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Spectrophotometric Study of Stability Constants of Co(II), Ni(II) and Cu(II) Complexes of 2, 2 – Bipyridine at Different Temperatures

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ABSTRACT

Complexation of Co(II), Ni(II) and Cu(II) with 2, 2– bipyridine (bpy) have been studied spectrophotometrically at absorption maxima for Co(bpy), Ni(bpy) and Cu(bpy), of 400, 400 and 680nm respectively. The complexations were carried out at temperatures 30°C, 40°C, 50°C and 60°C at the wavelengths of the respective complexes. The stoichiometry of the complexes were determined using Job's continuous variation method and the value was found to be 1:2 metal to ligand ratio. Stability constants (K) values were calculated using the continuous variation method and found to be in the order 3.51×10^3, 3.30×10^3 and 2.88×10^3 respectively for Cu-bpy, Ni-bpy and Co-bpy. The complexes were found to be stable over the temperature range used as there was slight change in the color intensity and absorbance values. From the thermodynamic parameters ΔG, ΔS and ΔH values, the reactions were all spontaneous and exothermic.

Keywords: Cobalt(II), Copper(II), Nickel(II), Spectrophotometric, Stability constant, Thermodynamic parameters

INTRODUCTION

Stability constants of metal ion complexes of various ligands and especially chelating ligands using different methods such as potentiometric and spectrophotometric techniques have been determined (Na'aliya and Aliyu 2010; Payehghadr *et al*., 2009; Sandra *et al*., 2007; Syed *et al*., 2010; Adedibu *et al*., 2011). Stability constant of a complex ion is influenced by factors such as ligand type, metal ion type, counter-ions and solvent (Reza, 2012).

Similarly, thermodynamic study of complex formation between metal ions and various ligands have been reported (Paola and Raffaele 1989; Nezhadali and Taslimi 2003; Smith and Martell, 2005).

However, despite the numerous work carried out in the area of stability constant and thermodynamic parameters and the fact that stability constant dependence on temperature during complexation reaction have been found useful in obtaining thermodynamic parameters as reported by Thakur and Conca (2013). It is still desirable to carryout more of such determinations owing to the various roles played by chelating ligands and the numerous uses of the corresponding chelate complexes in biological systems (Balaji, 2008).

Co(II) is used by animals to make essential enzymes which function as catalyst and its role in the natural production of B-12 vitamins that ensures the production of adequate red blood cells in animals. Ni(II) is important because of its ability to replace other metal ions in enzymes and proteins or to bind to cellular compounds containing O^-, S^- and N^- atoms such as enzyme and nucleic acids. It is essential for healthy life of humans and animals and its deprivation profoundly impairs intestinal absorption of iron and thus causes anaemia. Both glucose and glycogen concentrations in the liver and serum are reduced by 90% on nickel depletion. Albumin is the principal nickel (II) binding protein in human serum (Cempel and Nikel, 2005). Cu(II) which occurs in plants in smaller quantity is found in diets such as cereals, meat and vegetables and it has been reported to form stable complex with N, O, and S ligands (Nursen and Arslan 2003).

2, 2-bipyridine, a bidentate ligand, is a colorless solid and soluble in water. Upon bonding to metal ions, the related N, N-heterocylic ligand phenanthroline, does not incur an enthalpic and entropic penalty, hence its complexes become stable (Smith and Martel, 2005).

Chelating ligands are useful in detoxification of poisonous metals (Adedibu *et al*., 2011) and can form more bonds to the metal ion thereby enhancing higher affinity for the metal ions when compared to the monodentate ligands.

Stability constant values of various metal ion complexes involving chelating ligands such as Ni(II) – famotidine $C_8H_{15}N_7O_2S_3$ complex, Cu-Dapsone complex, Co(II), and Ni(II) – mixed ligand complexes of amino acids and imidazole, Cu(II)-amino acids that have polar uncharged groups and Be(II) / Co(II) – proline complexes have been reported (Syed *et al*., (2010); Adedibu *et al*., (2011)). Based on the available literature no study have been reported for the determination of mole ratio, stability constant, thermodynamic parameters $(\Delta G, \Delta H \text{ and } \Delta S)$ using spectrophotometric for the Co(II), Ni(II) and Cu(II) complexes of 2,2-bipyridine at different temperatures.

