Interaction of Cobalt(II) and Nickel(II) ions with Amino acids in Aqueous solution: A Spectrophotometric Study

Devajani Boruah

Department of Chemistry, Dibrugarh University, Dibrugarh-786 004, Assam, India

Abstract- The interactions of transition metals cobalt(II) and nickel(II) ions with the amino acids L-threonine(L-thr), L-proline(L-pro) and L-lysine(L-lys) in aqueous solution have been studied by using visible spectroscopic method. On addition of amino acids to the aqueous solution of the metal ions, a change in the visible spectra is observed due to the replacement of the water molecules from the coordination sphere of the aquo-complex $[M(H_2O)_6]^{2+}$ by the amino acid molecules.

$$[M(H_2O)_6]^{2+} + L = [M(H_2O)_5L]^{2+} + H_2O$$

(where M = Co(II) and Ni(II); L = L-thr, L-pro and L-lys). The equilibrium constants and the change of Gibbs free energy ΔG^o of the water exchange process at room temperature have been determined. For Ni(II)-H_2O-amino acid systems the equilibrium constants have been determined for five variable temperatures (318-298 K) and the corresponding thermodynamic parameters ΔG^o, ΔH^o and ΔS^o have been calculated.

Index Terms- Visible spectrophotometry, cobalt(II), amino acids, equilibrium constant, thermodynamic parameters.

I. INTRODUCTION

Amino acids are the chemical units of proteins, which construct the structure for all living organism [1] and essential for variouus biochemical processes that support the maintaining of life in the individuals [2,3]. They are good chelating agents [4] and can coordinate to transition metals through their amino or carboxylic groups [1,5]. During the last few decades the complexation of transition metal ions with amino acids have been studied [6,7,8,9]. The amino acid-metallic ion interactions are found to be responsible for enzymatic activity and stability of protein structures [10,11,12]. The metal-amino acid complexation is important field of study as they can be used as representative model systems to understand the metal-protein interaction in biological systems. Moreover the study of thermodynamic parameters will help to investigate the driving forces that lead to the formation of metal-amino acid complexes in biological systems. The anticancer, antibacterial and antifungal effects of Cobalt(III) complexes with amino acid are well proved [13]. Cobalt is an essential trace element in animal nutrition and in the form of vitamin B_{12} it is essential for human health as it stimulates the production of red blood cells. For the treatment of pernicious anaemia a small amount of cobalt is invaluable. It associates with important synthetic reactions in the metabolic process [14, 15]. Nickel is also essential for healthy life of animal. It associated with several enzymes [16]. Nickel is play a role in physiological processes as a co-factor in the absorption of iron from the intestine [17]. Any change in its concentration leads to metabolic disorder [18]. With the discovery of biological importance of cobalt and nickel, it is important to study its complexation with amino acids in order to understand more about functions of their complexes.

In the present work the interaction of L-thr, L-pro and L-lys with Co(II) and Ni(II) ions in the aqueous solution have been studied spectrophotometrically and some thermodynamic parameters are reported.
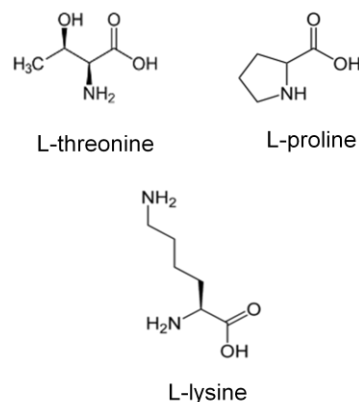

Figure 1: Used amino acides

II. MATERIALS AND METHODS

The salts $CoCl_2.6H_2O$ and $NiCl_2.6H_2O$ used in this study were of AR grade which were purchased from E.Merck. The amino acids L-lysine, L-threonine and L-proline were purchased from Loba Chemie which were used as received. The metal and amino acid solutions were prepared just before each measurement by direct dissolution salts and amino acids in doubly distilled water. The concentration of the amino acids in the sample solutions were kept as low as possible.

The visible spectra were recorded in aqueous solution by using 1 cm^3 quartz cell in the range 800-360 nm on Shimadzu UV-240 spectrometer. The variable temperature (318-298 K) experiments were performed by using temperature regulated cell holder. The pH of the solutions was measured by using Elico Li-120 pH meter.

