Est. 1984

ORIENTAL JOURNAL OF CHEMISTRY
An International Open Free Access, Peer Reviewed Research Journal

www.orientjchem.org

ISSN: 0970-020 X
CODEN: OJCHEG
2011, Vol. 27, No. (4):
Pg. 1803-1806

Thermodynamics of Complexation of Cytidine 5'- monophosphate (CMP) with Mn (II), Co(II), Ni(II) Cu(II) and Zn(II) ions in Aqueous Media

MUKUL KUMAR SINGH[1]* and NAMITA BHARDWAJ[2]

[1]Department of Chemistry, Government E.R.R. Science PG College Bilaspur (India).
[2]Department of Chemistry, C.V. Raman University, Kota, Bilaspur (India).

(Received: September 10, 2011; Accepted: October 22, 2011)

ABSTRACT

Crow's mean diffusion coefficient method applied to diffusion currents in the polarographic study of complexation of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with cytidine 5'- monophoshate yielded the $\log K_1$ and $\log K_2$ values as Mn(II) 2.76, 1.76; Co(II) 2.37, 1.46, Ni(II) 2.86, 0.843; Cu(II) 3.06, 1.90 and Zn(II) 3.93, 2.01 at 293 K. The overall stability constants followed Irving-William natural order. Thermodynamic parameters ΔG, ΔH and ΔS values calculated in the range 293-303 K were all negative, proving the formation of strong complexes with greater order in their molecule.

Key words: Thermodynamics, Aqueous media, Polarographic study.

INTRODUCTION

The Importance of metal ion-nucleic acid interactions in the metabolic machinery is well recognized in medicinal chemistry. These reaction provide an opportunity to identity the nature of such interactions as they serve as model for many metalloenzyme reactions.

Cytidine 5'- monophosphate (CMP), a nucleotides, consists of cytidine, (a nucleoside) plus monophosphate residue attached to the five membered sugar phosphate-ester linkage. Polynucleotides such as DNA and RNA contain a repeating sugar phosphate backbone with a single phosphate residue linked at 3' of one sugar and to of the next; this alternation provides a directional sense to the .

The present communication involves description of the chemical knowledge accumulated regarding complexes of CMP with above mentioned metal ions in aqueous solution. The stability constant of the metal nucleotide complexes has been determined at three temperatures 293, 298 and 303K by Crow's mean diffusion coefficient method assuming 1:1 complaxation in . Thermodynamic quantities have been calculated by usual thremodynamic equations.

There are a number of possible interaction sites between metal ions and CMP. Specifically these sites can be one or more of the phosphate oxygen, substituents on the bases, and a simultaneous interaction of the metal ion with the phosphate backbone and some position on the .

EXPERIMENTAL

The reagents used in this work were of AR grade. Reagent grade CMP was procured from SRL India. Metal perchlorates were prepared from reagent grade oxide, hydroxides or carbonate of metals by dissolving them in perchloric acid (AR) and crystallizing the salts twice from double distilled water.

Stock solution were prepared in triple distilled water. A typical 25ml test solution contains (A) 2.0 ml 5 mmol dm^{-3} metal perchlorate, 2.5 ml 1.0 mmol dm^{-3} lithium perchlorate, 0.5ml 0.2% gelatin and rest distilled water (B) 2.0 ml 5 mmol dm^{-3} metal perchlorate, 2.5 ml 1.0 mol dm^{-3} lithium perchlorate, 0.5ml 0.2% gelatin, increasing volume of CMP (0.8× mol dm^{-3} to 200× 10^{-4} mol dm^{-3}) and water to make up to 25ml, The pH of the solutions were adjusted by using perchloric acid or lithium hydroxide as required prior to addition of water the preparation of test solution. The ionic strength of the solution were kept constant at 0.1 mol dm^{-3} $LiClO_4$.

The apparatus used were ELICO polarograph (model CL-25D) with chart recorder, digital pH meter (LI-120), Julabo (HC, West Germany) circulating water cryostat and sargent capillary, m= 1.722 , t=5.3 sec for 70 cm Hg head in aqueous solution at zero potential (SEC). The double-walled Kalousek cell with built-in SCE was used for the investigation.

RESULTS AND DISCUSSION

Test solution containing Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) and varying concentration of CMP (0.8×10^{-4} mol dm^{-3} to 200×10^{-4} mol dm^{-3}) were taken and polarogram were recorded at three temperateres, 293, 298 and 303K, the pH being maintained at 7.0, 6.0, 6.3, 5.1 and 6.0 for respective metal ions below precipitation pH. A well defined single polarographic reduction waves were obtained for all metal ions except Cu(II), the slope of waves indicating quasireversibility of the reduction process. Increase in concentration of the ligand makes the reduction processes more reversible in each case. Negative shift in half-wave potential values as well as decrease in reduction wave were observed on addition of ligand. In the case of Co(II) and Ni(II) reduction wave show some different behavior. For Co(II) at low concentration of the ligand, the half wave potential shifts to more positive values at first then at a higher ligand-metal ratio, the usual negative shifts were observed. For the case of Ni(II) in the presence of CMP reduction exhibits two ill-defined diffusion controlled waves, i.e., splitting of waves occurs on addition of ligand. As the ligand concentration is increased , the splitting of the waves become more pronounced with a tendency of the lower wave to shift towards more positive value and the upper wave towards more negative values than the waves obtained for the preceding ligand concentration. Also the lower wave height increases while the upper wave-hight