MATERIALS AND METHODS

All the reagents used in this work were of analytical grade purity and were used without further purification. All weighings were carried out using Adventurer AR3130 analytical balance, while spectrophotometric measurements were obtained on Jenway 6305 Spectrophotometer.

0.01M $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ and $CuCl_2.2H_2O$ were prepared by dissolving 0.238g, 0.237g, and 0.171g respectively in a 100cm^3 volumetric flask each. Similarly, 0.01M solution of 2, 2-bipyridine was prepared by weighing 0.156g of $C_{10}H_8N_2$ and dissolved in 100cm^3 volumetric flask.

The stoichiometric ratio of M(II) to ligand in the complexes were determined by Job's continouos variation method as described by Syed, (2010) and Adedibu *et al*. (2011). Series of volumes (0, 1, 2, 3, 4, 5, 6cm^3) of the 0.01M of M(II) solutions were respectively pipetted into seven 50cm^3 volumetric flasks and aliquot (6, 5, 4, 3, 2, 1 and 0cm^3) of the 0.01M ligand were added, keeping the mole fraction of the solution constant. The absorbances of each of the solution was taken at the wavelength of maximum absorbance of the complex which was initially determined by varying the wavelengths from 400 – 800nm. The procedure was repeated for each of the mole fractions of the complex at various temperatures 60^{0}C, 50^{0}C, 40^{0}C, and 30^{0}C and the respective absorbances recorded at the point of mixing.

RESULT AND DISCUSSION

The stoichiometric study of the complexation reaction using the continous variation method gave a 1:2 (metal : ligand) in all the Co(II), Ni(II) and Cu(II) 2, 2 –bipyridine chelate complexes. (Figs. 1 – 3). This result is consistant with the findings of Eugenijus *et al*. (2011), Aliyu and Bilyaminu (2011). This value suggests that the ligand bounds to the central metal ion via four N-atoms forming a ring.

Values of the stability constant K, for the complexes (Table 1) were obtained as reported by Syed, (2010) and Adedibu *et al.* (2011) from the relation;

$$K = \frac{{A_2}/{A_1}}{\left(1 - \frac{A_2}{A_1}\right)(C_M - C_L)(\frac{A_2}{A_1})}$$

Where A_2 = Absorbance value at peak point, A_1 = Absorbance at break point, C_M = Concentration of metal ion and C_L = concentration of ligand

The values were found to vary according to the order 3.51 x 10^3, 3.30 x 10^3 and 2.88 x 10^3 respectively for Cu(bpy) > Ni(bpy) > Co(bpy) indicating high stability of the complexes. This high stability of the chelates can be attributed to resonance, from the benzene rings where there could be delocalization of electrons between the ligand-metal π-bonding thereby providing extra stability for the chelates, Chelate rings prevent complexes from distorting either by elongation or compression of bonds, which consequently stabilizes the complex ion. In the case of bpy complexes, this could be higher due to its bulkiness/sterric hindrances which is capable of preventing the dissociation of the complex in solution.

Thermodynamic parameters of the complexes (Table 1) were obtained from the various Van't Hoff's plots of lnK against 1/T (natural logarithm of stability constant against absolute temperature) from the relation;

$$lnK = \frac{\Delta H}{R} - \frac{\Delta S}{RT}$$

From the slope (-ΔS/R), where R is universal gas constant, the values of entropy change (ΔS) were obtained, while the intercept (ΔH/R) allows for the computation of the respective enthalpy change (ΔH). Values of Gibb's free energy change ΔG, were obtained from the relation;

$$\Delta G = \Delta H - T\Delta S$$

and all the values were found to be negative, suggesting a feasible exergonic process; which agrees closely with the findings of Sung-Nak *et al.* (2001). The exothermicity of the complexation varies in the order Co(bpy) < Ni(bpy) < Cu(bpy) which may be related to increased nuclear charge across the period. ΔS values were all large and positive, indicating spontaneous complexation reactions.

