



pH –METRIC STUDIES OF AZOLE-BASED TRANSITION METALS COMPLEXES



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Received: June 02, 2016 Accepted: September 06, 2016

Abstract: Metal-ligand complexations in solution of the transition metals with azole based ligands (triazole and benzimidazoleligand) in water-methanol medium by pH-metric titration with the glass electrode; ionic strength 0.1M KNO₃ and buffer solutions at pH 7 and 9 were carried out. Titration were carried out for the ligand against 0.05M NaOH solution as well as on metal complexes (metal ligand) at various temperatures 35, 45 and 55°C. The pK_a values (stability constants) were determined at the respective temperatures and found to decrease as the temperature increased. The results of thermodynamic studies have revealed that the metal complexes were exothermically favourable while the negative Gibb's free energy explained the spontaneity of the metal-ligand system and that the metals complexes were feasible at the respective temperatures.

Keywords: Metal-ligand, pH-metric, stability constant, thermodynamic studies, benzimidazole

Introduction

Azoles containing ligands actively participated in complex forming reaction with ions of transition metals. Derivatives of azole-based ligand are widely used in medical practice as drugs (Horton *et al.*, 2003). Its compounds are also applied for analytical determination of ions of different metals due to their donor properties (Kennedy and Lever, 1997). Benzimidazole is an alicyclic compound having imidazole ring containing two nitrogen atom at non-adjacent position fused to benzene (Finar, 1998).

The stability of metal complexes depends both on the metal ion and ligand. Generally, the stability of the metal complexes increase with increasing charges, decrease in size and increase in electron affinity. For the transition metal ions, the electronic configuration is significant with regards to the stability of the complexes. The stability of the complexes of bivalent transition metal is Mn > Fe > Co > Ni > Cu > Zn. (Wilkinson, 1998). Alfred Werner (1890) had proposed the correct structures for the coordination complexes also Bjerrum (1941). The key to Bjerrum method was use of the recently developed glass electrode and pH meter to determine the concentration of the hydrogen ions in solution. Irving and William (1945) series were discovered, where calculations were done by hand using the so called graphical method later Rossotti and Rossotti (1964) developed the use of a computer programme.

Oxidation –reduction system involved in the titration gives an insight of the processes of complexation of the metal and ligands in solution. The formation constants are used to derive the proportions of the various complexes formed as function of equilibrium-ligand concentration (Okoronkwo and Aminjanov, 2003).

The thermodynamic stability of a species is a measure of the extent to which the species will be formed from other one species under certain conditions provided that the system is allowed to reach equilibrium (Basset *et al.*, 2005). It is useful in distinguishing between enthalpic and entropic effects. Enthalpic effects depend on the bond strength and entropic effects have to do with changes in the order or disorder of the solution as a whole (Rossotti and Rossotti, 1964). Potentiometric studies for the determination of deviation constant of 1-aryl-4-(2-nitrophenyl) 3-thiosemicarbazides with some binary metal ions and their formation constant have been studied and characterized (Sireesha *et al.*, 2006). Mn(II) Fe(II) Co(II),

Ni(II) and Cu(II) halide complexes with 1,2,4 –triazole as ligands have also been synthesized and studied (Zaydoum and Saidi, 1995).

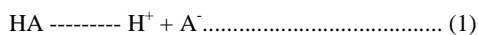
Potentiometric studies on complexes of Gabapentin (chemically 2-[1-(aminomethyl) cyclohexyl]ethanoic acid) with Cu(II), Cd(II), Co(II), Ni(II), Pb(II) and Zn (II) have been studied. The results of the potentiometric studies on complexes of Gabapentin (2-[1-(aminomethyl) cyclohexyl]ethanoic acid) using Calvin-Bjerrum pH titration technique indicates that the order of stability is as follows Cu(II) > Pb(II) > Co(II) > Ni(II) > Zn (II) (Agarwaal *et al.*, 1982). This order is also in accordance with Irving-Williams order of stability. The negative free energy change indicates the spontaneity of the complex formation process. This paper deals with pH –metric studies of azole-based ligands with iron(III), Ni(II) and Zinc(II) ions in water-methanol medium with a view of determining their stability constants and thermodynamic stabilities.

