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Solution Equilibrium Studies on Metal(II) Complexes with 3-Amino-2-benzofurancarboxamide Schiff Base

M.B. Halli[*], Kinni. Mallikarjun, Vijayalaxmi. B. Patil and R.B. Sumathi

Department of Chemistry, Gulbarga University, Gulbarga-585 106, India

*Corresponding author: E-mail: mbhalli@rediffmail.com

The stability constant of Cu(II), Ni(II), Co(II), Cd(II), Ba(II), Mg(II) and UO_2(II) complexes were determined with Schiff base derived from condensation of 3-amino-2-benzofuran-carboxamide with 8-formyl-7-hydroxy-4-methyl-coumarin by pH metric method. Irving-Rossotti technique was used to determine pK^H_{OH} and log K values, at constant ionic strength of 0.1M $NaNO_3$ at 30 ± 1 °C in 60:40 % (v/v) alcohol and water medium. The order of stability constant was found to be UO_2 > Cu > Ni > Cd > Co > Ba > Mg. The negative values of free energy change suggest that the reactions are spontaneous one.

Key Words: Equilibrium constant, 3-Amino-2-benzofurancarboxamide, Schiff base, Metal complexes.

INTRODUCTION

The compound with benzofuran moiety are well known as biodynamic agents possessing various antimicrobial agents[1], analgesic[2], analeptic, antiviral[3], cardiovascular[4] *etc*. Some of the natural compounds with benzofuran nucleus are used as effective medicines[5] in the treatment of heart diseases and whooping cough, Baker's yeast contains a benzofuran derivative which acts as an oxidant and prevents hemorrhagic liver necrosis in rats and haemolysis of red cells in vitamin-E deficient rats[6].

The coumarin derivatives have been of great interest because of their role in natural and synthetic chemistry, they also exhibit biological activity such as anticoagulant agents[7], florescent brighteners, insecticides[8] *etc*. The biological activity is associated with hydrazone compounds attributed to the presence of the active pharmacophore (-CONH-N=C-). Hence many hydrazone compounds containing this active moiety showed good anticancer activities[9].

From the literature survey it is observed that both benzo-furan and coumarin derivatives are biologically active compounds. In the present study we report solution stability constant of metal complexes of Co(II), Cu(II), Ni(II), Cd(II), Ba(II), Mg(II) and UO_2(II) ions with 3-amino-2-benzofuran-carboxamide Schiff base in 60:40 % (v/v) ethanol-water medium at 30 ±1 °C temperature at 0.1 M ionic strength ($NaNO_3$).

Schiff base is derived from condensation of 3-amino-2-benzofuran-carboxamide with 8-formyl-7-hydroxy-4-methylcoumarin.

EXPERIMENTAL

All chemicals used were of analytical grade. The comp-ounds 3-amino-2-carboxamide[10] and 8-formyl-7-hydroxy-4-methyl-coumarin[11] were prepared as per literature methods.

Preparation of Schiff base: The Schiff base was prepared by the condensation of 3-amino-2-benzofuran-carboxamide (0.01 mol) in alcohol (20 mL) with 8-formyl-7-hydroxy-4-methyl-coumarin (0.01 mol) in ethanol (20 mL). The reaction mixture was refluxed on water bath for about 8 h. On partial removal of the solvent and cooling the reaction mixture to room temperature, the separated light yellow coloured Schiff base was collected by filteration, washed with alcohol and recrystallized from alcohol. The purity of Schiff base was tested with TLC. The synthesis of Schiff base is shown in Fig. 1. m.f.: $C_{20}H_{14}N_2O_5$, m.w. 362.33, Yield = 75 %, m.p. 222 ºC.

Infrared spetra of the Schiff base was taken in KBr pallet on Perkin-Elmer 783 model FTIR spectro-photometer in the region 4000-350 cm^{-1}. The Schiff base exhibits band at 3250 cm^{-1} due to primary amino group. The bands at 2923 and 2852 cm^{-1} are due to hydrogen bonded ν(OH) stretching vibrations. The stretching frequencies of C=O ($CONH_2$) appears at 1699 cm^{-1} and ν(C=O) stretch of lactone appears at 1627cm^{-1}. All these spectral data suggests that the proposed structure for the Schiff base.