The replacement process for Co(II)-L-lysine system can be represented on the basis of the report that only one water molecule has been replaced by the amino acid ligand from the coordination sphere of the metal ion [19].

$$[Co(H_2O)_6]^{2+} + L\text{-pro} = [Co(H_2O)_5(L\text{-pro})]^{2+} + H_2O$$

The equilibrium constants for the replacement process have been evaluated by Srivastava and Newman's linearised equation [20].

$$\frac{1}{\varepsilon - \varepsilon_o} = \frac{1}{\varepsilon_1 - \varepsilon_o} \frac{[H_2O]_f}{K[L]_f} + \frac{1}{\varepsilon_1 - \varepsilon_o} \quad \text{-------(1)}$$

where ε is the apparent extinction coefficient of the sample solution; ε_o and ε_1 are those of $[Co(H_2O)_6]^{2+}$ and $[Ni(H_2O)_6]^{2+}$ respectively. $[H_2O]_f$ and $[L]_f$ are the concentration of free solvent and free amino acid. A plot of $\dfrac{1}{\varepsilon - \varepsilon_o}$ against $\dfrac{[H_2O]_f}{[L]_f}$ gives a straight line of slope $\dfrac{1}{(\varepsilon_1 - \varepsilon_O)K}$ and intercept $\dfrac{1}{\varepsilon_1 - \varepsilon_0}$. The equilibrium constants K for the metal-amino acid systems have been calculated putting the values of the slopes and intercepts in equation (1).

The thermodynamic parameters have been calculated by using the following equations.

$$\Delta G^o = -2.303RT \log K = \Delta H^o - T.\Delta S^o$$

$$\log K = -\frac{\Delta H^o}{2.303RT} + \frac{\Delta S^o}{2.303R}$$

$$\Delta S^o = (\Delta H^o - \Delta G^o)/T \quad \text{----------(2)}$$

Where ΔG^o is the Gibbs free energy change, ΔH^o is the change of enthalpy and ΔS^o is the change of entropy. ΔH^o were calculated from the slope($-\Delta H^o/2.303R$) of the straight line found from the plot of log K against 1/T. The standard entropy change, ΔS^o of the replacement process can be calculated by using equation (2).

III. RESULTS AND DISCUSSION

The absorption peak for $[Co(H_2O)_6]^{2+}$ ion has been observed at 502 nm. The spectra of $[Ni(H_2O)_6]^{2+}$ ion shows three peaks at 392 nm, 656 nm and 736 nm respectively. The equilibrium constants for Ni(II) ions have been determined with respect to the sharper peak at 392 nm. The peaks of Ni(II) shifted towards blue to ~385 nm on addition of amino acids to their aquo-complexes.

The both amino acids L-threonine and L-lysine are tridentate with the three coordination sites –COOH, –NH₂, –OH and COOH, –NH₂ –NH₂ respectively while L-proline has two viz., –COOH, –NH–. In aqueous solution Co(II) and Ni(II) ions exist as octahedral $[M(H_2O)_6]^{2+}$ [21] aquo ions. When amino acid is added to the aquo ion, replacement of water molecules by amino acids occur from the coordination sphere of the metal ions. The

coordination mode of amino acids to the metal center depends on the pH of the solution. In solution amino acids exist as zwitter ion predominantly at pH ≤ 7 [22,23] and the amino acids behave as monodentate ligand coordination of the amino acids to the metal centre occurs through the oxygen atom of its carboxylate group. When the pH of the solution is 12, both the nitrogen and oxygen atoms take part in coordination with the metal ions [24]. The equilibrium constants for Co(II) and Ni(II) ions complexes with the L-threonine, L-proline(L-pro) and L-lysine(L-lys) are listed below (Table 1).

