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Complexing Capacity of Salicylaldoxime with Nickel and Zinc by Differential Pulse Polarography

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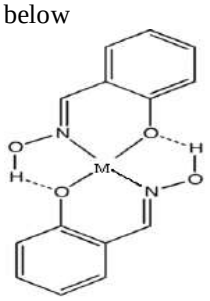
Abstract:- Differential Pulse Polarography was used to study the complexation of Ni(II) and Zn(II) with Salicylaldoxime in highly dilute solutions. The stability constants for both Ni(II) and Zn(II) complexes were calculated for three different metal to ligand concentration ratios viz 1:10, 1:50 and 1:100, from the shift in peak potential. The Log K_f values were found to be 9.39, 9.49 and 9.49 for Ni(II) complex and 8.82,8.28 and 8.89 for Zn(II) complex in 10, 50 and 100 times concentrated solution of Salicylaldoxime respectively. For ten and fifty times concentrated solution of Salicylaldoxime, the complex formation was stepwise while for hundred times concentrated solution of Salicylaldoxime, the complex formation was found to be a single step process. The molar combining ratio of metal to ligand was found to be 1:2 for both Ni(II) as well as Zn(II).

Keywords:- *Salicylaldoxime, Differential pulse polarography, stability constant, concentration ratio, peak potential.*

I. INTRODUCTION

Environmental pollution due to heavy metals is a serious problem since decades and is increasing at an alarming rate. Due to their hazardous effects, speciation of heavy metals in the environment becomes important. Speciation determines the toxicity, mobility and bioaccumulation of a substance in the environment. A comprehensive collection, critical analysis and interpretation of data for complexation of heavy metals become necessary. Physico-chemical parameters like total metal concentration, total ligand concentration, metal to ligand ratio and the stability constant have to be determined. A critical study of complexing capacity of heavy metals is therefore essential.
Salicylaldoxime is known to form highly stable chelates with many metals. Ni(II) and Zn(II) form ML_2 type of complexes with Salicylaldoxime. The structure of the complex is as given below



M = Ni(II) or Zn(II)

The stability of the complex in the solution phase depends on many factors like pH, ionic strength, metal concentration, ligand concentration, etc. The complex formation may be a stepwise or single step process. The process of complex formation, whether stepwise or single step, depends upon the concentration of the ligand in the solution. The present work aims at studying the complex formation process of Ni(II) and Zn(II) with Salicylaldoxime and determination of its stability in solution phase.

II. MATERIALS AND METHODS

A. Instrument

Voltammetric measurements were made using Metrohm 663 VA Stand. The three electrode system consisted of HMDE as the working electrode, Calomel Electrode with 3M KCl as reference electrode and Platinum rod as the counter electrode. Autolab PGSTAT 30 was used to control the potential. Polarograms were recorded with the help of 757 VA Computrance software. pH measurements were made using Equiptronics Digital pH meter (EQ 614A) with a glass electrode.

B. Reagents

0.001M solutions of Ni(II) and Zn(II) were prepared by dissolving appropriate amount of $NiSO_4.6H_2O$ and $ZnSO4.7H_2O$ respectively in distill water and then diluting to 100 cm^3 in a volumetric flask. 0.2 cm^3 of conc. H_2SO_4 was added to prevent hydrolysis. Acetate buffer of pH 3.4 was prepared by mixing appropriate volumes of 0.2M Sodium acetate and 0.2M acetic acid solution. 0.04M Britton Robinson buffer was prepared by mixing appropriate amount of Boric acid, phosphoric acid and glacial acetic acid and diluting with distilled water. The initial pH was 1.90 which was adjusted to 2.0 by dropwise addition of 0.2M NaOH solution. 0.1M solution of Salicylaldoxime in 20% methanol was used as the stock solution. 0.01M and 0.05M solutions of Salicylaldoxime were prepared from stock solution by appropriate dilution. 0.1M KCl solution was prepared by dissolving 0.745g of KCl in Acetate buffer for Ni(II) complexes and Britton Robinson buffer for Zn(II) complexes and diluting each to 100 cm^3 in a volumetric flask.

C. Experimental

The study was carried out with three different ***metal to ligand concentration ratios***

- 0.001M metal ion solution and 0.01M ligand (1:10 ratio)
- 0.001M metal ion solution and 0.05M ligand (1:50 ratio)
- 0.001M metal ion solution and 0.1M ligand (1:100 ratio)

➢ *Nickel Complex*

20 cm^3 of 0.1M KCl prepared in Acetate buffer (pH 3.4) was taken in a voltammetric cell and was purged with nitrogen gas for 5 minutes. A polarogram was recorded for this blank solution. 5.0 cm^3 of 0.001M Ni(II) solution was then added to the same cell and it was purged with nitrogen gas for 5 minutes. A polarogram was recorded. Then, 0.2 cm^3 aliquots of 0.01M Salicylaldoxime were added and polarograms were recorded after each addition. The same procedure was repeated for 0.05M and 0.1M Salicylaldoxime solution.

