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Thermodynamic and kinetic studies on interaction of some transition metal ions with tryptophan

Ebrahim Ghiamati * and Zahra Abazari

Chemistry Department, University of Birjand, Birjand, 971-743-4765, Iran

* *Corresponding author at: Chemistry Department, University of Birjand, Birjand, 971-743-4765, Iran.*
Tel.: +98.056.32202065. Fax: +98.056.32202065. E-mail address: eghiamat@birjand.ac.ir (E. Ghiamati).

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ABSTRACT

Amino acid of tryptophan (Trp) was chosen as a drug. A systematic approach was made to study its interaction with some transition metal ions, and qualitatively and quantitatively examine the thermodynamic and kinetic phenomena on this model drug. To accomplish these tasks, the stability constants of Trp complexes with Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Pb(II) at temperatures of 25, 30, 35, and 40 °C were determined potentiometrically, utilizing modified Bjerrum's method. Potentiometric titrations were carried out in water, and water:dioxane mixture (50:50, *v*:*v*). Our findings showed that the stability constants of the complexes increased as the dioxane content was raised or temperature was elevated. The negative values of $\Delta G°$ are indication of spontaneity of the processes. $\Delta H°$ values are positive, conveying the complex formation is an endothermic process and $\Delta S°$ values are positive contributing more to spontaneity, causing reaction favoring and disordering. The variations of natural logarithm of the stability constants versus 1/T are linear leading to evaluation of the stability constant of the complexes at any temperature. Moreover, kinetic study gave rise to estimation of rate constant and activation energy for each complex formation process. It was concluded that the order of increasing stability of the complexes is: $k_{f\ \mathrm{Co(II)\text{-}Trp}} \approx k_{f\ \mathrm{Zn(II)\text{-}Trp}} < k_{f\ \mathrm{Pb(II)\text{-}Trp}} < k_{f\ \mathrm{Ni(II)\text{-}Trp}} < k_{f\ \mathrm{Cu(II)\text{-}Trp}} < k_{f\ \mathrm{Fe\ (III)\text{-}\ Trp}}$. Furthermore the activation energy values for the aforementioned complexes in water-dioxane mixture obeyed the following trend $E_{a\ \mathrm{Zn(II)\text{-}trp}} < E_{a\ \mathrm{Fe(III)\text{-}Trp}} < E_{a\ \mathrm{Ni(II)\text{-}trp}} < E_{a\ \mathrm{Co(II)\text{-}trp}} < E_{a\ \mathrm{Cu(II)\text{-}trp}} < E_{a\ \mathrm{Pb(II)\text{-}trp}}$.

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1. Introduction

The secondary, tertiary and quaternary structures and biochemical function of peptides and proteins are controlled by noncovalent interaction among constituent amino acids, and with various metal or organic cations [1]. The interaction between metal ions and amino acids which mimics metal-protein reactions is an interesting phenomenon. One way to understand how well these interactions could occur is evaluation of their stability constants. Among various methods for determining the stability constant of metal ion complexes, potentiometry has its own advantages. Potentiometric titration of amino acids in the presence of metal ions is generally used as a method for measuring metal complex stability constants. This technique which first was described by Bjerrum [2] and later modified by Calvin and Wilson [3,4] has been utilized extensively by numerous researches [5-18]. The solvent and temperature effect have also been examined by quite number of researchers [19-34].

L-tryptophan (Trp) is an oxidizable amino acid plays an important role in many biochemical processes. It is an essential amino acid for human and herbivores as the precursor of hormones, neurotransmitters and other relevant biomolecules. The level of Trp in plasma is closely related to the extent of hepatic disease [35]. The present study focuses on the i) Determination of the stability constant of complexes of tryptophan with Fe(III), Co(II), Ni (II), Zn(II), Cu(II) and Pb(II) metal ions in water and dioxane mixture, ii) Examination of the nature of solvent and temperature on their stability, (iii) Evaluation of thermodynamic parameters of $\Delta G°$, $\Delta H°$, and $\Delta S°$ and finally estimation of kinetic parameters, i.e., rate constant, k and activation energy, E_a.

