

Stability study of complexation of transition metals with schiff base 2-hydroxy-5-bromoacetophenone-N-(4-methoxyphenyl) imine: Thermo dynamic aspect

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Abstract:

Stability constant of schiff base 2-hydroxy-5-bromoacetophenone-N-(4-methoxyphenyl) imine with divalent transition metal Cu^{2+} , Ni^{2+} , Cd^{2+} , Co^{2+} , Mn^{2+} and Zn^{2+} using pH metric titration technique in 50% (v/v) ethanol-water mixture at three different temperatures 25°C, 35°C & 45°C at an ionic strength of 0.1M NaClO_4 were studied. The method of Calvin-Bjerrum as adopted by Irving-Rossotti has been employed to determine metal-ligand stability constant $\log K$ values. The trend in the formation constants is as: $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+}$. The thermodynamic parameters such as, Gibb's free energy change (ΔG), entropy change (ΔS) and enthalpy change (ΔH) associated with the complexation reactions were calculated. The formations of metal complexes were found to be spontaneous, exothermic in nature and favorable at lower temperature.

Keywords: stability constant, transition metal ions, schiff base, pH metric, thermodynamic parameter etc.

1. Introduction: Metal complexes of schiff bases have played a central role in the development of coordination chemistry. pH metric titration is accepted as a powerful and simple electro analytical technique for determination of stability constants. It is also well known that some schiff bases exhibit increased activity when administered as metal complexes. Most of the d-block elements form complexes. There are different kinds of ligands used for complexation. For the present investigation, schiff base 2-hydroxy-5-bromo acetophenone-N-(4-methoxyphenyl) imine, having molecular formula $\text{C}_{15}\text{H}_{14}\text{O}_2\text{NBr}$, was selected.

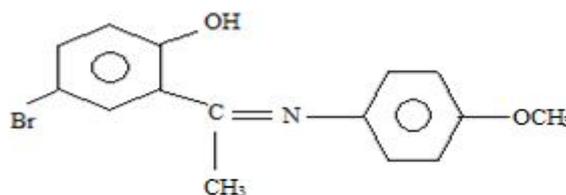


Figure: 2-hydroxy-5-bromo acetophenone-N-(4-methoxyphenyl) imine

In continuation of earlier work with complexation of schiff base¹⁻⁹ and after literature survey it was thought of interest to study the effect of temperature on thermodynamic parameters such as Gibb's free energy change ΔG , enthalpy change ΔH and entropy change ΔS of complexes of 2-hydroxy-5-bromo acetophenone-N-(4-methoxyphenyl) imine with transition metal ions Cu^{2+} , Ni^{2+} , Cd^{2+} , Co^{2+} , Mn^{2+} and Zn^{2+} pH metrically in 50% (v/v) ethanol-water mixture.

2. Experimental

2.1 Materials and Solution

All transition metal salts, HClO_4 , NaOH , NaClO_4 , were of AR grade. The solutions were used in the pH metric titration were prepared in double distilled CO_2 free water. The NaOH solution was standardized against oxalic acid solution and standard alkali solution was again used for standardization of HClO_4 . The transition metal salt solutions were standardized using EDTA. All the measurements were made at three different temperatures 25°C, 35°C and 45°C in 50% (v/v) ethanol-water mixture at constant ionic strength of 0.1M NaClO_4 . The water thermostat model SL-131 was used to maintain the temperature constant. The solutions were equilibrated in the thermostat for 10-15 minutes before titration. The pH measurement was made using a digital pH meter model Elico L1-120 in conjunction with a glass and reference calomel electrode (reading accuracy ± 0.01 pH units). The instrument was calibrated at pH 4.00, 7.00 and 9.18 using the standard buffer solutions.

2.2 pH metric procedures

For evaluating the protonation constant of the ligand and the formation constant of the complexes in 50% (v/v) ethanol-water mixture with different metal ions the following sets of solutions were prepared (total volume 50 ml) and titrated pH metrically against standard NaOH solution at three different temperature 25°C, 35°C and 45°C.

- Free acid HClO_4
- Free acid HClO_4 + Ligand (schiff base)
- Free acid HClO_4 + Ligand (schiff base) + Metal solution

The above mentioned sets were prepared by keeping M:Lratio, concentration of perchloric acid and sodium perchlorate constant for all sets.