Materials and Methods

All chemicals used are of good analytical grades were used without further purification. The reagents involved are benzimidazole and 1,2,3-triazole (ligands), nickel (II) sulphate hexahydrate, zinc (II) sulphate heptahydrate and iron (II) chloride hexahydrate, distilled water, methanol, pH meter (model 132E), thermometer, magnetic stirrer with hot plate and buffer solution pH 5 and 9.

The ligand (benzimidazole) and the metal salts in 1:2 molar ratios were prepared in 50% v/v water and methanol mixture in order to fulfil the maximum coordination number of the metal ions. All pH-metric measurements were carried out at a constant ionic strength 0.01M KNO₃, being a soluble salt and temperatures of 298K, 308K and 328K. Measurements were performed with ATC pH meter (model 132E) equipped with glass calomel electrode assembly. The prepared solutions were titrated against sodium hydroxide of 0.05 Mol/dm³. The pH readings were stabilized in a few minutes and converted to hydrogen ions concentration according to method of Bjerrum (1941) as modified by Aliyu and Garba (2009). The difference in the volume of NaOH utilized for the ligand and metal titrations was a measure of the extent of complexation. The complex titration curve was found to be well separated from the ligand titration curve indicating that the liberation proton was due to chelation.

The expression for the acid dissociation constant for the reaction is as follows;



$$pK_a = \frac{[H^+][A^-]}{[HA]} \dots\dots\dots (2)$$

Where: $[H^+]$, $[A^-]$ and $[HA]$ are known concentrations (Gregory *et al.*, 1977).

Average number of ligands bound per metal in the complex (n_A) were obtained from the equation;

$$T_A^0 - \frac{T_H - [H^+]}{nH} \dots\dots\dots (3)$$

Where: T_H = Total concentration of the hydrogen ion present

T_A^0 = Total concentration of ligand

T_M^0 = Total concentration of metal

n_A = Average number of ligands bound per metal

nH = Protonated hydrogen

Results and Discussion

The values of n_A obtained for metal-ligand indicate the formation of 1:1 and 1:2 complexes Bjerrum half-integral method at various n_A values, graphical method extended to water- methanol mixture by Van Ultert and Hass (1959) was used to calculate the logK values. The values of n_A calculated for benzimidazole complexes of Fe (II), Ni(II) and Zn(II) and stability constants were presented in Table 1 shows that the n_A , the coordination number of the ligand to the metal ions is within the range of 1.79 – 1.99, indicating the ML_1 and ML_2 complex formation while stability constant of the ligand and complexes decreases as the temperature increases, this reveal that complexes are better formed at 35°C .

The n_A values for 1,2,3-triazole and the complexes 1.5 for the ligand but complexes have shown values ranged between 1.84 – 2.05. This is an indication that 1,2,3-triazole can easily form complexes with Fe (II), Ni(II) and Zn(II) within the temperature ranges of 35 – 55°C which is an approximate of 2. Therefore ML_1 and ML_2 metal complexes are feasible in ratio 1:1 and 1:2. The pK_a values for 1,2,3-triazole which predict stability constants for both ligand and its complexes show that triazole/ligand is not stable at temperatures 45 and 55°C (Table 2) which indicates that the ligand is thermodynamically unstable. Whereas, the metal complexes at those temperatures are feasible and be studied. The results obtained have indicated that the stability constants decrease as temperatures increased that is the optimum temperature for metal complex formation is 35°C.

The average number of metal coordination to the ligand at 35, 45 and 55°C (n_A) is between 1.79 – 1.99, giving an approximate value of 2 which is an indication of both ML_1 and ML_2 types of metal complexes with benzimidazole for Fe(III), Ni(II) and Zn(II) ions in water-methanol medium as shown in Table 1. The ligand show n_A values ranging between 0.5-1.5 but a high stability at 35°C with pK_a value 11.98 and log k of 9.549×10^{11} as a sign of good stability however the stability decreases as the temperature increases, which is a common feature of first row of transition metals (Holm and O'connom, 1971). The stability of Zn(II) complexes with benzimidazole is higher than the corresponding metal ions Fe(III) and Ni (II) complexes due to its complete filled $3d^{10}$ orbitals therefore made it more stable at that particular temperatures (Wilkinson and Bochman, 1999; Lee, 1998). Table 1 result shows that the stability constants of the metal ions follows

the Irving and William (1953) order, but Zn(II) complexes appeared more stable. However, no precipitate was observed in the titration vessels, indicating that the possibility of formation of metal hydroxides can be excluded.