2. Experimental

2.1. Materials and procedure

Highly pure Trp, nitrate salt of the respective metals as reagent grade, dioxane and $HClO_4$ all were purchased from Merck, Germany. All of the solutions were made by doubled distilled water (DDW). A 25.00 mL solution mixture was made containing 5.000×10^{-3} M Trp, 3.000×10^{-3} M metal ion and 1.690×10^{-2} M $HClO_4$. The sufficient amount of 0.10 M $NaNO_3$ was added to adjust the ionic strength. The solution was poured into a double walled glass reactor; it was thermosstatted to desired temperatures of 25, 30, 35 and 40 °C and then titrated with an accurately standardized NaOH solution. During the experiments the reactor was purged with N_2. The pH was corrected and recorded after each addition of titrant in increments of 0.05 mL. Each titration consumed 6-8 mL of the

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titrant, and five replicate measurements were conducted in order to check the reproducibility of the data. The calculation of the stability constants of the complexes were performed using our developed computer programme. Spectrophotometric measurements were done with a UV-Vis Specord 210 plus with a GDU computer and using thermostated matched 10 mm quartz cells. IR spectra were acquired as KBr disc by Avatar, USA 370 FT-IR.

2.2. Calibration of the glass electrode

All pH titrations were performed using a Metrohm 794 basic automatic titrator (Titrino), coupled with a thermostating bath Hero (±0.1°C). The pH meter was calibrated using Merck standard buffer solutions with pH of 4.0, 7.0 and 9.0. A combination of calomel and glass electrode was used. To compensate for acid error (pH = 2-4) of the electrode, 30 mL solution containing KCl, 0.1 M was titrated with standardized perchloric acid, following a plot of calculated pH versus read pH, and producing the equation for pH correction. To account for alkaline error (pH = 10-12) the same volume of KCl, 0.1 M solution was titrated with standardized sodium hydroxide and the pH correction equation was acquired [36].

2.3. The method for determination of stability constant

The method for determination of stability constant was established by J. Bjerrum [2]. He measured the stability of metal amines using the concentration of metal free ligand and the total ligand concentration. The key to his method was the use of the then recently developed glass electrode and pH meter. Later M. Calvin and K.W. Wilson [3] modified the method so that pH measurements made during titration of a solution containing chelating agent in the presence and in the absence of a metal ion, with a base could be used to calculate the amount of hydrogen ions released in the reaction vessel, the free ligand exponent, the degree of formation of the system, $\bar{n}$, and the stability of the metal-ligand complex. If we assume the presence of the reacting species H_2L^+ as protonated amino acid, HL as the amino acid, and L^- the anion of amino acid, then the following reactions may occur in the solution.

$$H_2L^+ \rightleftharpoons HL_{(aq)} + H^+_{(aq)} \qquad (1)$$

$$K_{a1} = \frac{[HL][H^+]}{[H_2\,L^+]} \qquad (2)$$

$$HL_{(aq)} \rightleftharpoons L^-_{(aq)} + H^+_{(aq)} \qquad (3)$$

$$K_{a2} = \frac{[L^-][H^+]}{[HL]} \qquad (4)$$

$$M^{2+} + HL \rightleftharpoons ML^+ + H^+ \qquad (5)$$

$$K_{f1} = \frac{[ML^+][H^+]}{[M^{2+}][HL]} \qquad (6)$$

$$ML^+ + L^- \rightleftharpoons ML_2 \qquad (7)$$

$$K_{f2} = \frac{[ML_2]}{[ML^+][L^-]} \qquad (8)$$

Here K_{f1} and K_{f2} are the first and the second stability constants of the complex. We define $\bar{n}$ as:

$$\bar{n} = \frac{\text{Total concentration of L bont to M}}{\text{Total concentration of M}} = \frac{C_{L_{bound}}}{C_M} = \frac{C_{L_{total}} - C_{L_{free}}}{C_M} \qquad (9)$$

The concentration of free ligand is the sum of concentration of contained ligand species at different form, i.e.