2.3 Determination of the thermodynamic parameters

The thermodynamic parameters such as Gibb's free energy change (ΔG), entropy change (ΔS) and enthalpy change (ΔH) for formation of complexes were determined. The change in Gibb's free energy (ΔG) of the ligands was calculated by using the following equation. $\Delta G = -2.303RT \log K$

Where R (ideal gas constant) = $8.314 \text{ JK}^{-1}\text{mol}^{-1}$,

K is the dissociation constant for the ligand or the stability constant of the complex and

T is absolute temperature in Kelvin.

The change in enthalpy (ΔH) was calculated by plotting $\log K$ vs $1/T$

The equation used for the calculation of change in enthalpy was $\text{Slope} = -\frac{\Delta H}{2.303R}$

The evaluation of change in entropy (ΔS) was done by the following equation.

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

Table 1: Proton-ligand stability constant of schiff base with transition metal ions

| Temperature | Proton-ligand stability constant | |
|-------------|----------------------------------|--------|
| | pK_1 | pK_2 |
| 25°C | 4.99 | 9.77 |
| 35°C | 4.67 | 9.57 |
| 45°C | 4.20 | 9.38 |

Table 2: Metal-ligand stability constant and thermodynamic parameters of transition metal complexes of schiff base at 25°C

| Metal ion | $\log K_1$ | $\log K_2$ | $-\Delta G_1$ (KJmol^{-1}) | $-\Delta G_2$ (KJmol^{-1}) | $-\Delta H_1$ (KJmol^{-1}) | $-\Delta H_2$ (KJmol^{-1}) | ΔS_1 (KJmol^{-1}) | ΔS_2 (KJmol^{-1}) |
|-----------|------------|------------|--|--|--|--|---|---|
| Cu (II) | 7.45 | 6.34 | 42.510 | 36.177 | 15.018 | 15.045 | 0.0923 | 0.0709 |
| Ni (II) | 6.52 | 4.77 | 37.204 | 27.218 | 15.231 | 11.047 | 0.0737 | 0.0543 |
| Cd (II) | 6.25 | 5.20 | 35.663 | 29.671 | 12.433 | 13.834 | 0.0780 | 0.0531 |
| Co (II) | 5.88 | 4.70 | 33.552 | 26.818 | 14.669 | 14.469 | 0.0634 | 0.0414 |
| Mn (II) | 4.59 | 3.78 | 26.191 | 21.569 | 15.060 | 14.654 | 0.0374 | 0.0232 |
| Zn (II) | 6.04 | 5.11 | 34.465 | 29.158 | 15.609 | 13.055 | 0.0633 | 0.0540 |

3. Results and Discussion

Results obtained were analyzed by the computer programme and stability constant values were calculated. The proton-ligand stability constant (pK_a) of schiff base 2-hydroxy-5-bromo acetophenone-N-(4-methoxyphenyl) imine was determined by point wise calculation method as suggested by Irving and Rossotti. Metal ligand stability constant ($\log K$) of transition metal ions with schiff base 2-hydroxy-5-bromoacetophenone-N-(4-methoxyphenyl) imine were calculated by point wise and half integral method of Calvin and Bjerrum as adopted by Irving and Rossotti. The $\log K_1$ and $\log K_2$ values were calculated by point-wise calculation method and half integral method, which indicates simultaneous formation of 1:1 complex. Since we got values of proton-ligand formation number (\bar{n}_A) between 0.2 to 0.8 and 1.2 to 1.8 indicating 1:1 and 1:2 complex.

The order of stability constants for these transition metal complexes found to be: $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+}$

The graphs of $\log k$ vs atomic number, atomic radii were plotted & found in good agreement with earlier studies.

The negative ΔG values indicates that both dissociation of the ligand and the complexation process are spontaneous. Metal-ligand stability constant ($\log K$) decreases with increase in temperature and the negative values of enthalpy change (ΔH) for the complexation suggests that all the complexation reactions are exothermic, favorable at lower temperature and the metal-ligand bonds are fairly strong. Positive entropy changes (ΔS) accompanying a given reaction are due to the release of bound water molecules from the metal chelates. During the formation of metal chelates, water molecules from the primary hydration sphere of the metal ion are displaced by the chelating ligand. Thus there is an increase in the number of particles in the system i.e. randomness of the system increases. According to Martell and Calvin positive entropy effects was predicted towards an increase in the number of particles after the reaction and positive ΔS is responsible to give more negative ΔG .

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