CONCLUSION

Complexes resulting from the coordination of the metal ions with the chelating ligand (2,2 – bipyridine) are thermodynamically stable, a property which accounts for the numerous applications of the complexes.

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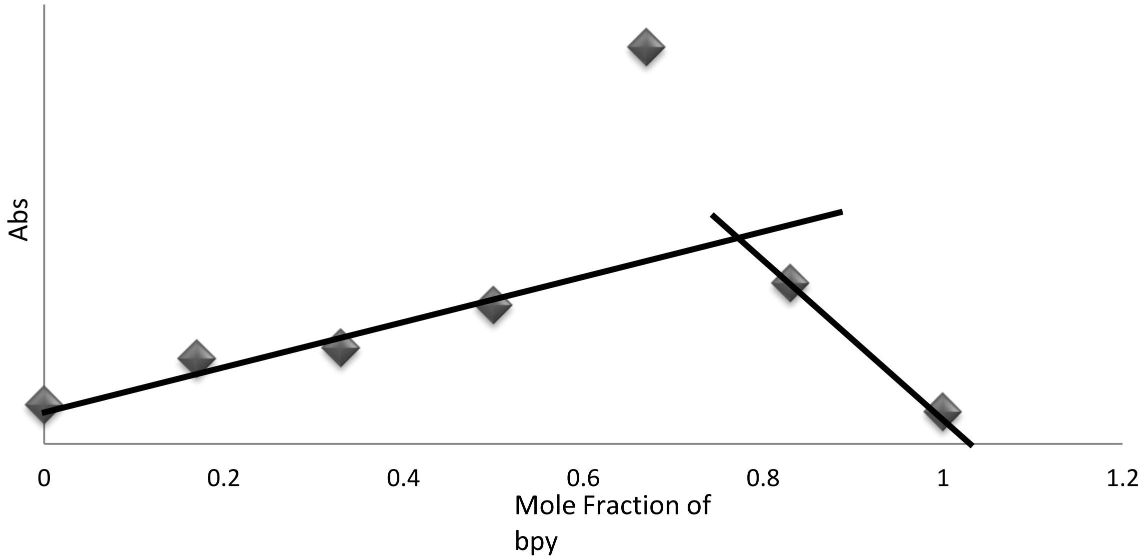