$$[L_{free}] = [H_2L] + [HL] + [L^-] \qquad (10)$$

The bound ligand concentration is then estimated as:

$$C_{L_{bound}} = C_{L_{total}} - C_{L_{free}} \qquad (11)$$

After rearrangement and substitutions we have:

$$\bar{n} = \frac{T_{H_2L^+} - [H_2L^+] - [HL] - [L^-]}{T_{M^{2+}}} \qquad (12)$$

where T_{H2L^+} is the total concentration of H_2L^+. Then:

$$\bar{n} = \frac{[ML^+] + 2[ML_2]}{[M^{2+}] + [ML^+] + [ML_2]} \qquad (13)$$

We know that:

$$T_{M^{2+}} = [M^{2+}] + [ML^+] + [ML_2] \qquad (14)$$

$$T_{HL} = [HL] + [L^-] + [ML^+] + 2[ML_2] \qquad (15)$$

Perchloric acid was added to titrand solution in excess to prevent the hydrolysis of metal ion.

$$[ClO_4^-] = T_{HClO_4} + 2\,T_M^{2+} \qquad (16)$$

T_{HClO_4} is total concentration of added perchloric acid to titrand.

$$[ML^+] + 2[ML_2] = [Na^+] - T_{HClO_4} + [H^+] \qquad (17)$$

$$\bar{n} = \frac{[Na^+] - [HClO_4] + [H^+]}{T_{M^{2+}}} \qquad (18)$$

Finally, we will have:

$$[HL] = \frac{K_a(T_{H_2L^+} - \bar{n}T_{M^{2+}})}{K_a + [H^+]} \qquad (19)$$

From plot of pH_L versus $\bar{n}$, the stability constant could be calculated.

$$K_{f1} = \frac{1}{[HL]_{\bar{n}=\frac{1}{2}}} \qquad (20)$$

$$K_{f2} = \frac{1}{[HL]_{\bar{n}=\frac{3}{2}}} \qquad (21)$$

All our calculations in this work were executed by GRCβeta computer-program developed in our lab. The software inputs are

a) Initial volume of solution containing the amino acid, metal ion, and perchloric acid,

b) The concentration of perchloric acid,

c) The concentration of sodium hydroxide,

d) The concentration of amino acid, and

e) pK_{a1} and pK_{a2} of the amino acid in the specified medium and at desired ionic strength which was found in the literature [37].

In water:dioxane mixture (50:50, *v*:*v*) and 0.1 M $NaNO_3$, Trp has pK_{a1} = 3.47 and pK_{a2} = 10.22. After insertion of the pertinent values, the software plots the corrected pH of the titrand solution versus the concentration of added standardized NaOH, plus drawing two curves, one for a $\bar{n}$ = 0.5 and the other for $\bar{n}$ = 1.5. The intersections of the potentiometric titration curve with these two curves produce two points (Figure 1) whose corresponding pHs will be used to evaluate the respective stability constants of the metal ion-amino acid complexes.

Table 1. Comparison between our obtained logarithm stability constants of Trp complexes in water at 25 °C with literature (in parenthesis) reference [14].

Log K_f	**Co (II)-Trp**	**Ni (II)-Trp**	**Fe(III)-Trp**	**Zn (II)-Trp**	**Cu (II)-Trp**
log K_{f1}	4.41 (3.86)	5.81 (5.76)	8.79 (9.00)	4.85 (5.01)	8.37 (7.80)
log K_{f2}	7.98 (-)	9.98 (10.20)	17.21 (-)	8.75 (8.20)	15.83 (15.90)

Additionally the software is capable of plotting first and second derivative of d-pH versus d-V_{NAOH} to clarify the end points.

