

Thermodynamics and stability of Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} complexes with DL-2-amino butanedioic acid

SHARDA SONI^{1*} and K.D. GUPTA

¹Department of Chemistry, Swami Keshvanand Institute of Technology, M&G, Jaipur - 302 025 (India).
Department of Chemistry, Malaviya National Institute of Technology, Jaipur - 302 017 (India).

(Received: December 30, 2009; Accepted: February 01, 2010)

ABSTRACT

pH metric titration technique has been employed to study the formation and composition of complexes of divalent Co, Ni, Cu and Zn with DL-2-amino butanedioic acid. Formation curve reveals the formation of 1:1 and 1:2 metal ligand complexes in the pH range 4.30-8.85. Their stability constant have been determined at 20°C, 30°C and 40°C and a different ionic strength viz. 0.05M, 0.1M, 0.15M and 0.2M NaClO_4 by Irving Rossotti method which follow the order $\text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$ which is in agreement with Irving Williams series. The change in thermodynamic parameter ΔG , ΔH and ΔS accompanying complexation have been evaluated at 30°C. The stability constant and thermodynamic function of these metal complexes are discussed in relation to ionic radii, electronegativity and ionization potential of title metals.

Key words: Thermodynamics, stability of Co^{2+} , Ni^{2+} , Cu^{2+} and DL-2-amino butanedioic acid.

INTRODUCTION

From the survey of chemical literature¹⁻⁹ it has been found that, the scanty work has been reported on the behaviour and metal complexes of DL-2-amino butanedioic acid as such the present work has been undertaken reporting the formation, composition and stability constant of Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} complexes at different temperature 20°C, 30°C and 40°C and varying ionic strengths 0.05M, 0.1M, 0.15M and 0.2M by pH metric titration technique. The thermodynamic function viz. free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) of the complexation reaction have also been determined and explained.

The stability constants and thermodynamic parameters of these metal complexes are discussed on the basis of several physical properties of the title metals such as ionic radii, electronegativity and second ionization potential of the title metal ion.

EXPERIMENTAL

DL-2-amino butanedioic acid was obtained from E. Merck Nickel sulphate, Copper sulphate, Cobalt chloride, Zinc chloride and other reagents of Anala-R B.D.H. grade.

Procedure

pH measurements were made on a EC digital pH-meter (accuracy ± 0.01 pH) with combined glass-calomel electrode assembly in a nitrogen atmosphere. The instrument was standardized with standard buffers. A thermostat having an accuracy of $\pm 0.1^\circ\text{C}$ maintained the temperature of the cell. Requisite amounts of NaClO_4 were added to the solution mixture for maintaining the ionic strength.

The experimental procedure as described earlier (1) involves a series of pH titration of ligand with 0.1M NaOH in the absence and presence of

metal ions at different metal ligand ratio, keeping the total volume 25 ml in each case. For qualitative detection of complex formation, stoichiometric pH titration were performed for the solutions having metal ligand ratio 1:1, 1:2, 1:3 and 1:4. After each addition of titrant NaOH, pH meter readings were noted on reaching equilibrium. Curves were plotted between pH and moles of alkali required per mole of ligand 'm' the inflections in the curves reveal the formation of complexes in solutions from which the stoichiometry has been evaluated.

The stability constants of metal ligand complexes were evaluated by employing Irving Rossotti method¹⁰⁻¹¹ pH titration technique keeping the ratio of metal to ligand constant at 1:5 using 8×10^{-3} M HClO_4 for initial lowering of buffer region.

RESULT AND DISCUSSION

The values of formation function \bar{n} were plotted against the corresponding free ligand concentration (pL) values to get the formation curves of the metal complexation equilibrium. From these formation curves, the values of stability constants, $\log K_1$ and $\log K_2$ were calculated which correspond to pL values at = 0.5 and 1.5 respectively. The $\log K$ stab values were determined at different temperature 20°, 30°C and 40°C and at varying ionic strength 0.05M, 0.1M, 0.15M and 0.2M in the pH range 4.25-8.85 are summarized in table 1 and 2 which follow the sequence.



which is in agreement with Irving William¹²⁻¹³ order of stability constants of bivalent metal complexes.

Effect of Temperature and Ionic strength

It is seen from Table 1 that the stability constants gradually increase with rise in temperature showing thereby that higher temperature favours the formation of stabler complexes. The effect of increase in ionic strength from 0.05M to 0.2M on the stability has been examined and it is observed that $\log K$ increases with rise in ionic strength. These changes have shown in Table 2.