➢ *Zinc Complex*

Polarograms for Zn(II) complexes were recorded in 0.1M KCl in Britton Robinson buffer (pH 2) in the same way as that for Ni(II) complex, using 0.01M Salicylaldoxime. The process was repeated for 0.05M and 0.1M solution of Salicylaldoxime.

III. RESULT AND DISCUSSION

For a complex formation process, the shift in peak potential obtained, after successive addition of aliquots of the ligand, is related to the concentration of ligand as follows:

$$\Delta E_p = \frac{0.05916}{n}\log K_f + \frac{q0.05916}{n}\log c_L$$

Where n is the no of electrons transferred, K_f is the overall formation constant of the complex, C_l is the concentration of ligand and q is the molar comining ratio of ligand.

A plot of ΔE v/s Log C is a straight line with slope **q*0.05916/n** and intercept **0.05916/n log Kf**. The shift in potential obtained can be plotted against the log of concentration of the ligand. From the intercept, the stability constant Kf can be calculated and from the slope, the molar combining ratio of metal to ligand can be calculated.

A. Effect of pH

Polarograms for Ni(II) and Zn(II) complexes were recorded in various buffers like Acetate buffer, Britton Robinson buffer, Phthalate buffer and ammonia-Ammonium chloride buffer. The best response was obtained in Acetate buffer of pH 3.4 for Ni(II)-salicylaldoxime complex and Britton Robinson buffer of pH 2 for Zn(II)-salicylaldoxime complex. No shift in potential was observed in Brittion Robinson and phthalate buffer for Ni(II) complex. For Zn(II) complex, no shift was observd in acetate buffer and phthalate buffer. In Ammonia buffer, both Ni(II) and Zn(II) form hydroxides and complexation with Salicylaldoxime cannot take place.

B. Effect of Supporting Electrolye Concentration

Polarograms for Ni(II) and Zn(II) complexes were recorded in solutions of different concentrations of KCl viz. 1M, 0.1M 0.01M, each prepared in the respective buffer solution. For both Ni(II) and Zn(II) complexes, a reproducible shift in potential and highest stability constant was obtained in 0.1M KCl.

C. Effect of Metal: Ligand Concentration Ratio

The process of complex formation depends upon the concentration of ligand. When Salicylaldoxime is ten or fifty times concentrated than the metal i.e 0.01M, the complex formation takes place in two steps both for Ni(II) as well as Zn(II). However when the concentration of Salicylaldoxime is hundred times more than that of the metal, i.e. 0.05M and 0.1M, the complex formation takes place in a single step for Ni(II) as well as Zn(II).

The shift in peak potential obtained for Ni(II) and Zn(II) complex for 0.001M (ten times concentrated) solution of Salicylaldoxime is shown in Figure 1 and Figure 2 respectively. Similar type of shift is obtained for all other concentrations.

IV. CONCLUSION

Nickel complex is slightly more stable than Zinc complex. The stability of both Ni(II) and Zn(II) complexes goes on increasing with the increasing concentration of ligand. This is seen from the log K_f values given in Table 1 and Table 2 When the [M]:[L] ratio is 1:10 and 1:50, the complex formation occurs in two steps. This can be seen from Figure 3. The two lines represent the two steps for complex formation. For [M]: [L] 1:100, the complex formation occurs in a single step. This can be seen from Figure 4. A single line is obtained that indicates single step The stability and mechanism of complex formation for both Nickel and Zinc complexes depends on the concentration of ligand. The method used is suitable to determine solution phase stability of Salicylaldoxime complexes with various metals under optimum conditions in highly dilute solutions.

FIGURES AND TABLES

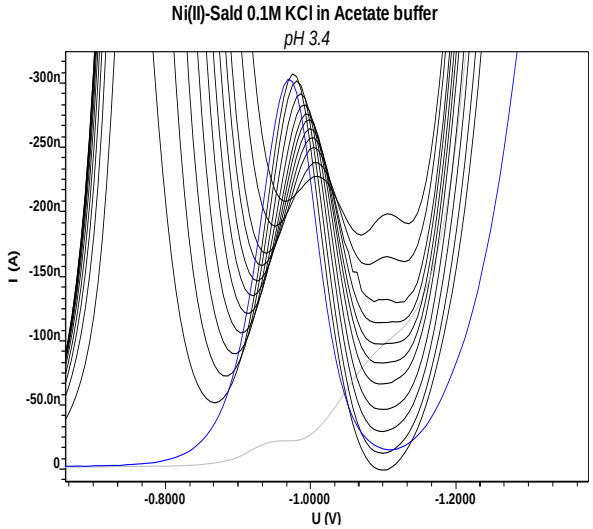


Fig 1:- Shift in peak potential obtained for 0.001M Ni(II) in 20 ml of 0.1M KCl in after successive additions of 0.01M Salicyladoxime (pH 3.4)