Fig. 1: Mole Ratio Determination (Job's Method) for Co(bpy) Complex

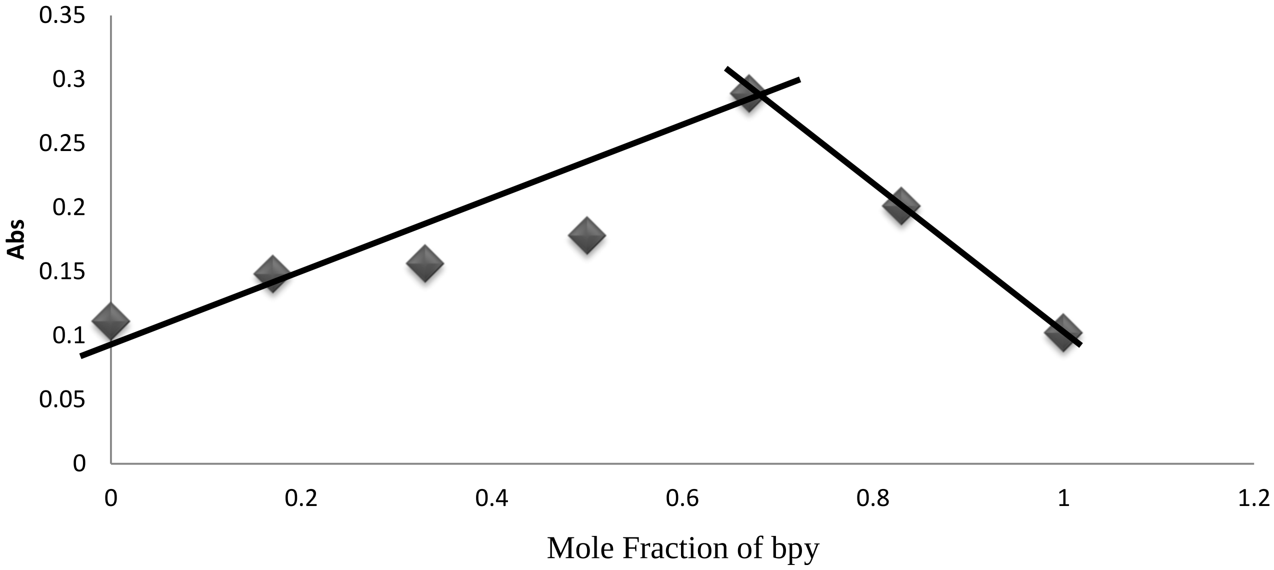

Fig. 2: Mole Ratio Determination (Job's Method) for Ni(bpy) Complex

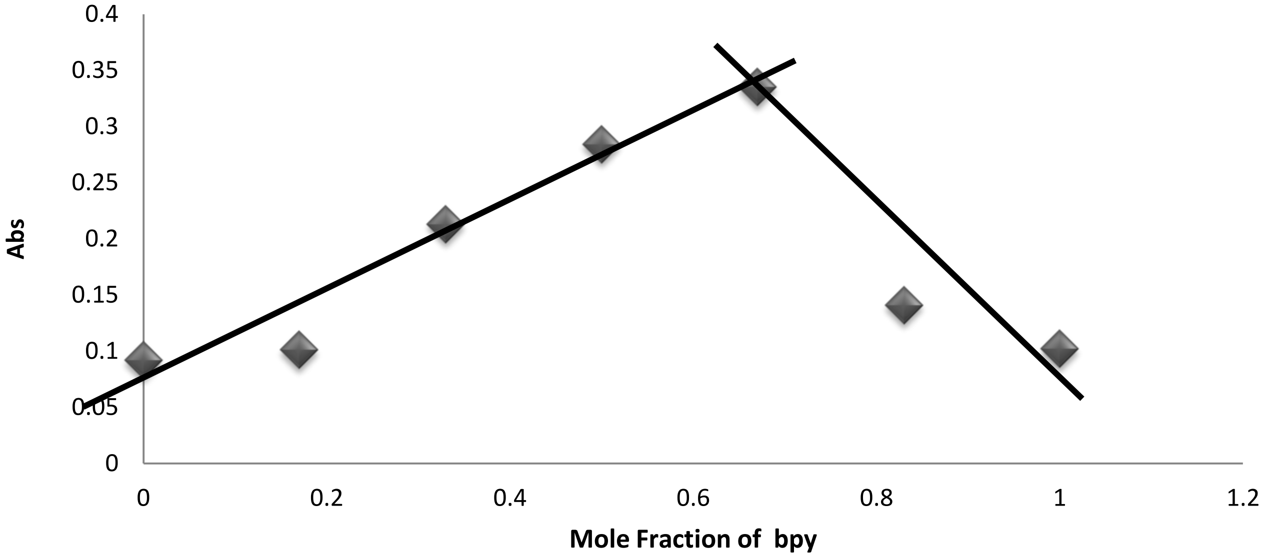

Fig. 3: Mole Ratio Determination (Job's Method) for Cu(bpy) Complex

Table 1: Thermodynamic Properties of the Complexes

	K (x 10^3)				ΔG(kJmol^{-1})				ΔH	ΔS
Complex	**303K**	**313K**	**323K**	**333K**	**303K**	**313K**	**323K**	**333K**	**(kJmol^{-1})**	**(kJmol^{-1}K^{-1})**
Co(bpy)	2.88	2.94	3.14	3.31	-6.516	-6.961	-7.407	-7.852	-6.983	44.55
Ni(bpy)	3.30	3.60	3.97	4.54	-2.232	-2.619	-3.006	-3.390	-9.478	38.65
Cu(bpy)	3.51	3.82	4.51	4.96	-1.486	-1.865	-2.242	-2.621	-9.976	37.83

REFERENCES

Adedibu, C. T., Joshua, A. O. and Gabriel, K. O. (2011). Spectrophotometric Study of Stability Constants of Dapsone – Cu(II) Complex at Different Temperatures. *J. Pharmacy Research*, 4(1):241 – 244.