Table 1: Complexation of M(II) of Cytidine 5'-monophosphate with Mn(II), C0(II), Ni(II),Cu(II) and Zn(II) in aqueous media at ionic strongly 0.1M$LiC10_4$

$MClO_4$ Mn(II), Co(II),Cu(II) : 0.4 mmol dm^{-3}, Ni(II), Zn(II): 0.3 mmol,

$LiCO_4$:0.1 mmol dm^{-3} **Temperature:298K**

00	1.35	1.35	1.00	1.47	0.97	1.40	0.01	1.470	1.02	1.720
0.8	1.33	1.33	0.98	1.46	0.96	1.38	0.02	1.460	1.01	1.710
4	1.32	1.32	0.98	1.45	0.96	1.37	0.01	1.420	1.01	1.690
8	1.29	1.29	0.99	1.44	0.96	1.36	0.01	1.370	1.01	1.685
16	1.24	1.24	1.00	1.43	0.96	1.335	0.01	1.315	1.01	1.665
40	1.16	1.16	1.02	1.40	0.98	1.32	0.01	1.210	1.01	1.610
80	1.08	1.08	1.02	1.38	0.98	1.295	0.01	1.100	1.02	1.550
200	-	-	1.06	1.31	0.98	1.240	-0.05	1.000	1.01	1.470

decreases. Such splitting of polarographic waves are attributed to the reduction of (Ni(II)- ligand) complex and hydrated nickel ion, Ni(II) , the two showing different half-wave potentials.

A plot of decrease in diffusion currents (“) against – log[L] gave sigmoidal shape curve called pseudoformation curve. The curve was integrated according to Fronaeous to obtain log data at each ligand concentration. The value thus obtained were plotted against log[L] and the limiting slopes of the curves and the maximum co-ordination number for each metal ion, the K value were calculated. By the multiplication of log value by the K value yielded logvalues. From the plot of L]Vs.[L], formation constants were , The values are shown in table 1.

Table 2: Stability constants and thermodynamic parameters of M(II) - Cytidine 5'-monophosphate complexes in aqueous medium at ionic strength 0.1 MLiC10$_4$

	T/K	$\log K_1$	$\log K_2$	$\frac{-\Delta G}{K J mol^{-1}}$	$\frac{-\Delta G}{K J mol^{-1}}$	$\frac{-\Delta G}{K J mol^{-1}}$
Mn(II)	293	2.76	1.76	15.48		
	298	2.73	1.81	15.58	12.19	-11.31
	303	2.69	1.75	15.61		
Co(II)	293	2.37	1.46	13.30		
	298	2.29	1.51	13.07	20.74	-25.72
	303	2.22	1.92	12.87		
Ni(II)	293	2.86	0.843	16.05		
	298	2.77	0.89	15.81	31.54	-52.81
	303	2.68	2.93	15.55		
Cu(II)	293	3.06	1.90	17.17		
	298	2.94	1.89	16.78	34.81	-60.31
	303	2.86	1.43	16.59		
Zn(II)	293	2.52	1.37	14.13		
	298	2.41	1.36	13.77	38.29	-82.35
	303	2.30	1.54	13.35		

For the calculation of thermodynamic parameters, the experiment were performed at three temperatures. The value of stability constant at three temperatures were used to determine thermodynamic and all the values for different metal ions are listed in table-2.

The stability constant values of 1:1 complexation of CMP with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) at 293K 2.76, 2.37, 2.86, 3.06 and 3.93 follows Irving and and Mellor and natural order. The stability constant values for complexes with CMP are nearly of the same order as that with 5-monophosphate and hence as proposed by, no base binding of the metal ions occur because of anticonformation of CMP in solution and the stability constant measured by polorographic method are due to phosphate binding of the metal ion.

When the stability constant values at the three temperature are compared, it is found that the stability constant values decreases with increasing temperature. This is in agreement with the conclusion of that higher temperature are not favorable for complexation.

All the thermodynamic parameters ΔG, ΔH and ΔS were calculated and found to be negative there by indicative of complex formation to be spontaneous and enthalpy and entropy stabilized.

REFERENCES

1. C.K. Mathews, K.E. vanttolde and K.G. Ahem, *Biochemistry*, 87 (2000).
2. D.R. Crow, *Electochim Acta*, **28**: 1799 (1983).
3. D.R. Crow, *Talanta*, **29**: 733 (1982).
4. D.R. Crow, "Polarography of metal complexes", Academic press. N.Y. (1969)
5. R. Bruce Martin and Y.H. Marian, Metal ions in Biological systems, H Sigel Ed. Vol-8, Dekker, New York, 57(1979)
6. H. Sigel, Angew. Chem., Int. Ed., **14**: 394 (1975), *Angew. Chem.*, **87**: 391 (1975)
7. L. Meites, Polarographic techniques, *Inter science* N.Y.(1965).
8. S Fronaeous, *Acta. Chim. Scand.*, **4**: 72 (1950).
9. I. Leden, Z. *Phys Chem.* (A), **188**: 160 (1941).
10. J. Koryta, *Chem Listy,* **51**: 1544 (1957).
11. Y. Yatsimirshii and V.P. Vasilev, "Instability constants of complex compounds, Pergamon Oxford (1962)
12. H. Irving and R.Williams, *Nature*, **162**: 746 (1948).
13. D.P. Mellor and L.E. Maley, *Nature*, **159**: 370 (1947).
14. H. Sigel and S.S.Massoud, *Inorg.Chem* **27**: 1447 (1988).
15. K.S. Pitzer, *J.Am.Chem, Soc.*, **59**: 2965 (1937).