The stability constants of these transitional

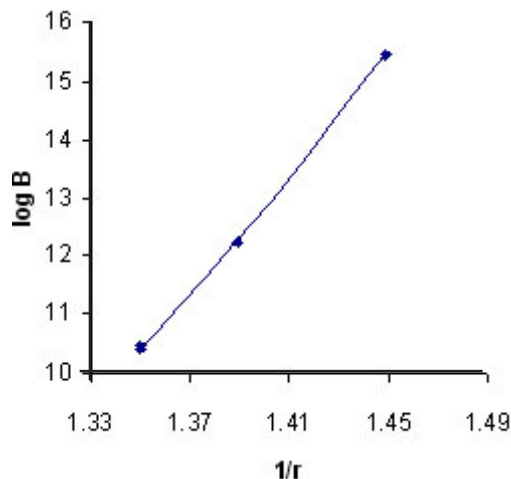


Fig. 1: Plot of log B vs 1/r at 30°C

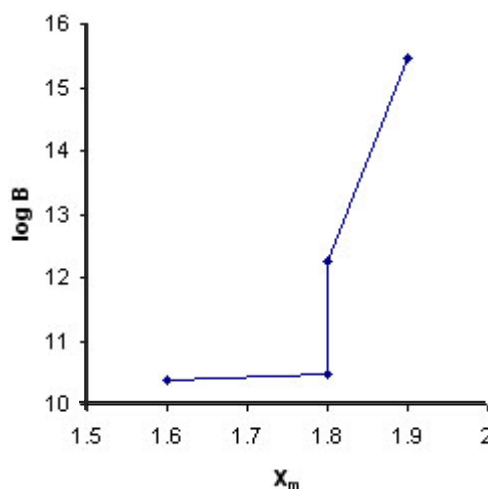


Fig. 2: Plot of log B vs $X_m \times$ at 30°C

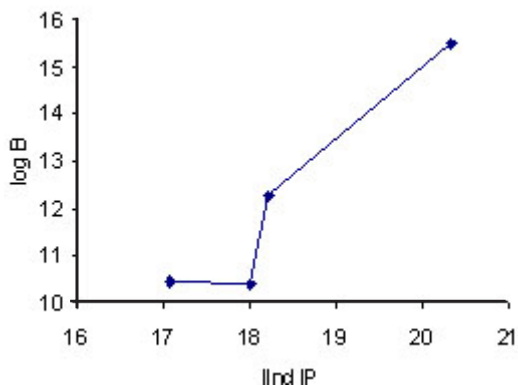


Fig. 3: Plot of log B vs ionization potential at 30°C

Table 1: Stability constant of Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ Complexes of DL-2-Amino-butanedioic acid at varying temperatures (Ionic strength 0.10 M)

Metal complexes	Log K	20°C	30°C	40°C
Co ²⁺	Log K ₁	5.8631	6.0532	6.2930
	Log K ₂	4.3676	4.4188	4.5184
	Log β	10.2391	10.4720	10.8114
Ni ²⁺	Log K ₁	6.8914	7.0914	7.2200
	Log K ₂	5.0663	5.1677	5.2305
	Log β	11.9577	12.2591	12.4505
Cu ²⁺	Log K ₁	8.4759	8.6833	8.8501
	Log K ₂	6.6564	6.7891	6.9665
	Log β	15.1323	15.4724	15.8166
Zn ²⁺	Log K ₁	5.6955	5.9002	6.0938
	Log K ₂	4.3686	4.4905	4.5681
	Log β	10.0641	10.3907	10.6619

Table 2: Stability constant of Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ Complexes of DL-2-Amino-butanedioic acid at varying ionic strengths(Temp.30°C)

Metal complexes	Log K	20°C	30°C	40°C
Co ²⁺	Log K ₁	5.9785	6.0532	6.1959
	Log K ₂	4.3173	4.4188	4.4682
	Log β	10.2958	10.4720	10.6641
Ni ²⁺	Log K ₁	6.9977	7.0914	7.1958
	Log K ₂	5.1316	5.1677	5.2339
	Log β	12.2930	12.2591	12.4297
Cu ²⁺	Log K ₁	8.5829	8.6833	8.7822
	Log K ₂	6.7177	6.7891	6.8659
	Log β	15.3006	15.4724	15.6481
Zn ²⁺	Log K ₁	5.7925	5.9002	6.0536
	Log K ₂	4.4165	4.4905	4.5699
	Log β	10.2090	10.3907	10.6235

Table 3: Thermodynamic function of Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ Complexes of DL-2-Aminobutanedioic acid at 30° C

Metal complexes	Thermodynamic Function at 30°C (μ= 0.1M)		
	-ΔG (kcal/mole)	ΔH (kcal/mole)	ΔS (cal/degree/mole)
Co ²⁺	14.52	12.08	87.79
Ni ²⁺	16.99	12.23	96.43
Cu ²⁺	21.45	14.36	118.18
Zn ²⁺	14.41	12.50	88.81

metals have also been interpreted in relation to atomic properties of these metals such as ionic radii (A°) electronegativity (Pauling) and 2nd ionization potential (eV).

