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RESEARCH ARTICLE

DETERMINATION OF ASSOCIATION AND DISSOCIATION CONSTANTS OF Co(II), Ni(II), Cu(II), Zn(II), Cd(II) AND Hg(II) METAL ION COMPLEXES WITH 3-(((3-(2-HYDROXYPHENYL)-1-PHENYL-1H-PYRAZOL-4-YL)METHYLENE)HYDRAZONO)INDOLIN-2-ONE.

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3-(((3-(2-hydroxyphenyl)-1-phenyl-1H-pyrazol-4-yl)methylene)hydrazono)indolin-2-one, Dissociation constants, Association constants.

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Abstract

The proton-ligand stability constants and metal-ligand stability constants of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with 3-(((3-(2-hydroxyphenyl)-1-phenyl-1H-pyrazol-4-yl)methylene)hydrazono)indolin-2-one has been investigated potentiometrically using pH metric technique in aqueous, ethanol-water (50% v/v) and dioxane-water (50% v/v) mixtures at different ionic strengths (0.1 M and 0.2 M) of $NaClO_4$ and at 25 ± 1 ^oC temperature. Proton-ligand stability constants values fall in the range of 9.642 to 11.751 attributable to ionization of phenolic –OH. The method of Calvin and Bjerrum as adopted by Irving and Rossotti has been employed to determine log K and log β values.

Introduction:-

pH-metry has been effectively adopted for the determination of stability constant J. Bjerrum and Ido-Laden's work enlightened the interest in the investigation of equilibrium of metal-chelates and ionic complexes in solution. Schwarzenbach and Ackermann **(**Schwarzenbach and Ackemann, 1948**)** found that stability of the chelates decreases as the increase of size ring. The present work provides a systematic solution study of the complex formation of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with different acids. As the coordination chemistry of metal-complex play a crucial role in biological system of organism (Ayesha, 2014), hence the formation, stability and reactivity of these complexes have been an active field of research (Brij, 2009). The stability constant gives the formation of metal-ligand. Metal ions plays essential role in the development of stable complexes is of interest to the analytical chemists and bio-inorganic researchers (Ayesha, 2011).

Hydrazones are very significant group of analytical regents for the fortitude of various metal ions by using assorted analytical techniques. Besides this use of hydrazones are also having biological activities also (Lakshmi et al., 2012). Hydrazone compounds obtained by the reaction of aromatic and heterocyclic hydrazides with mono and di-aldehydes or ketones have revealed very versatile behavior in metal coordination. Many researchers have synthesized a number of new hydrazones because of their relieve of synthesis. Hydrazones have been studied as a group of the most useful spectrophotometric reagents. Combining suitable starting materials (carbonyl compounds and hydrazine), the sensitivity as an analytical reagent and/or solubility of the hydrazones could be improved and the donating environment could be altered. The shortcoming of hydrazones was their lack of selectivity for metal ions. Much attempt has been devoted to emergent masking agents for use with hydrazones (Ajaykumar et al., 2009).

Metal complexes with Schiff bases of isatin derivatives exhibited notable biological activity (Nursabah and Gazi, 2005). Hydrazones derivatives of carbonyl compounds comprise a significant class of biologically active compounds. Metal complexes of Schiff bases represent an essential class of coordination compounds. Isatin Schiff base containing hetero donar atom continue to provide the interesting facts in the fields of coordination chemistry (Kamalaker, 2015). In present work an attempt has been made to study the interactions between Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) metal ions at different ionic strengths (0.1 M and 0.2 M) with 3-(((3-(2-hydroxyphenyl)-1-phenyl-1H-pyrazol-4-yl)methylene)hydrazono)indolin-2-one, at 25 ± 1 ^{o}C temperature, pH metrically in aqueous, ethanol-water (50% v/v) and dioxane-water (50% v/v) mixtures.

Experimental:-

The Schiff base ligand has been synthesized by the condensation of equimolar amounts of 3-(2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde with isatin monohydrazone in methanol and has been confirmed by its melting points and spectral studies (Siddappa and Nabiya sultana mayana, 2015). Afford Schiff base (HDPPPMHI) as shown in Figure 1.

