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Study of metal ions with Benzofuran-2-carbohydrazone

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Abstract

The stability constants of 1:1 and 1:2 complexes formed between Cu^{+2} , Ni^{+2} , Cd^{+2} and UO_2^{+2} with Schiff base derived from condensation of benzofuran-2-carbohydrazone with 2-hydroxy-1-naphthaldehyde has been determined by pH metric titration method as suggested by Irving-Rossodi [13]. The titrations were carried out at four different ionic strengths viz. 0.05, 0.10, 0.15 and 0.20 M NaClO_4 solution in non-aqueous medium 60:40% (v/v) alcohol-water and at constant temperature of $30 \pm 1^\circ\text{C}$.

Keywords: Schiff base, proton-ligand and metal-ligand stability constants.

Introduction

Simple 2,3-substituted benzofuran and their derivatives are used as bactericide [1], cardiovasculars [2], antiinflammatory [3], local anesthetic [4] agents. Some of the benzofuran compounds viz. 2-nitrobenzofurans 2-acetylbenzofurans are used as microbicidal [5], nematocidal, diuretic and choleric [6] agents. The compound aminodarone hydrochloride is used as antiarrhythmic drug which contains benzofuran nucleus. The schiff bases derived from aromatic aldehydes with hydrazides and amines form widely studied ligands. Hydrazides and hydrazones are widely used as antitubercular compounds, inhibitors of enzymes [8], and they possess wide range of biological activity. The most of the nucleotide-revelent enzymes [9] like DNA and RNA polymerases, kinase and ATP synthases are metal ion i.e. Zn^{+2} dependent and they use nucleotides as substrates only in the form of complexes i.e. Mg^{+2} . This has led to the intensive studies of metal ion bonding properties of organic molecules. In view of the above facts we here report stability constants of complexes formed between Cu^{+2} , Ni^{+2} , Zn^{+2} , Co^{+2} , Cd^{+2} and UO_2^{+2} with schiff base derived from condensation of benzofuran-2-carbohydrazone with 2-hydroxy-1-naphthaldehyde. Titrations were carried out by Calvin-Bjerrum pH titration technique in 60:40% (v/v) alcohol-water medium at four different ionic strength of 0.05, 0.1, 0.15 and 0.2M NaClO_4 and at $30 \pm 1^\circ\text{C}$ temperature.

Experimental

All chemicals used in the present investigations were of analytical grade.

Preparation of ligand solution

The solutions of ligand 0.002M was prepared by dissolving requisite quantity of the schiff base in distilled alcohol. This solution was used for all titrations.

Preparation of NaClO_4 , NaOH and HClO_4 solutions

These solutions were prepared in CO_2 free double distilled water by dissolving appropriate quantity of NaClO_4 , NaOH and HClO_4 to give final concentrations of 1M, 0.105M and 0.0109M respectively.

Metal salt solutions

The metal salt solutions of 0.02M were prepared in the double distilled CO_2 free water using metal nitrates. The metal contents were determined by standard method [10].

pH meter and other accessories

An Elico digital pH meter model LI-122 equipped with combined glass electrode type CL-51, with an accuracy of ± 0.01 unit having pH range 0-14 and the temperature range of 20-100 $^\circ\text{C}$ was used for the pH measurements. The pH meter was calibrated with the standard r

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buffers (pH 4.00 and 9.18), before taking readings. The pH meter reading were corrected in non-aqueous medium [11]. All titrations were carried out in double walled glass cell in an inert atmosphere of nitrogen at different ionic strength i.e. 0.05, 0.1, 0.15 and 0.2M NaClO₄ and at 30±1 °C temperature. The following solutions were titrated pH metrically against standard (0.105 N) NaOH₄ solution and total volume being 50 ml in each case.