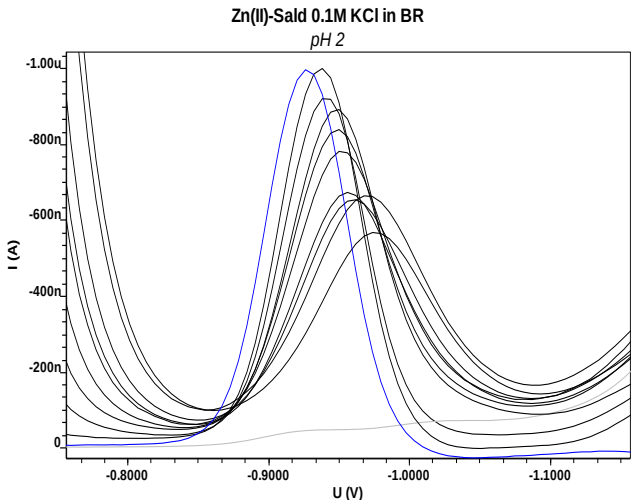


Fig 2:- Shift in peak potential obtained for 0.001M Zn(II) in 20 ml of 0.1M KCl in after successive additions of 0.01M Salicyladoxime (pH 3.4)

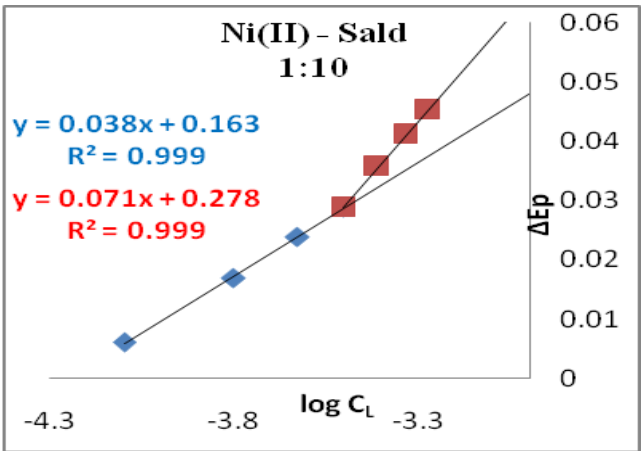


Fig 3:- Plot of shift in potential v/s Log C_l for Ni(II)-Salicylaldoxime complex (1:10)

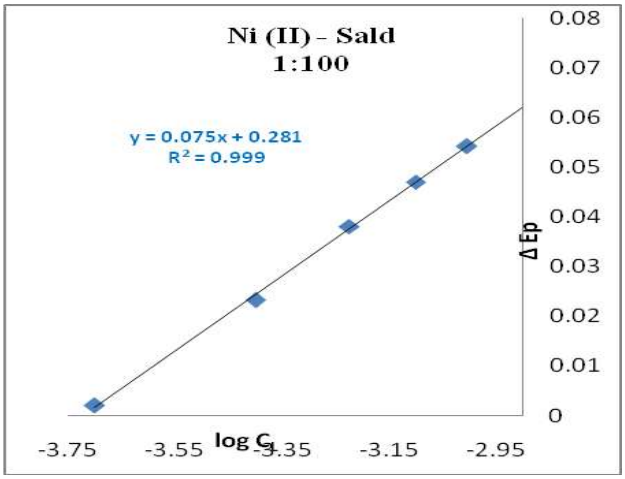


Fig 4:- Plot of shift in potential v/s Log C_l for Ni(II)-Salicylaldoxime complex (1:100)

[M]:[L]	Log K_1	Log K_f	q 1	q
1:10	5.51	9.39	1.28	2.36
1:50	5.27	9.49	1.25	2.46
1:100		9.49		2.46

Table 1:- Stability constant and molar conbining ratio for Ni(II)-salicylaldoximecomplex at different metal to ligand concentration ratios

[M]:[L]	Log K_1	Log K_f	q 1	q
1:10	3.98	8.82	0.84	2.26
1:50	3.98	8.88	1.04	2.36
1:100		8.89		2.36

Table 2:- Stability constant and molar conbining ratio for Zn(II)-salicylaldoxime complex at different metal to ligand concentration ratios

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