Acta Chimica & Pharmaceutica Indica

Acta Chim. Pharm. Indica: 3(1), 2013, 35-39
ISSN 2277-288X

STUDY OF BINARY COMPLEXES OF TRANSITION METAL IONS AND LANTHANIDE METAL IONS WITH ADENOSINE DRUG IN MIXED SOLVENT SYSTEM

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(*Received : 01.01.2013; Revised : 12.01.2013; Accepted : 15.01.2013*)

ABSTRACT

The interaction of transition metal ions and lanthanide metal ions with adenosine drug has been investigated in 20% (v/v) ethanol-water mixture at 0.1 M ionic strength at temperature 25°C by potentiometric titration. The data obtained is used to calculate the values of proton-ligand stability constant (pK) and metal-ligand stability constant (log K). It was observed that transition metal ions and lanthanide metal ions forms 1 : 1 and 1 : 2 complexes.

Key words: Stability constant, Transitional metal ion, Lanthanide metal ion, Potentiometric titration, Adenosine drug.

INTRODUCTION

Metal complexes are widely used in various fields, such as biological processes pharmaceuticals, separation techniques, analytical processes etc. Most of the d-block and f-block elements form complexes. There are different kinds of ligand used for complexation. For the present investigation, the ligand selected was Adenosine (ADO). It is analgesics, anti-arrhythmia agents, anti-arrthmic agents, cardiac drugs, vasodilator agents. In USA, it is marketed as adenocard. ADO plays an important role in biochemical processes, such as energy transfer. It is also an inhibitory neurotransmitter, believed to play a role in promoting sleep and suppressing arousal with levels increasing with each hour an organism is awake. ADO has molecular formula $C_{10}H_{13}N_5O_4$ and IUPAC name (3R, 4S, 5R)-2(6-aminopurin-9-yl)-5-(hydroxy methyl) oxolane-3,4 diol.

The physical properties of medicinal drugs adenosine is shown below -

(i) Molecular weight = 267.24 g/mol

(ii) Phase = Solid (at STP)

(iii) Melting point = 234ºC

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(iv) Boiling point = 676ºC

(v) Density = 0.99224 g/cm^3

(vi) Solubility = Soluble in water 8230 mg/L or 1.40 e + 01 g/L

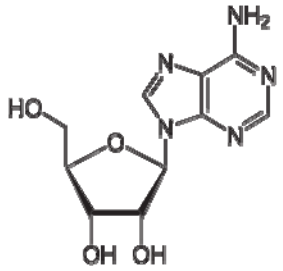

Fig. 1: **Structure of Adenosine**

Literature survey reveals that a very few researchers have done such type of work using medicinal drug as a ligand[1-15]. There for we decided to study stability constant of binary complexes of Adenosine with transition metal ions Fe (III), Co (II), Ni (II), Cu (II), Zn (II) and Cd (II) and lanthanides La (III), Ce (III), Nd (III), Sm (III), Gd (III), Tb (III) and Dy (III) using pH metry.

EXPERIMENTAL

Materials and solution

The ligand ADO is soluble in double distilled water. NaOH, $NaClO_4$, $HClO_4$ and metal salts were of AR grade. The solutions used in the potentiometric titration were prepared in double distilled water. The NaOH solution was standardized against oxalic acid solution (0.1 M) and standard alkali solution was again used for standardization of $HClO_4$. The metal salt solutions were also standardized using EDTA titration[14]. All the measurements were made at 25ºC in 20% ethanol-water mixture at 0.1 M $NaClO_4$ strength. The thermostat Model SL-131 (Adar Dutt and Co (India) Pvt. Ltd. Mumbai) was used to maintain the temperature constant. The pH measurement were made using a digital pH meter model Elico L1-120 in conjunction with a glass and reference calomel electrode (reading accuracy ± 0.01) The pH-meter was adjusted with buffer of pH 4.00, 7.00 and 9.18.

Potentiometric procedure

For evaluating the protonation constant of the ligand and the formation constant of the complexes in 20% ethanol-water mixture with different metal ions we prepared the following three sets of solutions.