^{1}H NMR spectrum of ligand was taken in DMSO-d_6 solvent on AV-300 MHz NMR spectrophotometer using TMS as an internal standard. The Schiff base shows a sharp signal at δ 11.90 (s, 1H, OH) due to phenolic proton, another sharp
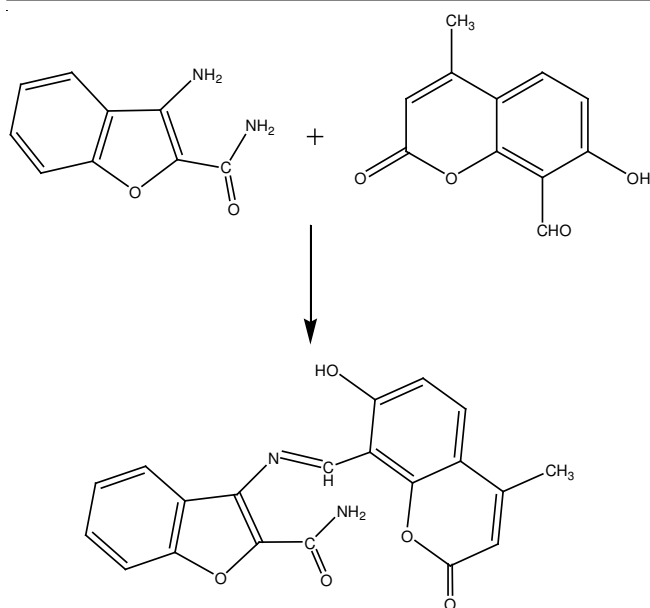
Fig. 1. Synthesis of ligand (LH)

signal appeared at δ 10.45 (s, 2H, CONH$_2$) assigned to -CONH$_2$ protons. The fine signal at δ 9.73 (s, 1H, -N=CH-) is due to azomethine proton. The 16 aromatic protons of the ligand have resonated as multiplets in the region δ (7.96-6.31) (m, 16H, ArH). FAB-Mass spectra of the Schiff base shows molecular ion peak at M/Z 362. This indicates the assigned structure to the Schiff base.

Preparation of solutions

The solution of the Schiff base (LH) was prepared by dissolving the requisite amount of the compound in distilled alcohol just before use.

Preparation of HNO$_3$, NaOH, NaNO$_3$ solution: The stock solution of 0.01M HNO$_3$, 0.101M NaOH and 1M NaNO$_3$ were prepared by dissolving appropriate quantity of AR grade respective compounds in CO$_2$ free double distilled water. The same solutions were used for all titrations.

Preparation of metal ion solution: The stock solution of metal ion (0.002M) were prepared in CO$_2$ free double distilled water using metal nitrates, the metal contents were determined using standard methods.

Procedures: All titrations were carried on Elico-122 digital pH meter equipped with combined glass electrode type CL-52 having pH range (0-14) at temperature range of 0-100 ºC was used. To account for the difference in acidity, basicity, dielectric constant and ionic activity in non-aqueous solvent, the pH meter readings were corrected as per literature method[12]. All measurements were carried out 100 mL glass beaker at 30 ± 1 ºC. The solution were allowed to attain equilibrium at the experimental temperature and titrated against 0.101N NaOH solution at a constant ionic strength of 0.1M NaNO$_3$.

RESULTS AND DISCUSSION

Proton-ligand stability constant: The proton-ligand stability constant pKa is calculated from the acid and ligand titration curves using Irrving-Rossoti method. The graphs of $\tilde{n}_A$ against B (B corrected pH) were plotted, $\tilde{n}_A$ values at various B values were determined. Sample titration curves are shown