Plot of $\log \beta$ against reciprocal of ionic radii of metal ions (Fig.1) shows that the ligand forms less stable complexes with Co^{2+} and Zn^{2+} and more stable complexes with Cu^{2+} in comparison to Ni^{2+} complex.

The plot of X_m (Electronegativity of metal) against $\log \beta$ (Fig.2) shows that stability of these metal complexes increases with increasing electronegativity which suggest that the metal ligand bond would be covalent. Similar observation has been reported by Van Uitert¹⁴ and Selbin¹⁵.

The second ionization potential rises along the transition series and it becomes maximum Cu^{2+} . A correlation of potential and stability was pointed out by Irving Williams¹³ and Schwarzenbach Ackermann and Prue¹⁶. A similar correlation was observed in the present case of the plots of $\log \beta$ against second ionization potential (Fig. 3).

Thermodynamic Parameters

Thermodynamic functions such as free

energy (ΔG), enthalpy (ΔH) and entropy (ΔS) accompanying complexation are determined at 30°C with the help of standard equations¹⁷ and are summarized in Table 3.

The negative values of ΔG show that the reaction tends to proceed spontaneously. The positive values of enthalpy indicate the endothermic nature of the reaction process in fair agreement with increasing stability suggesting higher temperature favours the chelation process. A positive change in the entropy strongly indicates the complex formation. The very large entropy changes are also justified by considering the greater availability of coordination sites of these metal ions.

To study the bonding nature of complexes, it is necessary to observe the relation between ionic radii of metal ions and thermodynamic parameters ΔG , ΔH and ΔS , by plotting them against reciprocal of ionic radii of divalent transition metals ions, which show somewhat linear relationship. Martell¹⁸ has suggested a dependence of linear relationship between ΔS and $1/r$, for divalent metals. This indicate the pre-dominant role of electrostatic force involved in ion association process, a fact which is in agreement with Bjerrum's ion pair concept.

REFERENCES

1. Sharma S., Saxena, K.K., and Saxena R.S.; *Anales De Quimica.*, **83** B: 125 (1987).
2. Sharma S., Saxena, K.K., and Saxena R.S.; *J. Indian Chem. Soc.* **53**: 479 (1986).
3. Saxena R.S., and Dhawan S.K.; *J. Indian Chem. Soc.*, **50**: 87 (1983)
4. Sharma S., Saxena, K.K., and Saxena R.S.; *J. Electro. Chem. Soc. India*, **37**: 267 (1988)
5. Sharma S., Saxena K.K., and Saxena R.S.; *J. Chem. Soc. Pak.*, **7**: 105 (1985).
6. Agarwal Vishakha and Saxena K.K.; *U. Scientist Phyl. Sciences*, **6**: 230 (1994)
7. Taquikhan Badar, Vijaya Kumari S., and Murli Mohan K.; *Indian J. Chem.* **31A**: 28 (1992).
8. Kanodari M., Mansour H., Gndaur M.A., and Salah Haman.; *J. Electro. Chem. Soc. India*, **43**(1): 35 (1994).
9. Rathore O.P. and Lavale S.C.; *Asian J. Chem.*, **10**(3): 613 (1998).
10. Irving H., and Rossotti H.S.; *J. Chem., Soc.* **76**: 2904 (1954).
11. Irving H., and Rossotti H.S.; *J. Chem. Soc.*, **74**: 3397 (1953).
12. Irving H. and Williams R.J.P.; *J. Chem. Soc.*, 3192 (1953).
13. Irving H., and Williams R.J.P., *Nature*, **162**: 148 (1948).
14. Van Uitert, L.G. Fernetus W.C. and Douglas

- B.E.; *J. Amer. Chem. Soc.*, **75**: 2736 (1953).
15. Dey, M.C. and Selbin J.; "Theoretical Inorganic Chemistry", Reinhold, N.Y. 114 (1957).
16. Scharzenbach G., Ackerman H. and Prue J.E.; *Nature*, **163**: 723 (1949).
17. Yatrimiriski K.B. and Vasilev V.P.; Instability constant of complex compounds, Pergamon Press Oxford (1960).
18. Martell A.E.; *Rec. Trav. Chim.*, **75**: 781 (1956).