Acid titration: 5ml of (0.0109N)

- HClO₄+2.44 ml of (1.0M)
- NaClO₄ + 35ml of alcohol + 7.56 ml of H₂O

Ligand titration:

- +5ml of (0.002 M) Ligand + 25 ml of alcohol

Metal titration:

- (ii) +0.5 ml of (0.02 M) metal ion solution + 7.06 ml of H₂O

In other sets requisite amount of NaClO₄ was added to maintain the ionic strength of 0.1, 0.15 and 0.2M. The ratio between metal: ligand was kept that 1:1 in all titrations. All titrations were carried out 70:30% (v/v) alcohol-water medium at constant temperature 30±1 °C.

Preparation of ligand

The Schiff base used in this work was prepared as follows: The benzofuran-2-carbohydrazide¹² (1 mol) in alcohol was treated with 2-hydroxy-1-naphthaldehyde (0.1 mol) in the same solvent the mixture was refluxed on water bath for about 5 hrs. during which light yellow coloured schiff base separated out. The solution was cooled, filtered and washed with alcohol. The schiff base was crystallized from alcohol. The purity of the compound was tested with TLC. [Mol. Formula = C₂₀H₁₄O₃N₂, m.p. = 271-272°C, Yield = 85%, IR in KBr pallets : νC = N 1622 cm⁻¹, νNH 3485 and 3207 cm⁻¹ and νC=O 1689 cm⁻¹]

Results and Discussion

Proton ligand stability constant

The value of proton-ligand stability constant (-log K_a) was calculated using Irving Rossotti [13] equation. The values of \bar{n}_A at various B values were calculated by using acid and ligand titrations curves. The formation curves are extended over the range 0.216 < \bar{n}_A < 0.750, at 0.05, 0.1, 0.15 and 0.20 M ionic strengths. These values of \bar{n}_A suggests that only one proton was liberated per ligand molecule and presence of HL species. The protonation of HC=N group does not take place at this experimental condition. The values of pK_a was calculated by three different methods, by plotting the graph of \bar{n}_A vs B, the pK_a value of schiff base decreases with increase in ionic strength of the 'medium, which is in agreement with Debye-Huckel¹⁴ equation.

Metal ligand stability constants

The comparison between acid and metal titration curves indicates that the metal curves are well separated from the ligand curves. This suggests the formation of metal-ligand complex in solution. The metal ligand formation constant \bar{n} and pL values were calculated using three different methods i.e.

- half integral method i.e. form the graph n vs. pL, at $\bar{n} = 0.5$ and 1.5
- graphical method, log (n/l-n) vs. pL, at log ($\bar{n} / l - \bar{n}$) = 0
- point wise calculation method log K₁ = pL + log $\bar{n} / l - \bar{n}$ as suggested by Irving-Rossotti [13].

The values of \bar{n} varies between 0.15 < \bar{n} < 2.10 for all ionic strengths. These values indicates that there is formation of 1:1 and 1:2 compexes in the solutions. The average values of all these methods are given in table-1.

Table I: Metal-ligand, protot-ligand-stability constants, standard free energy change and thermodynamic stability constants of the complexes at various ionic strength at 30±1 °C

Metal ion	Stability constant	μ=0.05	μ = 0.10	μ = 0.15	μ = 0.2	Log K ⁰ at μ = 0.0M
H ⁺ Cu(II)	pKa	9.70	9.016	8.975	8.751	-
	Log K ₁	10.624	9.906	-	9.782	-
	Log K ₂	7.376	7.194	-	6.717	11.4
	Log β ₂	18.00	17.10	-	16.50	7.6
	-ΔG ⁰ Kcal	24.957	23.709	-	22.878	
Ni(II)	Log K ₁	5.866	5.530	5.003	4.982	6.3
	Log K ₂	4.961	4.659	4.619	4.585	5.2
	Log β ₂	10.827	10.189	9.622	9.567	
	-ΔG ⁰ Kcal	15.012	14.127	13.341	13.265	
Zn(II)	Log K ₁	7.004	6.950	6.419	5.640	8.5
	Log K ₂	6.250	5.803	5.792	5.273	6.7
	Log β ₂	13.254	12.753	12.211	10.913	
	-ΔG ⁰ Kcal	18.377	19.703	17.069	15.131	
Co(II)	Log K ₁	6.813	6.035	5.563	5.114	7.7
	Log K ₂	5.225	4.764	4.760	4.473	5.7
	Log β ₂	12.038	10.799	10.328	9.587	
	-ΔG ⁰ Kcal	16.691	19.973	14.32	13.292	
Cd(II)	Log K ₁	5.875	5.394	5.012	4.740	6.5
	Log K ₂	5.313	4.950	4.728	4.660	5.8
	Log β ₂	11.188	10.344	9.740	9.400	
	-ΔG ⁰ Kcal	15.512	14.342	13.504	13.03	
UO ₂ (II)	Log K ₁	9.579	9.210	8.835	8.605	10.1
	Log K ₂	8.519	7.826	7.672	7.620	9.0
	Log β ₂	18.098	17.086	16.507	16.330	
	-ΔG ⁰ Kcal	25.098	23.62	22.88	22.643	

