ISSN: 0976-3031

International Journal of Recent Scientific Research

Impact factor: 5.114

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Volume: 6 Issue: 9

THE PUBLICATION OF
INTERNATIONAL JOURNAL OF RECENT SCIENTIFIC RESEARCH
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International Journal of Recent Scientific Research
Vol. 6, Issue, 9, pp.6417-6421, September, 2015

International Journal of Recent Scientific Research

ISSN: 0976-3031

RESEARCH ARTICLE

PHYSICOCHEMICAL STUDIES ON BIOLOGICALLY IMPORTANT 3-(((2-HYDROXYQUINOLIN-3-YL) METHYLENE) HYDRAZONO) INDOLIN-2-ONE WITH Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) METAL IONS: IONIZATION CONSTANTS AND STABILITY CONSTANTS

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ARTICLE INFO

Article History:

Received 06th June, 2015
Received in revised form 14th July, 2015
Accepted 23rd August, 2015
Published online 28st September,2015

Key words:

3-(((2-hydroxyquinolin-3-yl) methylene) hydrazono) indolin-2-one, Ionization constants, Stability constants.

ABSTRACT

Objective: Influence of ionic strength on the proton-ligand stability constants and metal-stability constants of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with 3-(((2-hydroxyquinolin-3-yl) methylene) hydrazono) indolin-2-one (HQMHI).

Material and methods: The interaction of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) metal ions with 3-(((2-hydroxyquinolin-3-yl) methylene) hydrazono) indolin-2-one (HQMHI). has been investigated in aqueous, ethanol-water (25% v/v) and dioxane-water (25% v/v) mixtures at different ionic strengths (0.1 M and 0.2 M) of $NaNO_3$ at temperature 30 ± 1 ^oC by potentiometric titration.

Findings and conclusion: The data obtained is used to calculate the values of proton-ligand stability constants and metal-ligand stability constants. The pKa and stability constants values decreased with increase in ionic strength and the polarity of the media, which indicated the opposite charges on reacting species.

INTRODUCTION

Dissociation of organic acids and their interactions with metal ions (complex formation) may be extremely sensitive to ionic strength of the medium. If charges on the reacting species are opposite then there is a decrease in the reaction rate with increasing ionic strength whereas if the charges are identical, an increase in the reaction rate will occur and if one of the reactant is charge less the reaction rate does affect by ionic strength of the medium. Ionic strength measures the intensity of an electric field of solution due to the presence of ions in a solution. Ionic strength of medium affects the rates at which ions react with each other and hence the extent to which the reaction occurs. It is related to the concentration of electrolytes and indicates how effectively the charge on a particular ion is shielded or stabilized by other ions in an electrolyte (Deosarkar *et al.*, 2011).

Hydrazones are azomethines characterized by the presence of the triatomic group C=N-N< and form an interesting class of compounds that find different applications in biological, clinical, analytical and various other fields (Mohanan and Murukan, 2005). Various hydrazones which have applications such as biologically active compounds and analytical reagents are obtained depending on the experimental conditions. In analytical chemistry, hydrazones find application in detection, determination, and isolation of compounds containing the carbonyl group (Raman *et al.*, 2011). Isatin, an endogenous indole, and its derivates have exhibited a wide range of biological activities (Mohamad *et al.*, 2014). Although much work has been reported with heterocyclic monohydrazones, very little information is available on bishydrazones (Murukan *et al.*, 2007). In the view of analytical application, it was an interest to know the physicochemical properties such as stability constants of complexes with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) metal ions at various ionic strength (Tambatkar *et al.*, 2010). The present paper describes study of ionization and stability constants of 3-(((2-hydroxyquinolin-3-yl) methylene) hydrazono) indolin-2-one with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) metal ions in aqueous, ethanol-water (25% v/v) and dioxane-water (25% v/v) mixtures at different ionic strengths (0.1 M and 0.2 M) of $NaNO_3$ and at 30 ± 1 ^oC temperature by pH metric study.