Thermodynamic study involved evaluating ΔG°, ΔH°, and ΔS° values. The Gibb's free energy change, ΔG°, could be calculated from the equation below:

$$\Delta G^\circ = -\mathrm{RT}\ln K_\mathrm{f} \qquad (22)$$

The plot of log K_f versus 1/T produces straight line with slop equals to:

$$\mathrm{Slope} = \frac{-\Delta H^\circ}{2.303\times\mathrm{R}} \qquad (23)$$

Using the Equation (23), enthalpy changes were computed. For calculating ΔS° we have:

$$\Delta G^\circ = \Delta H^\circ - \mathrm{T}\Delta S^\circ \qquad (24)$$

Regarding kinetics study, the rate of a chemical reaction depends on the concentrations of the reacting species. For the reaction of:

$$\mathrm{aA + bB \rightarrow product} \qquad (25)$$

The rate law could be described as:

$$\mathrm{Rate = k\times[A]^n\times[B]^m} \qquad (26)$$

where n and m are the orders of the reactants and their values depend on the detailed reaction mechanism. For the n order reaction, the integrated rate equation could be represented as:

$$\frac{1}{[\mathrm{A}]^{\mathrm{n}-1}} - \frac{1}{[\mathrm{A}]_0^{\mathrm{n}-1}} = (\mathrm{n}-1)\times\mathrm{k}\times\mathrm{t} \qquad (27)$$

Regarding half-life definition, i.e., as [A] reaches to half of initial concentration we have:

$$\mathrm{t}_{\frac{1}{2}} = \frac{2^{\mathrm{n}-1}-1}{\mathrm{k}\,(\mathrm{n}-1)}\,[\mathrm{A}]_0^{1-\mathrm{n}} \qquad (28)$$

By taking logarithm from both sides of the Equation (28), we have:

$$\log\mathrm{t}_{\frac{1}{2}} = \log\frac{2^{\mathrm{n}-1}-1}{\mathrm{k}\,(\mathrm{n}-1)} + (1-\mathrm{n})\log[\mathrm{A}]_0 \qquad (29)$$

The output of plotting log $t_{1/2}$ versus log [A] is a linear with slope of (1-n) and intercept of log $\frac{2^{\mathrm{n}-1}-1}{\mathrm{k}\,(\mathrm{n}-1)}$. In practice, the amino acid is allowed to react with metal ion and the progress of the reaction is measured at different times. The plot of concentration of one component is drawn against the time. On the obtained curve an arbitrary point could be selected and its concentration is regarded as initial concentration and its corresponding time is initial time. Then the point equivalent to half of this concentration is chosen and its pertinent time is recorded. The discrepancy between these two values is the time required to reduce the concentration of the component to half. By finding other points on the cure this task could be repeated until enough data to be produced to plot log [A] versus log $t_{1/2}$.

Using experimental data the value of n could be calculated. By substituting n in the Equation (28), the rate constant, k, could be estimated. The relation between the rate constant and activation energy has been shown by the following equation:

$$\mathrm{k} = \mathrm{A}e^{\frac{-\mathrm{E_a}}{\mathrm{RT}}} \qquad (30)$$

where E_a is the activation energy in J/mol, R has the value of 8.3145.J/K.mol. Taking the natural logarithm of each side of the Equation (30), yields:

$$\ln(\mathrm{k}) = -\frac{\mathrm{E_a}}{\mathrm{R}}\left(\frac{1}{\mathrm{T}}\right) + \ln(\mathrm{A}) \qquad (31)$$

A plot of ln(k) versus 1/T produces a straight line with the slope of -E_a/R, or E_a = -R (slope) and R = 8.3145 J/K.mol.

3. Results and discussion

Figure 1 illustrates a potentiometric titration curve for Zn (II)-Trp complex in water at 25 °C. The structure of Trp has been shown on Figure 2. Table 1 exhibits a comparison between the stability constant values of the pertinent metal ion-Trp complexes in water at 25 °C. The results indicate that they are in a good agreement with the works in the literature. Table 2 demonstrates the stability constant values of the respective complexes in water-dioxane mixture (50:50, *v*:*v*) at temperatures of 25-40 °C.

