| **303** | 11618.90359 | -23580.1 | | |
| **308** | **10292.57068** | **-23658.9** | | |

These tables' shows that the equilibrium constant valuesincrease with increase in temperature for Cd (II) with Catechin and decrease with increase in temperature for Ni (II) with Catechin. The negative value of Gibbs free energy for this interaction indicates the spontaneous process in the direction of equilibrium. The positive value or negative value of enthalpy and entropy change refers to the type of interaction between Cd (II) and Catechin have positive $\Delta H^o$ that means endothermic process and suggest a week hydrophobic interaction, and positive $\Delta S^o$, so spontaneously are entropy driven. For Catechin-Ni(II) complexes $\Delta H^o$ were negative and $\Delta S^o$ also positive that means the process were enthalpy driven and the interaction may be ionic interaction.

## 4. Conclusion

The complex of the chelating agent (Catechin) with Cadimum (II) and Nickel(II) shows a high tendency of this antioxidant to Ni (II),Cd(II) this were obvious from the values of their equilibrium constant with the comparison with Ni(II), which were considered as a good complexing agent used. The thermodynamic parameter shows that this complexation is a spontaneous and may be entropy or enthalpy driven or both depend on a chelator's structures.

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