Table 1: The equilibrium constants and ΔG^o at 25°C

Metal ions	Amino acids	pH	Log K	$-\Delta G^o$ kJmol⁻¹
Ni(II)	L-pro	5.19	3.245	18.515
	L-thr	5.67	3.186	18.179
	L-lys	5.97	3.069	17.511
Co(II)	L-pro	5.04	2.350	13.409
	L-thr	5.29	1.981	11.303
	L-lys	5.88	1.785	10.185

The equilibrium constants for Co(II)-amino acid complexes are lower than the Ni(II)-amino acid complexes which reflects the good agreement of the results of Irving-Willium order [25]. For both the metals-amino acid complexes the equilibrium constants for the amino acids is of the order L-pro > L-thr > L-lys. The lower value of equilibrium constants of Co(II) and Ni(II) complexes of L-threonine and L-lysine than L-proline complexes is due to the presence of bulky substituent into the ligand molecules [26]. The lowest value of equilibrium constants for L-lysine is due to the formation of sterically hindered eight membered ring [27] as it bearing another –NH₂ group in its structure which make the sample solution more basic lead to the formatin of the big ring which causing lower stability in the complex. The higher stability of the complex of L-threonine over L-lysine can be attribute to the intramolecular hydrogen bonding in threonine complex that forms due to the presence of polar –NH and –OH groups [28,29,30]. The negative value of ΔG^o of all the complexes indicates the spontaneity of the reactions and the most stable complex having hight $-\Delta G^o$ value.

The equilibrium constants for Ni(II)-amino acid complexes at temperature range 318 K-298 K are given bellow (Table 2). With the increase of temperature, the equilibrium constants for the Ni(II)-amino acid system decreases (Figure 2) which may be attributed to the exothermic nature of the reaction.
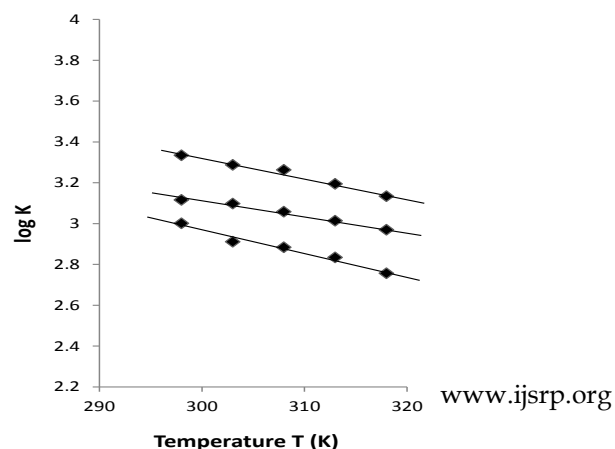
[7] A. Marcu, A. Stanilaa, O. Cozar, L. David; *Journal of Optoelectronics and Advanced Materials*, **2008**, 10(4), 830–833.

[8] C. Auclair, E. Voisin, H. Banoun, C. Paoletti, J. Bernadou, B. Meunier, *J. Med.Chem*. **1984**, 27, 1161.

[9] Y. Baran, S. Baran, N. K. Tunali, *Tr.J. of Chemistry*, **1997**, 21, 105-110.

[10] L. R. Dinelli, T. M. Bezerra, and J. J. Sene, *Curr. Res.Chem.,* **2010**, 2, 18-23.

[11] URL:http://scialert.net / abstract. Acessed on 21/08/2010. 2.

Figure 2: Variation of log K with temperature T

Table 2:

Thermodynamic parameters for Ni-amino acid-H_2O systems

Metal ions	Amino acids	pH	Temp. T K	$(I/T) \times 10^{-3}$ K^{-1}	log K	$-\Delta G^o$ kJ mol^{-1}	$-\Delta H^o$ kJ mol^{-1}	ΔS^o Jk^{-1} mol^{-1}
Ni (II)	L-pro	5.17	298	3.36	3.334	19.023	15.557	11.631
			303	6.30	3.287			
			308	3.25	3.262			
			313	3.19	3.194			
			318	3.14	3.133			
	L-thr	5.47	298	3.36	3.115	17.774	15.318	8.242
			303	6.30	3.097			
			308	3.25	3.057			
			313	3.19	3.013			
			318	3.14	2.969			
	L-lys	5.99	298	3.36	3.000	17.118	15.088	6.812
			303	6.30	2.910			
			308	3.25	2.883			
			313	3.19	2.833			
			318	3.14	2.756			

IV. CONCLUSION

The interactions of cobalt(II) and nickel(II) ions with the amino acids L-threonine, L-proline and L-lysine in aqueous solution have been studied by visible spectroscopic method. The equilibrium constants for Ni(II)-amino acid complexes are found to be higher than the Co(II)-amino acid complexes. The equilibrium constants for the amino acids follow the fellowing order L-pro > L-thr > L-lys. Different thermodynamic parameters have been calculated. Stability of the metal-amino acid complexes have been compared.