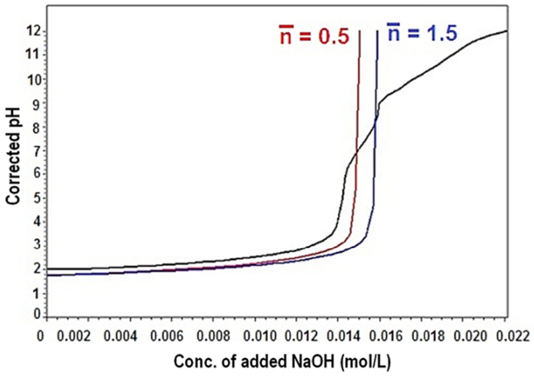

Figure 1. A plot of corrected pH versus the concentration of added standardized NaOH solution for Zn(II)-Trp in water at 25 °C.

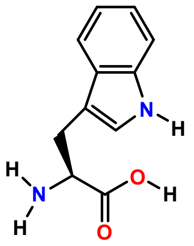

Figure 2. The structure of Trp.

The order of increasing stability is as follows:

$$\mathrm{k_{f\,Co(II)\text{-}Trp}} \approx \mathrm{k_{f\,Zn(II)\text{-}Trp}} < \mathrm{k_{f\,Pb(II)\text{-}Trp}} < \mathrm{k_{f\,Ni(II)\text{-}Trp}} < \ldots$$
$$\ldots\ \mathrm{k_{f\,Cu(II)\text{-}Trp}} < \mathrm{k_{f\,Fe\,(III)\text{-}\,Trp}} \qquad (32)$$

Table 2. Logarithm of the first and second stability constants of the respective Trp complexes in water:dioxane mixture (50:50, *v:v*).

Complex	**k_{f1} & k_{f2}**	**T (°C)**			
		25	**30**	**35**	**40**
Fe(III)-Trp	k_{f1}	9.86	9.99	10.24	10.35
	k_{f2}	19.02	19.25	19.91	20.23
Co(II)-Trp	k_{f1}	6.12	6.50	6.58	7.26
	k_{f2}	10.99	11.55	12.04	13.44
Ni(II)-Trp	k_{f1}	7.34	7.51	7.60	7.72
	k_{f2}	13.46	13.73	13.80	14.24
Cu(II)-Trp	k_{f1}	9.33	9.35	9.43	9.72
	k_{f2}	17.31	17.73	18.26	18.43
Zn(II)-Trp	k_{f1}	6.15	6.35	6.57	7.16
	k_{f2}	10.98	11.24	11.67	13.13
Pb(II)-Trp	k_{f1}	7.20	7.32	7.55	7.62
	k_{f2}	12.92	13.39	13.53	13.79

Table 3. $-\Delta G^{\circ}_1$ values for the corresponding Trp complexes in water:dioxane mixture (50:50, *v:v*).

Complex	**$-\Delta G^{\circ}_1$ (KJ/mol)**			
	25 °C	**30 °C**	**35 °C**	**40 °C**
Fe(III)-Trp	6.48	6.63	6.81	6.96
Co(II)-Trp	5.21	5.44	5.60	5.96
Ni(II)-Trp	5.69	5.84	5.96	6.12
Cu(II)-Trp	6.30	6.41	6.59	6.75
Zn(II)-Trp	5.21	5.44	5.60	5.96
Pb(II)-Trp	5.61	5.78	5.92	6.06

Table 4. ΔS°_1 and ΔH°_1 values for the related Trp complexes in water:dioxane mixture (50:50, *v:v*).

Complex	**ΔS°_1 (J/mol)**				**ΔH°_1 (kJ/mol)**
	25 °C	**30 °C**	**35 °C**	**40 °C**	
Fe(III)-Trp	33.15	33.07	33.13	33.08	3.40
Co(II)-Trp	47.55	47.51	47.26	47.65	9.52
Ni(II)-Trp	27.92	27.95	27.88	27.95	2.63
Cu(II)-Trp	30.65	30.51	30.60	30.62	3.07
Zn(II)-Trp	45.59	44.87	44.73	45.14	8.22
Pb(II)-Trp	29.51	29.65	29.65	29.51	3.18