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Experimental

Synthesis of 3-(((2-hydroxyquinolin-3-yl) methylene) hydrazono) indolin-2-one (HQMHI)

The 3-(((2-hydroxyquinolin-3-yl) methylene) hydrazono) indolin-2-one has been synthesized by refluxing the equimolar mixture of hot methanolic solution 2-hydroxyquinoline-3-carbaldehyde (0.01 mol, 30 mL) and methanolic solution of isatin monohydrazone (0.01 mol, 30 mL) for 6-7 h in presence of catalytical amount of Conc. HCl. The product obtained after the evaporation of the solvent was filtered, washed with cold methanol and finally recrystallized from methanol to afford HQMHI as shown in Figure I. The purity of the compound has been checked by TLC.

Reagents and materials

All the chemicals used in present study were of analytical grade. 3-(((2-hydroxyquinolin-3-yl) methylene) hydrazono) indolin-2-one were procured and used as a ligand.

Ethanol and dioxane were purified by the standard procedures (Vogel, 1968). Ligand solution was prepared by dissolving weighed portions of appropriate ligand in purified alcohol. Metal ion solutions were prepared from metal nitrates in double distilled water and standardized with EDTA (Jeffery *et al*., 1989). Solution of HNO3, 0.1M NaOH and 0.1 M and 0.2 M $NaNO_3$ was also prepared in double distilled water. A carbonate free sodium hydroxide solution was used as the titrant and standardized against oxalic acid. The measurements of pH (accuracy ± 0.01) were accomplished by means of Elico pH-meter model L1-122 using calomel and glass electrodes. The pH meter was switched on half an hour before starting the titration for the initial warm up of the instrument. Before making any measurement with the meter the electrodes were washed with distilled water and dried with filter paper. The readings were record only when the instrument registered a steady value for at least one minute (Meshram *et al*., 2014). The pH meter was standardized before each titration with a buffer solution of pH 4.0 and 9.2. The pH-meter readings were corrected by Van Uitert and Hass relation (Vanuitert and Hass, 1953).

Potentiometric measurements

Titrations were carried out in aqueous, ethanol-water (25% v/v) and dioxane-water (25% v/v) mixtures and a different ionic strengths was maintained by using $NaNO_3$ at 30 ± 1 °C in an inert atmosphere by bubbling oxygen free nitrogen gas through an assembly containing the electrode to expel out CO_2 (Phase *et al*., 2013). 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.

RESULTS AND DISCUSSION

Titration curves

Potentiometric titrations of the ligand with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) were carried out with standard NaOH, $NaNO_3$ (0.1 M and 0.2 M) and at 30 ± 1 °C temperature, in aqueous, ethanol-water (25% v/v) and dioxane-water (25% v/v) mixtures. The representative set of the potentiometric titration curves of the free ligand and complexed 3-(((2-hydroxyquinolin-3-yl) methylene) hydrazono) indolin-2-one as a typical example in ethanol-water (25% v/v) at 0.1 M and 0.2 M ionic strengths are shown in (Figure II and III). It is observed that the complex curves almost coincided with the ligand curve in the initial stage afterwards started diverging. This indicates the liberation of proton from HQMHI due to the formation of the respective metal complexes. The decrease in pH for the metal titration curves relative to the ligand titration curve can be attributed to the formation of metal ligand bonding (Bjerrum *et al*., 1941, Varam and Rajkumari, 2011).

Table 1 T = 30 ± 1 °C Aqueous medium μ = 0.1 M/ 0.2M $NaNO_3$

Solution (Initial concentration)	Acid titration	Ligand titration	Metal titration
HNO_3 (0.01M)	5.0 mL	5.0 mL	5.0 mL
$NaNO_3$ (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 = 30 ± 1 °C 25% Ethanol-water μ = 0.1 M/ 0.2M $NaNO_3$

Solution (Initial concentration)	Acid titration	Ligand titration	Metal titration
HNO_3 (0.01M)	5.0 mL	5.0 mL	5.0 mL
$NaNO_3$ (1M / 2M)	5.0 mL	5.0 mL	5.0 mL
Ethanol	12.5 ml	12.5 ml	12.5 ml
Water	27.5 ml	22.5 ml	17.5 ml
Ligand (0.01M)	-----	5.0 ml	5.0 ml
Metal (0.01M)	-----	----	5.0 ml

Potentiometric determination of the ionization constants

Proton-ligand formation number n_A are evaluated using Irving-Rossotti's expression (Irving and Rossotti, 1954).