Figure 1:- 3-(((3-(2-hydroxyphenyl)-1-phenyl-1H-pyrazol-4-yl)methylene)hydrazono)indolin-2-one (HDPPPMHI)

Reagents:-

The chemicals used for pH – metric determination were analytical grade. NaOH, metal cholrides, Perchloric acid, sodium perchlorate were used. These are prepared in deionized water and ethanol and dioxane were also distilled. 3-(((3-(2-hydroxyphenyl)-1-phenyl-1H-pyrazol-4-yl)methylene)hydrazono)indolin-2-one were procured and used as a ligand.

Apparatus:-

The titrations were carried out with a digital Elico pH-meter model L1-122 using combined electrode with the accuracy range ± 0.01 pH digits at 25 ± 1 ^{o}C. The magnetic stirrer for the continuous stirring of the solution during the titration, and a thermostat were used to maintain the temperature constant.

pH titrations:-

Titrations were performed in aqueous, ethanol-water (50% v/v) and dioxane-water (50% v/v) mixtures and a different ionic strengths was maintained by using $NaClO_4$ at 25 ± 1 ^{o}C in an inert atmosphere. The experimental procedures involve the acid titration, ligand titration and metal titration. The details of titrations are shown in the Table 1 to Table 3. The total volume in all the cases was 50 mL.

Table 1 to **Table 3.** The experimental procedures involve the acid titration, ligand titration and metal titration.

Table 1:-

T = 25 ± 1 ºC **Aqueous medium** **μ = 0.1M / 0.2M $NaClO_4$**

Solution (Initial concentration)	Acid titration	Ligand titration	Metal titration
$HClO_4$ (0.01M)	5.0 ml	5.0 ml	5.0 ml
$NaClO_4$ (1M / 2M)	5.0 ml	5.0 ml	5.0 ml
Water	40 ml	35 ml	30.0 ml
Ligand	-----	5.0 ml	5.0 ml
Metal	-----	----	5.0 ml

Table 2:-

T = 25 ± 1 ºC **50% Ethanol-water** **μ = 0.1M / 0.2M $NaClO_4$**

Solution (Initial concentration)	Acid titration	Ligand titration	Metal titration
$HClO_4$ (0.01M)	5.0 ml	5.0 ml	5.0 ml
$NaClO_4$ (1M / 2M)	5.0 ml	5.0 ml	5.0 ml
Ethanol	25.0 ml	25.0 ml	25.0 ml
Water	15.0 ml	10.0 ml	5.0ml
Ligand (0.01M)	-----	5.0 ml	5.0 ml
Metal (0.01M)	-----	------	5.0 ml

Table 3:-

T = 25 ± 1 ºC **50% Dioxane-water** **μ = 0.1 M/ 0.2M $NaClO_4$**

Solution (Initial concentration)	Acid titration	Ligand titration	Metal titration
$HClO_4$ (0.01M)	5.0 ml	5.0 ml	5.0 ml
$NaClO_4$ (1M / 2M)	5.0 ml	5.0 ml	5.0 ml
Dioxane	25.0 ml	25.0 ml	25.0 ml
Water	15.0 ml	10.0 ml	5.0ml
Ligand (0.01M)	-----	5.0 ml	5.0 ml
Metal (0.01M)	-----	-------	5.0 ml

Results and discussion:-

A large number of techniques of great diversity are now being employed for the determination of stability constants. The most generally utilized and probably the most accurate and reliable method for the determination of stability constant is based on the potentiometric measurement of hydrogen ion concentration. This depends on the fact that pH of the solution is directly affected by complex formation, which is accompanied by the displacement of a proton from the acidic ligand. The magnitude of the observed pH change may be employed to determine the stability constant of the metal complexes by Bjerrum's method, Calvin and Wilson's method (Bjerrum et al., 1941).