Table 1: Benzimidazole calculated coordinated number of ligand bound per metal, pKa and stability constants

Ligand/metal ions	Temp in Kelvin	n_A	pK_a	Logk (stability constant)
Benzimidazole(ligand)	35	1.5	11.98	9.55×10^{11}
	45	0.5	1.70	5.01×10^1
	55	0.5	1.69	4.90×10^1
Fe(III)	35	1.82	2.64	309.03
	45	1.88	2.32	234.43
	55	1.99	1.69	223.87
Ni (II)	35	1.98	2.13	323.59
	45	1.90	2.52	398.11
	55	1.84	2.66	239.88
Zn(II)	35	1.81	3.44	4570.88
	45	1.82	3.02	2691.53
	55	1.79	3.11	2230.87

Table 2: 1,2,3-Triazole calculated coordinated number of ligand bound per metal, pKa and stability constants

Ligand/ metal ions	Temp in Kelvin (°C)	n_A	pK_a	Log k (stability constant)
Triazole	35	1.5	11.90	7.94×10^{11}
	45	-	Not stable	-
	55	-	Not stable	-
Fe (III)	35	1.911	2.85	446.86
	45	1.944	2.58	308.18
	55	2.042	2.37	251.18
Ni(II)	35	1.857	2.85	707.9
	45	1.939	2.58	446.68
	55	2.057	2.37	251.18
Zn (II)	35	1.846	2.82	794.33
	45	1.869	2.72	660.69
	55	2.101	2.31	257.04

Table 3 shows the results of thermodynamic studies of the metal complexes of Fe (III), Ni (II) and Zn(II) ions with benzimidazole at 308K, 318K and 328K. The slopes of the plots of logK against the reciprocal of the temperatures were used to evaluate the enthalpy change ΔH for dissociation or complexation process, respectively at 308K, 318K and 328K. From the Gibb's energy change ΔG and ΔH values and one can deduce the entropy change ΔS using the well known relationship.

$$\Delta G = -2.303RT \log K \dots\dots\dots (4)$$

$$\Delta G = \Delta H - T\Delta S \dots\dots\dots (5)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \dots\dots\dots (6)$$

The results of the enthalpy changes for the metal ion shows that metal complexes were exothermically favourable with high negative values which results in great disorder. The combined changes in the enthalpy and entropy will lead to a large decrease in free energy making the reaction spontaneous. A negative value of ΔS obtained is due to the increased order as a result of solvation processes as shown by the Zn(II) complex with benzimidazole. Whereas, the entropy changes for Fe (III) and Ni (II) metal complexes gave positive values which

have suggested that the ions in aqueous solution with water molecules around them. During complexformation between oppositely charges ion (L^{2-} and M^{2+}) will lead to the breakdown of metal-water arrangement resulting in positive entropy. This confirms that the complex formation is entropically favourable, in that for a system to occur spontaneously, ΔS (total) must be positive as total energy must increase. Since $\Delta G = -T\Delta S$ for ΔS to be positive, ΔG must be negative (Wilkinson, 1998). However, Gibb's free energy negative results confirm the spontaneity of the metal complexes and the reactions are feasible and irreversible. The free energy of formation (ΔG°) of complexes has more negative values with increase of temperature, showing that complex formation is a spontaneous process.

The average number of metal coordination to the ligand at 308K, 318K and 328K in Table 1 ranged between (1.82 – 2.10) indicates that the coordination of metal to ligand in 1:1 and 1:2 are ML_1 and ML_2 as calculated from equation 3. Stability constant $\log K$ for triazole metal complexes Fe(III), Ni(II) and Zn(II) ion showed a decrease in the value of n_A and $\log K$. As the temperature increases in ΔG value reduces and the atomic mass increases. The free energies of formation (ΔG) of metal complexes have negative values indicating spontaneity of the reaction process. The volume of ΔG obtained show that at 35°C the formation of copper (II) benzimidazole complex is more spontaneous than the formation of iron(II) 1,2,3-triazole complex. However, as the temperature increases from 35 – 55°C (308 – 338K) the spontaneity of copper (II) Benzimidazole gives negative value of free energy formation (ΔG) which is an indication that the increase in temperature will decrease the stability of copper(II) benzimidazole complex.