$$\bar{n}_A = Y - \frac{(V_2 - V_1)(N + E^0)}{(V_0 + V_1)\, T^0_L} \quad \ldots\ldots\ldots\ldots(1)$$

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. HQMHI having only one dissociate H+ ion from –OH group and can therefore be represented as HL (Avinash and Marutil, 2013).

$$HL \rightarrow H^+ + L^-$$

pKa values were calculated from formation curves (pH vs n_A) by noting pH at which n_A = 0.5 at different ionic strengths. 3-(((2-hydroxyquinolin-3-yl) methylene) hydrazono) indolin-2-one exhibits only one pKa value in the range of 8.704 to 10.556 in 0.1 M ionic strength and 8.201 to 9.923 in 0.2 M ionic strengths (Table 4) respectively in different solvent media, this can be attributed to the ionization of –OH group of the (HQMHI). The proton-ligand stability constants increase with decreases the polarity of the media.

Table 3 T = 30 ± 1 °C 25% Dioxane-water μ = 0.1 M/ 0.2M $NaNO_3$

Solution (Initial concentration)	Acid titration	Ligand titration	Metal titration
HNO_3 (0.01M)	5.0 mL	5.0 mL	5.0 mL
$NaNO_3$ (1M / 2M)	5.0 mL	5.0 mL	5.0 mL
Dioxane	12.5 ml	12.5 ml	12.5 ml
Water	27.5 ml	22.5 ml	17.5 ml
Ligand (0.01M)	-----	5.0 ml	5.0 ml
Metal (0.01M)	-----	------	5.0 ml

Table 4 Ionization constants of HQMHI at 30 ± 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	8.704	8.201
25% Alcohol-water	9.310	8.908
25% Dioxane-water	10.556	9.923

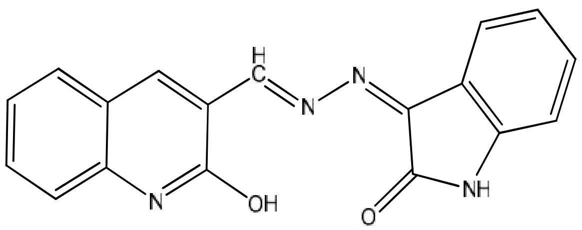
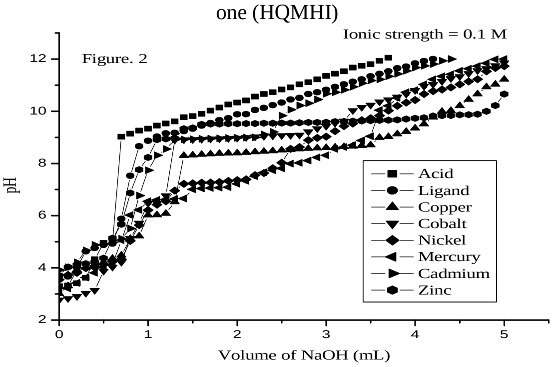


Figure I 3-(((2-hydroxyquinolin-3-yl) methylene) hydrazono) indolin-2-one (HQMHI)



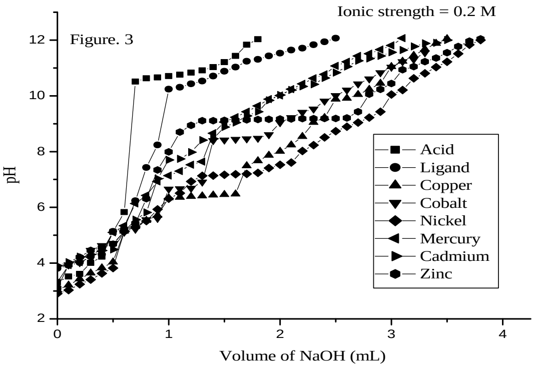


Figure II and III Plot of pH versus volume of NaOH added (water).

Potentiometric determination of the stability constants

Metal-ligand stability constants of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with 3-(((2-hydroxyquinolin-3-yl) methylene) hydrazono) indolin-2-one was determined by employing Bjerrum-Calvin pH titration technique as adopted by Irving and Rossotti (Irving and Rossotti, 1954).