Aliyu, H. N. and Bilyaminu, U. L. (2011). Studies on Bis (paranisidine acetylacetonato) Nickel (II) Complex. *Bayero Journal of Pure and Applied Sciences*, 4(1):32 – 35.

Balaji, R. J. (2008). Transition Metal Compleexes and Catalysis. *Resonance*, 4(9): 63 – 81.

Cempel, M. and Nikel, G. (2005). Nickel: A Review of its Sources and Ennvironmental Toxicology. *Polish J.Environ. Stud.* 15(3): 375 – 382.

Eugenijus, N., Ina, S., Aldona, J. and Kestutis, P. (2011). Cu(II) Complex Formation with Pentaethylene hexamine: Determination of Stability Constants by the Ligand Displacement Method. *Chemija*, 22(2): 131 – 137.

Naaliya, J. and Aliyu, H. N. (2010). Potentiometric Titration with Sodium Hydroxide for Determination of Stability Constants of Iron, Manganese, Cobalt and Nickel Complexes of Glycine in Aqueous Solution. *Bayero Journal of Pure and Applied Sciences*, 3(2): 101 – 106.

Nezhadali, A. and Taslimi, Gh. (2003). Thermodynamic Study of Complex Formation Between 3,5 – di iodo-hydroxy quinoline and Zn^{2+}, Ni^{2+} and Co^{2+} Cations in some Binary Solvents using Conductometric Method. *Alexadria Engineering Journal*, 52: 797 – 800.

Nursen, S. and Arslan, S. (2003). Antimicrobial Activities of some New Amino Acids Schiff Base. *Indian J. of Chemistry*, 16(2): 283 – 288.

Paola, A. and Raffaele, P. (1989). Ligand – Ligand Interactions in Metal Complexes. Thermodynamic and Spectroscopic Investigation of Simple and Mixed Copper (II) and Zinc (II) Substituted Malonate Complexes with 2,2 – Bipyridyl in Aqueous Solution. *J. Inorg. Chem*. 28(18):3555 – 3561.

Payehgadr, M., Ali Akbar, B. and Fraydoun, A. (2009). Spectrophotometric and Conductometric Studies of the Thermodynamics of Complexation of Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+} and Cd^{2+} ions with a New Schiff Base Ligand in Acetonitrile Solution. *African Journal of Pure and Applied Chemistry*, 3(5): 92 – 97.

Reza, E. S. (2012). Synthesis and Determination of Stability Constants of Bis – 1,2,4 – triazole Ligand for Complexation with Zn (II), Ni (II) and Cu (II) in Acetonitrile Medium. *AJAC*, 3(6): 437 – 442.

Sandra, S. K., Blaga, C. R., Zoran, B. T. and Slavica, B. I. (2007). Spectrophotometric Study of Co (II), Ni (II), Cu (II), Zn (II), Pd (II) and Hg (II) Complexes with Isatin – B – thisemicarbazone at 30°C. *J. Serb. Chem. Soc*. 72(10): 975 – 981.

Smith, R. M. and Martell, A. E. (2005). Thermodynamic Parameters of the Formation of 3d transition Metal Complexes.*J. Theoretical and Experimental Chemistry*, 41(2): 83 – 93.

Sung-Nak, C., Sun-Geum, P., Young-Jin, K, and Young-Inn, K.(2001). Thermodynamic Parameters for Complexation of some 3d – Divalent Transition Metal ions with L – proline, L – thiaproline and trans – 4 hydroxy – L – Proline in Aqueous Solution. *Bull. Korean Chem. Soc.* 22(7): 779 – 781.

Syed, A. T., Wattoo, M. H. S., Sarwar, S., Wattoo, F. H., Ghanghro, A. B. and Iqbal, J. (2010). Spectrophotometric Study of Stability Constants of Ni (II) – Famotidine Complex at Different Temperature. *Arabian Journal of Chemistry*, 3(2): 206 – 210..

Thakur, P. and Conca, J. (2013). Complexation Thermodynamics and Structural Studies of Am^{3+}, Cm^{3+} and Ln^{3+}. *Radiochim Acta*. 101: 221 – 232.