(A) $HClO_4$ (A)

(B) $HClO_4$ + ADO (A+ L)

(C) $HClO_4$ + ADO + Metal (A+ L+ M)

The above mentioned sets prepared by keeping M : L ratio, the concentration of perchloric acid and sodium perchlorate (0.1 M) were kept constant for all sets. The volume of every mixture was made upto 50 mL with double distilled water. The test solutions were magnetically stirred, NaOH was added stepwise and pH reading was recorded until stable values, within ± 0.002 pH units were obtained.

Table 1: Proton-ligand stability constant and metal-ligand stability constant of transion metal ions at 0.1 M ionic strength in 20% (v/v) ethanol-water medium

Metal ion	Proton-ligand stability constant	Metal-ligand stability constant			Log K_1/ Log K_2
		Log K_1	Log K_2	Log β	
Fe (III)		11.95	10.70	22.650	1.1168
Co (II)		5.807	4.906	10.713	1.1836
Ni (II)	PK_1 = 3.292	5.977	5.080	11.057	1.1765
Cu (II)		8.893	7.567	16.460	1.1752
Zn (II)	PK_2 = 11.659	7.042	6.360	13.402	1.1072
Cd (II)		5.704	4.687	10.391	1.2169

Table 2: Proton-ligand stability constant and metal-ligand stability constant of lanthanide metal ions at 0.1 M ionic strength in 20% (v/v) ethanol-water medium

Metal ion	Proton-ligand stability constant	Metal-ligand stability constant			$LogK_1/LogK_2$
		Log K_1	Log K_2	Log β	
La (III)		6.402	4.688	11.090	1.3656
Ce (III)	PK_1 = 3.292	7.094	5.148	12.242	1.3780
Nd (III)		7.363	5.658	13.021	1.3013
Sm (III)	PK_2 = 11.659	8.068	6.786	14.854	1.1889
Gd (III)		7.891	6.451	14.342	1.2232
Tb (III)		8.100	7.113	15.213	1.1387
Dy (III)		8.281	7.308	15.589	1.1331

RESULTS AND DISCUSSION

Titration curves were obtained for different sets. During titration no precipate was formed indicating that there is no tendency to form hydroxo complexes. The stability constants of the formed complexes were investigated in the pH range of 4-6. Proton ligand stability constants (pK) of ADO was determined by point wise calculation method as suggested by Irving and Rossotti.

Metal ligand stability constant (log K) of transition metal ions and lanthanides were calculated by point wise and half integral method as suggested by Irving and Rossotti.

In the present investigation, we have studied the stability constants of divalent transition metal ions except Fe which is in trivalent state. ADO contains three OH groups, out of these two are attached to cyclic ring and one is to the side chain. The deprotonation of side chain –OH is easier compaired to –OH directly attached to ring. Hence only one deprotonation in the acidic range (pK_1 = 3.292) and the other pKa in the basic region corresponds to $–NH_2$ group only (pK_2 = 11.659). ADO has N-atom as binding site. The functional group NH_2 is mostly responsible for Complexation, although there are nitrogen atoms present in the co-ordinate bond formation.

The probable structure of metal complex with ADO is difficult to predict only on the basis of solution study. Since we got $\overline{n}_A$ between 0.2 to 0.8 and 1.2 to 1.8 indicating 1 : 1 and 1 : 2 complex formation. It will be interesting to study the solid state formation of such complex and to study its biological activity,which is included in our future plan.

Till now very less or almost no work is observed on the complexation behavior of lanthanide with medicinal drug such as ADO. As Lanthanides are having less capacity to from complexes still there stability constant values (log β) are comparable with that of transition metal ions. This might be due to the pressure of diffused f-orbitals, the trivalent charge present and effective nuclear charge etc.

Observed trend in the order of stability constant of transition metal ions was -

$$Fe^{3+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} > Cd^{2+}$$

Which are accordance with the William-Irring series and the order of stability constant of Lanthanide metal ions was -

$La^{3+} < Ce^{3+} < Nd^{3+} < Sm^{3+} > Gd^{3+} < Tb^{3+} < Dy^{3+}$ and shows a break at gadolinium.

The ratio of log K_1/log K_2 is positive and greater than one in all cases. This implies that there is little or no steric hindrance to the addition of secondary ligand molecule.

ACKNOWLEDGMENT

Authors thankful to Principal Dr. Maqdoom Farooqui, Maulana Azad College, Aurangabad and Principal Dr. Md. Ilyas Fazil, Milliya Arts, Science and Management Science College, Beed for providing all research facilities.

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