However, as the temperature increases to 55°C, the triazole complex forms less rapidly than the benzimidazole complex. The negative value of the free energy also increases with the temperature in the Ni(II) benzimidazole complex but decrease with increase in temperature in the Ni(II) triazole complexes i.e less spontaneity. Although, the negative values of the free energy are higher in triazole (-16.3684-15141 kJ mol⁻¹) than in benzimidazole complexes (-15.10118-15.286 kJ mol⁻¹). This shows that Ni(II) triazole forms complexes more rapidly than that of Benzimidazole. In the Zn (II) benzimidazole complexes; they are more stable than that of Zn(II) triazole as the free energy values gave -21.460 – 20.835 kJ mol⁻¹. Benzimidazole and triazole have -17.4309 – 1508 kJ mol⁻¹ values. In both the benzimidazole and triazole the values of ΔG decrease with increase in temperature (Tables 3 and 4). These indicate that formations of metal complexes are less rapidly formed and less spontaneous. Iron(III) benzimidazole complexes have $-\Delta G$ which increase with increase in temperatures -14.593, 14.625 and 14.655 kJ mol⁻¹, showing their complexes form rapidly while that of Fe(III) triazole $-\Delta G$ (free energy) value decreases with rise in temperature. -15.7402, -15.4695 and 15.1998 kJ mol⁻¹ which is an indication that complex formation increases rapidly as the temperature increased (Olagboye and Okoronkwo, 2013).

Table 3: Determination thermodynamic properties of the benzimidazole metal complexes at three different temperatures

Metal ions	Temp. in Kelvin	ΔH (kJmol ⁻¹)	ΔS (Jmol ⁻¹ deg ⁻¹)	ΔG (kJmol ⁻¹)
Fe (III)	308	-13627.13	+3.10	-14593.35
	318	-13637.13	+3.10	-14624.40
	328	-13637.13	+3.10	-14655.44
Ni(II)	308	-12254.77	+9.24	-15101.18
	318	-12254.77	+9.24	-15198.59
	328	-12254.77	+9.24	-15286.04
Zn(II)	308	-31080.82	-31.23	-21460.53
	318	-31080.82	-31.23	-21148.19
	328	-31080.82	-31.23	-20835.84

Table 4: Determination of stability constant thermodynamic properties of 1, 2,3-triazole metal complexes at different temperatures

Metal ions	Temp. (Kelvin)	Stability constant (Log K)	ΔG (kJmol ⁻¹)	ΔH (kJmol ⁻¹)	ΔS (Jmol ⁻¹ deg ⁻¹)
Fe(III)	308	446.68	-15.74016	-24.0596	-27.01
	323	308.18	-15.4695	-24.0596	-27.01
	338	251.18	-15.1998	24.059	-27.01
Ni(II)	308	707.90	-16.8681	-	-86.32
	323	446.78	-	43.45721	-86.32
	338	251.18	-	43.45721	-86.32
Zn(II)	308	794.33	-17.43094	-47.0408	-96.14
	323	660.69	-16.46958	-47.0408	-96.14
	338	257.04	-15.50822	-47.0408	-96.14

Generally, the negative values obtained for the enthalpy change (ΔH) for all the metal complexes of benzimidazole and triazole at various temperature 35, 45 and 55°C (308, 323 and 338 K) reveal that the heat is liberated to the surrounding and the reactions are exothermic. On the other hand, the positive values for the entropy (ΔS) change for the metal complexes for Fe(III) and Ni(II) with benzimidazole and Zn(II) confirm that complex formation is entropically favourable and less entropy disorder is lost when the complexes are formed (Otuokere, 2011).

Conclusion

The results of the pH-metric studies on transition metal complexes of benzimidazole and 1,2,3-triazole in methanol-water medium using calvin-Bjerrum pH titration technique. The results obtained for calculated coordinated number of ligand bound per metal for both the benzimidazole and 1,2,3-triazole is approximately 2, indicating that coordination of metal – ligand is feasible within the ratio 1:1 and 1:2; i.e. ML_1 and ML_2 . The result of $\log K$ indicate that the order of stability is Fe(III)>Ni(II)>Zn(II). This order is in accordance with Irving-Williams order of stability. The negative values of the free energy changes for the metal complexes indicate the spontaneity of the complex formation process. The stability of the metal complexes decreases as the temperature increases.

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