Table 5 Stability constants of HQMHI at 30 ± 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
water	Cu(II)	log k	7.00	6.25
		log β	5.66	5.14
	Co(II)	log k	6.61	6.18
		log β	5.42	4.69
	Ni(II)	log k	6.23	5.96
		log β	5.14	4.44
	Hg(II)	log k	5.77	4.82
		log β	4.95	3.96
	Cd(II)	log k	4.75	4.11
		log β	3.31	3.22
	Zn(II)	log k	3.77	3.60
		log β	2.73	2.68
25% Alcohol-water	Cu(II)	log k	7.68	7.22
		log β	6.66	6.22
	Co(II)	log k	7.48	7.15
		log β	6.58	5.96
	Ni(II)	log k	7.33	6.86
		log β	6.14	5.69
	Hg(II)	log k	7.14	6.78
		log β	6.02	5.54
	Cd(II)	log k	6.09	5.59
		log β	5.38	4.11
	Zn(II)	log k	5.48	4.23
		log β	4.96	3.35
25% Dioxane-water	Cu(II)	log k	8.82	8.03
		log β	7.79	7.06
	Co(II)	log k	8.75	7.76
		log β	7.69	6.75
	Ni(II)	log k	8.69	7.69
		log β	7.45	6.33
	Hg(II)	log k	8.45	7.45
		log β	7.06	6.29
	Cd(II)	log k	8.09	7.26
		log β	6.86	6.09
	Zn(II)	log k	7.26	6.39
		log β	6.29	5.36

Irving–Bjerrum method gives the following equation for the complex formation function, n, i.e., average number of ligands bound to metal cation (Serap and Perihan, 2004). The stoicheiometric metal-ligand stability constants have been calculated from the formation curves obtained by plotting n against pL (Al-sarawy *et al.*, 2005).

$$\bar{n} = \frac{(V_3-V_2)\,(N-E^0)}{(V_0-V_2)\,T^0_M\,\bar{n}_A} \quad \ldots\ldots\ldots\ldots\ldots(2)$$

where V_3 and V_2 volumes of alkali required for acid+ligand+metal ion, T^0_M total concentration of the metal ion, rest of term symbols are as given in equation 1. pL values are calculated by equation 3 as given below.

log [antilog (pK $_a$ – pH)]

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

The stability constants of metal complexes can be very easily calculated by this method. As we increases the polarity of the media such as dioxane-water (25% v/v), ethanol-water (25% v/v) aqueous media, the metal-ligand stability constants are decreases. The stability constants indicate the formation of both 1:1 and 1:2 matal-ligand complexes and data is summarized in Table 5**.**

Variation of the association and dissociation constants with ionic strengths

The effect of variation of ionic strength on the stabilities of metal complexes of 3-(((2-hydroxyquinolin-3-yl) methylene) hydrazono) indolin-2-one has been determined. For this purpose the association and dissociation constants of these ligand have been evaluated at two different ionic strengths (0.1 and 0.2 M) using $NaNO_3$ as a supporting electrolyte at constant temperature (30 ± 1 ^oC). From above data it is observed that the association and dissociation constants decrease with raise in ionic strength of the media which in accordance with Debye-Hukel theory (Shakru *et al*., 2011, Agarwal *et al*., 1982).

CONCLUSION

The ionization and stability constants of complexes were determined pH metrically in aqueous, ethanol-water (25% v/v) and dioxane-water (25% v/v) mixtures at temperature 30 ± 1 ^oC with two different ionic strengths (0.1 M and 0.2 M) of $NaNO_3$. The calculated values of ionization and stability constants decrease with the increase in ionic strength and polarity of the media. Ionization and stability constants are also important parameters for the selection of the optimum conditions in the development of analytical methods.

Conflict of Interests

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

Acknowledgement

The authors are thankful to the Chairman, Department of Chemistry, Gulbarga University, Kalaburagi, for encouragement and facilities. One of the authors (NSM) is thankful to UGC New Delhi for the grant of research fellowship in science for Minority students Under MANF Scheme.

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How to cite this article:

Siddappa K and Nabiya Sultana M.2015, Physicochemical Studies on Biologically Important 3-(((2-Hydroxyquinolin-3-yl) Methylene) Hydrazono) Indolin-2-One With Co(Ii), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) Metal Ions: Ionization Constants and Stability Constants. *Int J Recent Sci Res*, 6(9), 6417-6421.

International Journal of Recent Scientific Research

ISSN 0976-3031

9 770976 303009