Calvin and Wilson have demonstrated that pH measurements made during titrations with alkali solution of ligand in the presence and absence of metal ion could be employed to calculate the formation functions $\overline{n_A}$, $\overline{n}$ and pL and stability constants can be computed. Irving and Rossotti **(**Irving and Rossotti, 1954), titrated following solutions against standard sodium hydroxide solution keeping total volume V_0 constant. The formation functions $\overline{n_A}$, $\overline{n}$ and pL can be computed from the following eqations:

$$\overline{n_A} = Y - \frac{(V_2 - V_1)\ (N + E^0)}{(V_0 + V_1)\ T^0_L} \qquad \text{.......…………(1)}$$

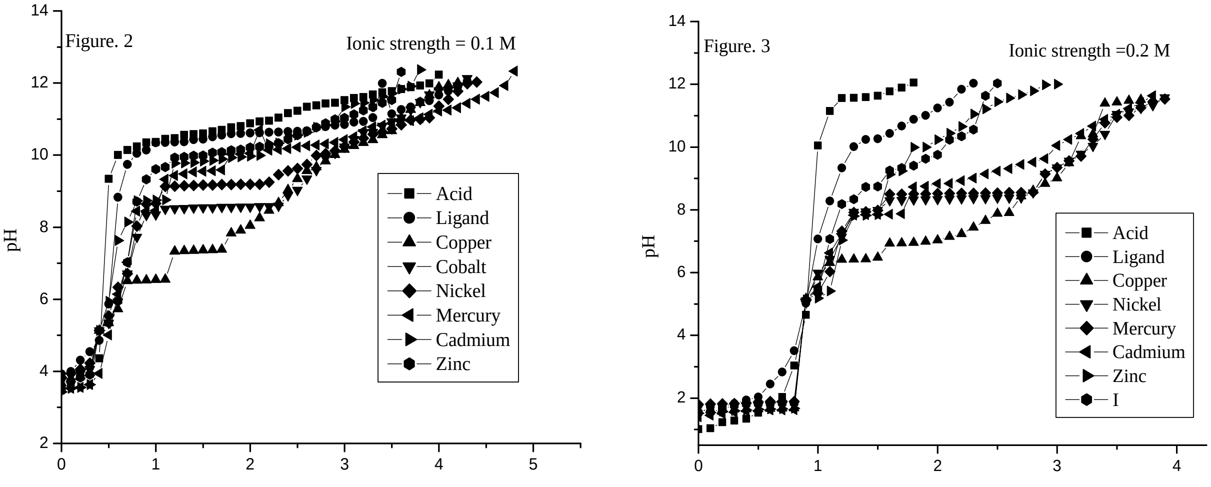
$$\overline{n} = \frac{(V_3 - V_2)\ (N + E^0)}{\qquad} \qquad \text{…....…………..(2)}$$

$(V_0 - V_2)\ T^0_M\ \overline{n}_A$

$$pL = \frac{\log [\text{antilog}\ (pK_a - pH)]}{T^0_L - \overline{n}\, T^0_M} \times \frac{V_0 + 2V_2}{V_0} \qquad \ldots\ldots\ldots\ldots\ldots.. (3)$$

where Y = is the number of replaceable hydrogen ion,
N = concentration of alkali,
T^0_L = total concentration of ligand,
V_0 = total volume 50 mL,
V_1 = volume of alkali required by the acid
V_2 = volume of akali used by acid and ligand
V_3 and V_2 = volumes of alkali required for acid+ligand+metal ion,
T^0_M = total concentration of the metal ion

pH titration data was utilized for determination of , dissociation constants, association constants. The plot of pH vs volume of NaOH given in the Figures 2 and 3. Dissociation constant and stability constant were evaluated by Irving-Rossotti methods and by computer pregame.



Figures 2 and 3:- Plot of pH versus volume of NaOH added (water).