REFERENCES

[1] K. Asemave, S. G. Yiase, S. O. Adejo and B. A. Anhwange, *International Journal of Inorganic and Bioinorganic Chemistry,* **2011**, 2 (1), 11-14.

[2] http://www.crystalyouth.co.za/Documents/Amino%20Acids.htm.

[3] R. H. Garret, C. M. Grisham, *Biochemistry*, Sanders, New York, **1995**, p. 216.

[4] J. H. Ottawa and D. K. Apps, *Biochemistry,* ELBS, London, **1984**.

[5] N. Visfiliumurthy and P. Lingaiah, *Ind. J. Chem.*, **1986**, 25 (A), 875.

[6] T.R. Rap, M. Sahay and R. C. Aggarwal, *InSt. J. Chem*., **1984**, 23 (A), 214.

[12] S. S. Dara, A textbook of *Environmental Chemistry and Pollution Control,* S. Chand and Company Ltd, India, **2005**, p. 67-69.

[13] Z. H. Chohan, M. Arif, A. M. Akhartar, C. T. Spuran, *Bioinorganic Chem. Appl.,* **2006**, 1-3.

[14] Agency for Toxic Substances and Diseases Registry, Toxicological Profile for Cobalt, US Department of Health and Human Services, **2004**.

[15] J. C. Bailer Jr., H. J. Emelens, Sir R.Nyhlom, A. F. T. Dickenson, *ComprehensiveInorganic Chemistry,*Pergamon Press, Oxford, New York, **1973**, 3, 1056.

[16] R. A. Poellot, T. R. Shuler, E. O. Uthus and F. H. Nielsen, *Proc. Natl Acad.Sci.*, USA, **1990**, 44, 80.

[17] F. H. Nielsen, *J. Nutr,* **1980**, 110, 965-73.

[18] A. F. Kolodziej, *Prog. Inorg. Chem.*, (ed. K.D. Karlin), Wiley, New York, **1994**, 41, 493.

[19] K. Ozutsumi and H. Ohtaki, *Bull. Chem.Soc. (Japan)*, **1984**, 57, 2605.

[20] M.T. Beck, *Chemistry of Complex Equlibria*, Von Nostrand Reinhold Company, London, **1970**, 188.

[21] J. D. Lee, *Concise Inorganic Chemistry*, 5th ed., Blackwell Science Ltd., **1996**.

[22] D. Feakins, R. D. O. Neill, W. E. Waghorne and A. J. I. Ward, *J. Chem. Soc. Fara. Trans*. I., **1982**, 78, 143.

[23] M. Castillo and E. Ramrez, *Trans. Metal*. , **1984**, 9, 268.

[24] Y. B. Yakolev and V. G. Ushakova, *Russ. J. Inorg. Chem*., **1983**, 28(8), 1217.

[25] Shriver and Atkins, *Inorganic Chemistry*. 3rd ed., Oxford University Press, **1999**, 244.

[26] A. K. Jain and F. Khan, *J. Indian Chem. Soc.*, **1998**, 75, 31.

[27] J. P. Greenstein and M. Winitz, *Chemistry of Amino Acids*, Wiley, New York, Vol.1, **1961**.

[28] F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, A comprehensive Text, 4th ed., John Wiley and Sons, New York, **1980**, p. 1310-1344.

4

[29] P. Satya, G. D. Tuli, S. K. Basu and R. D. Madan, *Advanced Inorganic Chemistry,* Vol. I, S. Chand and Company India, **2006**, p. 705-706.

[30] P. Satya, G. D. Tuli, S. K. Basu and R. D. Madan, *Advanced Inorganic Chemistry,* Vol.II, S. Chand and Company India, **2006**, p. 30-52.

First Author – Devajani Boruah, Research Scholar, Department of Chemistry, Dibrugarh University, Dibrugarh-786004, Assam, India
E-mail:devajani5bboruah@gmail.com