in Fig. 2. The formation curve is extended over the range $0.3022 < \tilde{n}_A < 0.6759$. This suggests that presence of only one dissociable proton from ligand molecule *i.e.*, phenolic OH. After deprotonation this takes part in coordination with metal ions. The dissociation equilibrium can be represented as:
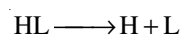
$$HL \longrightarrow H + L$$
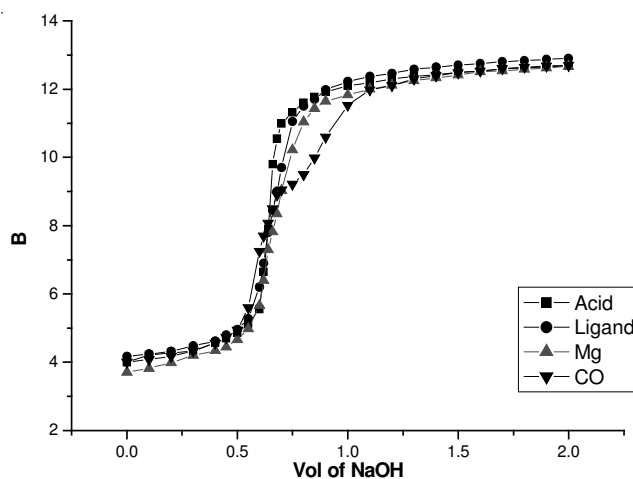
$$K_{OH}^{H} = \frac{[H][L]}{[HL]}$$

Fig. 2. Plot of B (corrected pH) *versus* volume of NaOH added

The proton-ligand stability constant was determined by using following methods.

(i) By half integral method, from the graphs of $\tilde{n}_A$ *versus* B. at $\tilde{n}_A = 0.5$.

(ii) By graphical method, from the plot of log [$\tilde{n}_A/(1 - \tilde{n}_A)$] *versus* B.

(iii) By the point wise calculation method $pK_{OH}^{H} = B + \log [\tilde{n}_A/(1 - \tilde{n}_A)]$.

The pK_{OH}^{H} average value obtained by three methods is 10.028. This pK_{OH}^{H} value is in good agreement with the reported ones[13] by varies workers for different Schiff base.

Metal-ligand stability constant (log K): The metal titration curves are separated by ligand and acid titration curves, this indicates the formation of metal chelates in solution. The values of $\tilde{n}$ are in the range of $0.051 < \tilde{n} < 1.873$. This shows the formation of both 1:1 and 1:2 complexes in solution.

The metal-ligand stability constant (log K$_1$ and log K$_2$) were calculated by using following methods.

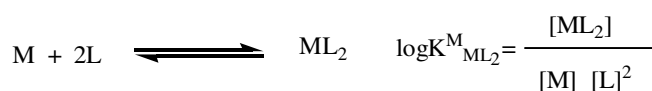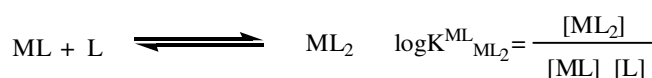(i) By half integral method, from plot of $\tilde{n}$ *versus* pL, at $\tilde{n} = 0.5$ and 1.5.

(ii) By graphical method, from plot of log [$\tilde{n}/(1 - \tilde{n})$] *versus* pL and log [$(2-\tilde{n})/(\tilde{n}-1)$] *versus* pL at log [$\tilde{n}/(1 - \tilde{n})$] = 0 and log [$(2-\tilde{n})/(\tilde{n}-1)$] = 0.

(iii) log K$_1$ and log K$_2$ were also obtained by point wise method.

The average values of all the three methods are given in Table-1. The values obtained are in good agreement. Generally log K$_1$ is more than log K$_2$, this may be in account of statistical and electrostatic point. This suggests that interaction of second ligand molecule is slower than the first one. The formation of complexes may be shown by the following equations.

TABLE-1
PROTON-LIGAND AND METAL-LIGAND
STABILITY CONSTANTS OF SCHIFF'S BASE
AT 30 ± 1 °C AND μ = 0.1M NaNO₃

Ligand/Complex	log K_1	log β_2	ΔG° (kcal/mol)
Ligand	pK^H_{OH} = 10.073	–	–
UO₂(II)	7.9475	15.00	11.019
Cu(II)	7.2213	13.0397	10.012
Ni(II)	6.7255	11.6683	9.325
Cd(II)	5.8065	11.5173	8.050
Co(II)	5.4162	10.2724	7.509
Ba(II)	4.5156	–	6.261
Mg(II)	4.2479	–	5.889

$$M + L \rightleftharpoons ML \qquad logK^M_{ML} = \frac{[ML]}{[M][L]}$$

$$ML + L \rightleftharpoons ML_2 \qquad logK^{ML}_{ML_2} = \frac{[ML_2]}{[ML][L]}$$

$$M + 2L \rightleftharpoons ML_2 \qquad logK^M_{ML_2} = \frac{[ML_2]}{[M][L]^2}$$