Dissociation constants:-

The proton-ligand equilibrium constant for the ligand (HDPPPMHI) under experimental conditions were determined by Calvin-Bjerrum pH –titration, as modified by Irving and Rossotti for calculation of n and pH from proton-ligand formation. The proton-ligand formation curve was obtained by plotting n values against pH. This indicates that the ligand has one dissociable proton. The pK values were estimated from formation curve by noting the pH at which $\overline{n}$ = 0.5. In Irving and Rossotti method, the pH titration of the three sets of mixtures against a carbonate free standard alkali, were performed. Dissociation constants decrease with the increase in ionic strength and polarity of the media (Table 4).

Table 4. Ionization constants of (HDPPPMHI) at 25 ± 1 °C and at 0.1 M and 0.2 M ionic strengths.

Solvent	Ionic strength =0.1 M	Ionic strength =0.2 M
	pKa	pKa
Water	10.339	9.642
50% Alcohol-water	11.258	10.600
50% Dioxane-water	11.751	11.443

Association constants:-

The formation constants have been determined by plotting a graph between n and pL value and in the case of a metal ligand curve by plotting n against pL, log K and log β were calculated from the formation curve by the known values of pL at which n = 0.5 and n = 1.5 corresponds to the values ~~of~~ log K and log β, respectively. The log K values decreases with increase ionic strength of the medium which is concordance with Debye-Hukel limiting law. It means that Bronsted relationship is valid for the dissociation of ligand and complex equilibria of chelates. The difference in the log K and log β is small which is due to the simultaneous formation of complexes. The thermodynamic metal-ligand stability constants are reported in Table 5.

Table 5:- Stability constants of (HDPPPMHI) at 25 ± 1 °C and at 0.1 M and 0.2 M ionic strengths.

Solvent	Metal ions	Stability constants	Ionic strength = 0.1 M	Ionic strength = 0.2 M
Aqueous media	Cu(II)	log k	6.832	6.502
		log β	6.311	6.132
	Co(II)	log k	6.345	5.915
		log β	5.233	4.788
	Ni(II)	log k	5.812	5.777
		log β	4.635	4.534
	Hg(II)	log k	5.642	5.555
		log β	4.455	4.366
	Cd(II)	log k	5.432	5.338
		log β	4.030	3.919
	Zn(II)	log k	5.145	4.938
		log β	3.838	3.759
50% Alcohol-water	Cu(II)	log k	8.518	8.439
		log β	7.839	7.116
	Co(II)	log k	8.348	8.232
		log β	7.569	6.916
	Ni(II)	log k	7.575	7.439
		log β	6.731	6.516
	Hg(II)	log k	7.245	7.159
		log β	6.636	5.936
	Cd(II)	log k	7.057	6.855
		log β	6.539	5.416
	Zn(II)	log k	6.948	6.638
		log β	6.169	4.916
50% Dioxane-water	Cu(II)	log k	10.039	9.731
		log β	9.244	8.755
	Co(II)	log k	9.955	9.635
		log β	9.131	8.417
	Ni(II)	log k	9.845	9.239
		log β	8.888	8.012
	Hg(II)	log k	9.736	9.135
		log β	8.314	7.915
	Cd(II)	log k	9.455	8.966
		log β	8.038	7.335
	Zn(II)	log k	9.011	8.885
		log β	7.551	6.136

Conclusion:-

Potentiometric measurement of hydrogen ion concentration employed when the degree of complex formation is sensitive to the hydrogen ion concentration thus the degree of complex formation undergoes increase/decrease with change in pH. In the present work, we investigate the dissociation and association constants of 3-(((3-(2-hydroxyphenyl)-1-phenyl-1H-pyrazol-4-yl)methylene)hydrazono)indolin-2-one with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) potentiometrically using pH metric technique in aqueous, ethanol-water (50% v/v) and dioxane-water (50% v/v) mixtures at different ionic strengths (0.1 M and 0.2 M) of $NaClO_4$ and at 25 ± 1 ^oC temperature. The calculated values of dissociation and association constants decrease with the increase in ionic strength and polarity of the media.

Conflict of interests:-

The authors declare that there is no conflict of interests regarding the publication of this paper.

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