It was found that in general $K_{f2} > K_{f1}$. This means that the first formation complex process is weaker than the second process (i.e. attraction between M^{2+} and L^- is weaker than ML^+ and L^-). Here electrostatic repulsion and steric hindrance between ligands are not important factors for the increase in the stepwise formation constant value of the complex. Figure 3 illustrates that the most stable configuration of Trp, in solution which is the outcome of quantum mechanical calculations. Regarding metal ion-Trp complexation, Indolyl group of tryptophan, does not contain any readily ionizable proton, and the side chain does not possess any clearly defined donor center to metal ions. Accordingly, the suggested structural formula for $M(Try)_2(H_2O)_2$ complex is showed in Figure 4.

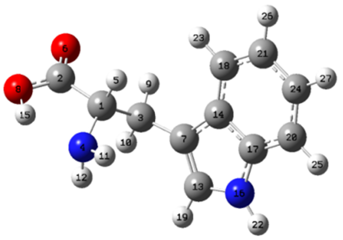

Figure 3. The most stable configuration of Trp in liquid phase, among 22 possible configurations according to quantum mechanical calculations (our unpublished results).

The variation of natural logarithm of k_{f1} versus 1/T for complex of Pb(II)-Trp has been shown in Figure 5, meaning that the stability constant for all the complexes could be evaluated at any temperature.

Table 3 shows $\Delta G_1°$ values for the respective complexes in the solvent mixture. The negative $\Delta G_1°$ values indicate that these complexation processes are spontaneous, and $\Delta G_1°$ values were increased by enhancing the temperature. The order of increasing $\Delta G_1°$ is as follows:

$$\Delta G_1°_{\text{Zn (II)-Trp}} \approx \Delta G_1°_{\text{Co (II)-Trp}} < \Delta G_1°_{\text{Pb (II)-trp}} < \ldots$$
$$\ldots \Delta G_1°_{\text{Ni(II)-Trp}} < \Delta G_1°_{\text{Cu(II)-Trp}} < \Delta G_1°_{\text{Fe (III)- Trp}} \quad (33)$$

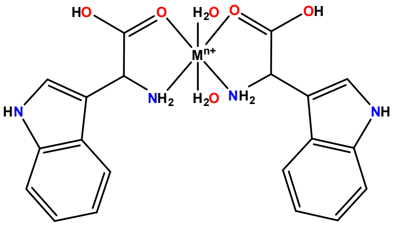

Figure 4. The proposed structure of metal ion-Trp complex.

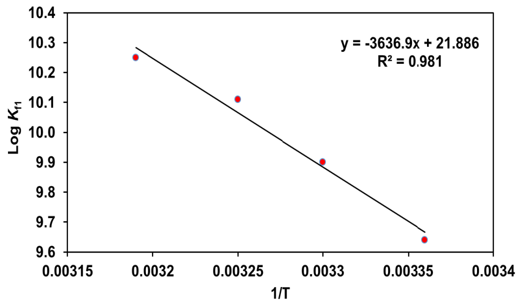

Figure 5. A plot of log K_{f1} *vs.* 1/T for Pb(II)-Trp complex in 50:50 (*v:v*) water:dioxane mixture.

The data in Table 4 shows that all $\Delta S_1°$ possessing positive values, for those complexes at 25-40 °C. Here the entropy change enforces the spontaneity of the reaction and favors the completion of the reaction because disordering has been increased.

Table 5. Activation energy (E_a) and the rate constant (k) values for the pertinent Trp complexes in water:dioxane mixture (50:50, *v*:*v*).