The stability order is observed as UO₂ > Cu > Ni > Cd > Ba > Mg. This order in good agreement with Irving and Williams[14] natural order the free energy change ΔG was calculated and the negative values indicate reactions tends to proceed spontaneously.

Correlation between log K_1 and the fundamentals properties of the metal ion: In order to explain the possible relationship between log K_1 values of metal ligand system and some of the fundamental properties of metal ions, in the present study the relationship explained are (i) Plots of log K_1 values *versus* atomic number of elements. (ii) Plots of log K_1 values vs electronegativity. (iii) Plots of log K_1 values *versus* first ionization energy. (iv) Plots of log K_1 values *versus* reciprocal of ionic radii. (v) Plots of log K_1 values *versus* sum of first and second ionization potential.

In case of plots of log K_1 *versus* atomic number of elements (Fig. 3) it was observed that in a monotonic rise to a maximum of Cu followed by lower value of Cd. A similar relationship was observed by Irving Williiams[15] this shows that stability seems to decrease with increase in bascity of the metal ions. *i.e.*, weakly basic metal like Cu(II) forms stronger chelates and strongly basic metal like Mg forms weaker chelates[16].

In the case of log K_1 *versus* second ionization potential (Fig. 4) it was observed that the second ionization potential increases along the transition series to a maximum of Cu(II). The same trend was observed by various workers[17]. The similar relation was observed in the present case. log K_1 *versus* sum of first and second ionization potential (Fig. 5). In the case of plot of log K_1 *versus* electronegativity (Fig. 6) also confirms the above observations. In the case of plot of log K_1 *versus* reciprocal of ionic radii (Fig. 7) this suggests that metal-ligand bond would be a covalent and hence it is seen that stability constant increases as electronegativity increases to a maximum of Cu(II) followed by lower value of Ni(II).
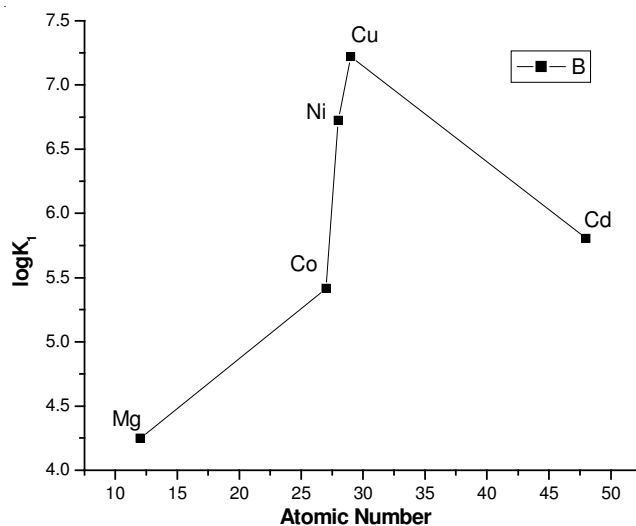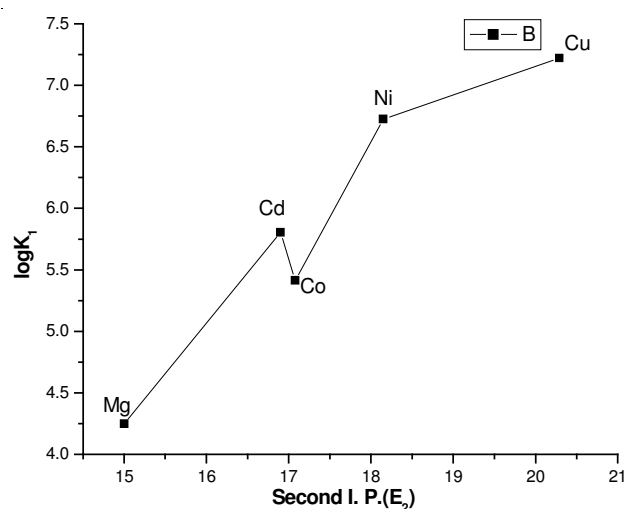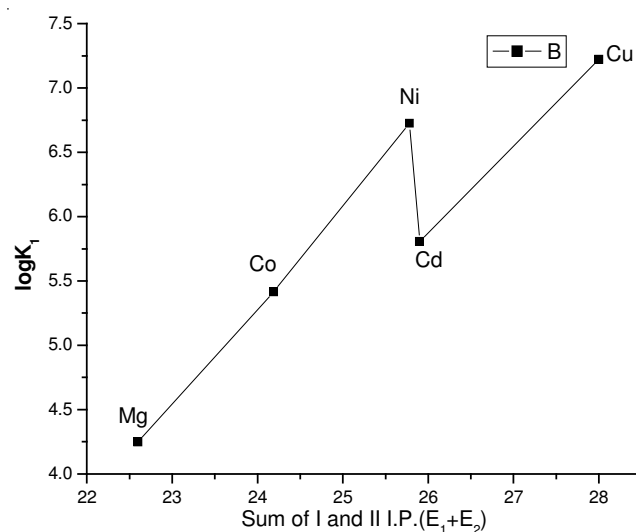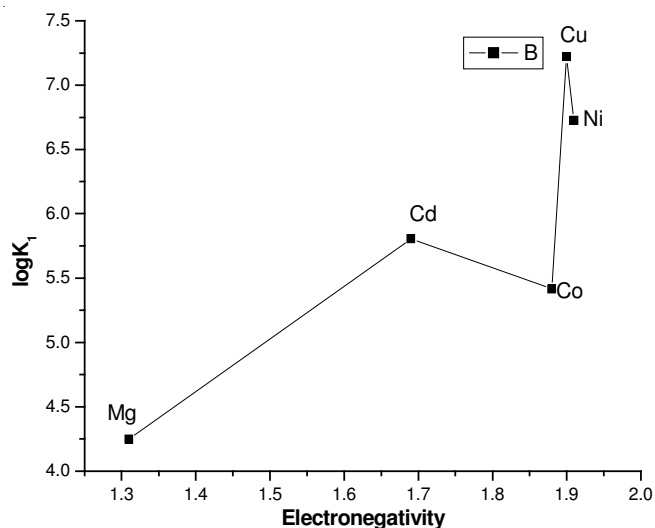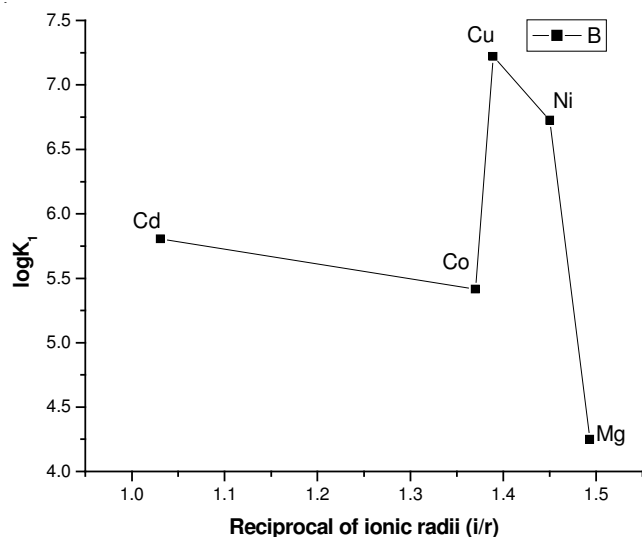

Fig. 3. Plt of log K_1 *versus* atomic number

Fig. 4. Plot of log k_1 *versus* second ionization potential

Fig. 5. Plot of log K *versus* sum of first and second ionization potential

Fig. 6. Plot of log K_1 *versus* electronegetivity

Fig. 7. Plot of log K_1 *versus* reciprocal of ionic radii (i/r)

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