Some cases $\log K_1$ is calculated equation $\log K_1 K_2 = 2pL$, pL at $\bar{n} = 1.0$, by interpolation of mid-point, Generally; $\log K_2$ is less than $\log K_1$ on account of statistical and electrostatic point. In, the present case we observe that $\log k_1 > \log K_2$ in all the. Systems, this may be due to interaction of second molecule of ligand is slower than the first one ^[15]. The order of stability constants for present metal chelates follows the order-

- $\log \beta_2$: $UO_2^{+2} > Cu^{+2} > Zn^{+2} > Co^{+2} > Cd^{+2} > Ni^{+2}$ at $\mu = 0.05$
- $Cu^{+2} > UO_2^{+2} > Zn^{+2} > Co^{+2} > Cd^{+2} > Ni^{+2}$ at $\mu = 0.10M$
- $UO_2^{+2} > Zn^{+2} > Co^{+2} > Cd^{+2} > Ni^{+2}$ at $\mu = 0.15M$
- $Cu^{+2} > UO_2^{+2} > Zn^{+2} > Co^{+2} > Ni^{+2} > Cd^{+2}$ at $\mu = 0.20M$

From the above sequence, it is observed that Irving-Williams ^[16] natural order is followed. The regularity of sequence can be correlated increase in second ionization potential in; passing from $Cd(II)$ to $Cu(II)$. The thermodynamic-Stability constant $\log K_1^0$ and $\log K_2^0$ of the complexes have been obtained by extrapolating the straight line of $\log K_1$ vs $\sqrt{\mu}$ to zero ionic strength. These values are given in the Table 1. The values suggests that metal ion combine predominantly with the ligand. The equilibrium involved between metal (II) ions and ligand molecule can be represented as:

- $LH \rightleftharpoons L + H$; pK_1
- $M + L \rightleftharpoons ML$; $\log K_1$
- $ML + L \rightleftharpoons ML_2$; $\log K_2$,
- $M + 2L \rightleftharpoons ML_2$; $\log K_2$

In order to explore any possible correlation between- $\log \beta_2$ of Metal ligand systems and some of the fundamental properties of metal ions the following graphs were plotted,

- a. $\log \beta_2$ vs atomic number
- b. $\log \beta_2$ vs second ionization potential
- c. $\log \beta_2$ vs electronegativity
- d. $\log \beta_2$ vs reciprocal of ionic radii
- e. $\log \beta_2$ vs sum of first and second IP

In the case of $\log \beta_2$ vs atomic number of metal ions reveals that there is a monoatomic increase to a maximum of Cu^{+2} followed by lower value of Zn^{+2} . Similarly in the plots of $\log \beta_2$ vs reciprocal of ionic radii of metal ions show that the ligand forms a least stable complex with Ni^{+2} and most stable complex with Cu^{+2} in comparison with other metal ions. The plots of $\log \beta_2$ vs electronegativity shows that the stability of these metal complexes increases with increase in electronegativity except Cd^{+2} and Ni^{+2} which suggest that metal ligand bond would be covalent¹⁷. It is also observed that stability of metal chelates increases as second ionization potential increases from Cd^{+2} , to Cu^{+2} except Ni^{+2} . Similar observations are made by Irving and Williams ^[16] and Ackermann and others ^[18].

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