Complex	**E_a (J/mol)**	**k (1/s)**			
		25 °C	**30 °C**	**35 °C**	**40 °C**
Fe(III)-Trp	9.56×10^4	2.84×10^{-7}	5.12×10^{-7}	9.15×10^{-7}	1.83×10^{-6}
Co(II)-Trp	1.09×10^5	1.76×10^{-7}	3.18×10^{-7}	7.05×10^{-7}	1.41×10^{-6}
Ni(II)-Trp	1.08×10^5	2.20×10^{-7}	4.24×10^{-7}	8.36×10^{-7}	1.79×10^{-6}
Cu(II)-Trp	1.13×10^5	2.41×10^{-7}	4.93×10^{-7}	9.75×10^{-7}	2.18×10^{-6}
Zn(II)-Trp	9.52×10^4	1.82×10^{-7}	3.40×10^{-7}	6.93×10^{-7}	1.11×10^{-6}
Pb(II)-Trp	1.29×10^5	2.00×10^{-7}	3.70×10^{-7}	8.11×10^{-7}	2.50×10^{-6}

$\Delta H_1°$ values are positive and independent of temperature, also the temperature increase affects the complexation. Because M^{+2} ions exert solvation effect and L^- and M^{+2} ions with opposite charge could break, causing $\Delta H°$ and $\Delta S°$ to become positive. Although the process of Trp complex formation with a metal ion has an endothermic nature as a result of the positive $\Delta H°$ value, it could be concluded that the second formation step of complex is highly spontaneous compared to the first formation step. Positive $\Delta H°$ and $\Delta S°$ means that the reactions become spontaneous at higher temperatures.

Regarding using dioxane as a co-solvent, 1,4-dioxane-water mixture is a well-defined solvent. Changes in stability constants upon addition of 1,4-dioxane to aqueous solution is due to increase in ion-ion interactions resulting from both the decreasing dielectric constant and the change in solvent-ion and solvent-solvent interactions. As the dielectric constant decreases, the ion interaction involving the proton and anionic oxygen on the amino acid decreases to a greater extent than the ion dipole interaction between the proton and the solvent molecules. Co-solvent influences the protonation-deprotonation equilibria in solution by changing the dielectric constant of the medium, which varies the relative contributions of electrostatic and non-electrostatic interacttions.

Our outcomes demonstrate that Cu(II) complexes are more stable than the other metal ion complexes as a result of the larger ratio of valance/radius and the Jahn-Teller effect. Figure 6 shows a potential energy diagram for an endothermic reaction. The energy difference between the reactants and complex transition state is called activation energy. Higher activation energy translates lower rate of ~~as~~ reaction and more dissimilarities between the reactants and the transition states. More discrepancy between bonds in the two states leads to higher activation energy. Table 5 shows the rate constant and activation energy values for the aforementioned complexes in water-dioxane mixture.

The following trend was acquired.

$$E_{a\ \mathrm{Zn(II)\text{-}trp}} < E_{a\ \mathrm{Fe(III)\text{-}Trp}} < E_{a\ \mathrm{Ni(II)\text{-}trp}} < E_{a\ \mathrm{Co(II)\text{-}trp}} < \ldots$$
$$\ldots E_{a\ \mathrm{Cu(II)\text{-}trp}} < E_{a\ \mathrm{Pb(II)\text{-}trp}} \quad (34)$$

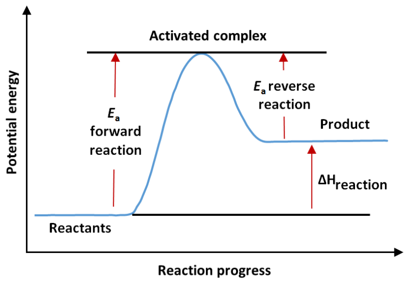

Figure 6. Potential energy diagram for an endothermic reaction.

4. Conclusions

In this study, a systematic approach was made to examine the interaction of some transition metals ions with tryptophan in water and water:dioxane mixture (50:50, *v*:*v*) at various temperatures. As was expected, cobalt and zinc complexes had the lowest stability and copper and iron the highest. Our results show that as the temperature rises, or on addition of dioxane to water, the stability constant increases, The Gibbs free energy change is negative correlating to the spontaneity of the complex formation. $\Delta H°$ and $\Delta S°$ values were positive The variations in logarithm of stability constants versus 1/T is linear evidencing that $\Delta H°_s$ are independent of temperature in temperature range of the study, and increase in entropy enforces the formation of these complexes. Regarding kinetic studies, the obtained rate constants were low, and evaluated activation energy for formation of each complex were reasonable.

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