Metal Complexes Stability Constant Determination by Paper Electrophoresis: The Case of 1:1 Metal-to-Ligand Stoichiometry

Shikha Sharma[1] and O.P. Rai[2]

[1] *Applied Chemistry (Faculty of Tech. and Eng.) M.S. University, Baroda, Gujarat, India*
[2] *Department of Chemistry, Govt.P.G. College, Satna, M.P. - 485 001, India.*

Abstract—A paper electrophoretic technique is described for the determination of the stability constants for Cu(II), Ni(II), Zn(II) and Cr(III) metal ion complexes with alizarin as ligand. The stability constants for different metal (II, III)-alizarin complexes indicated the following order of the stabilities of complexes formed between alizarin and metal (II, III) ions. The following values were obtained with a good precision for metal-(II)/(III)-alizarin; $10^{5.14}$, $10^{4.84}$, $10^{4.44}$ and $10^{4.14}$ for Cr(III), Cu(II), Ni(II) and Zn(II) respectively at 35^0C and ionic strength I=0.1 mole dm^{-3} (HClO4). These values are consistent with the literature data, showing paper electrophoresis potential for metal complexes stability constant determination.

Keywords— Metal complexes, overall mobility, paper electrophoretic technique, stability constant(s), metal-alizarin binarysystem.

I. INTRODUCTION

Coordination chemistry is about tuning properties of metal ions using different ligands. Alizarin with reactive hydroxyl groups in 1 and 2 positions with respect to quinoid oxygen can form coordination compounds with metal ions and stabilizes the complexes via hydrophobic interaction. The essential metals such as Cu, Zn, Ni, and Cr play vital various roles in biological processes in form of complexes and their stability contributes to their efficiency. The roles played by these metal complexes include storage, enzyme catalysing process, analysing metal toxicity at certain concentration. Knowledge of the appropriate stability data is essential in determining whether a particular ligand considered for use in ligand (or chelate) therapy can selectively remove (or reduce the toxic levels of) a given metal ion. The knowledge of stability of metal complexes are known to play an important role in many metabolic and toxicological functions [1]. Furthermore, the metal complex with dye is very important in the textile industry. Alizarin is one of the most known and stable organic dyes and is found as the main component, with purpurin and quinizarin, of the madder lake pigment, known to painters as Rose Madder and Alizarin Crimson. Extracted from Rubiatinctorum roots [2] since 3.000 BC, it has been widely used in Europe during the XVI century in both artistic painting and textiles. Moreover, its capability to form stable complexes with different metal atoms [3]-[4]], also shown by its most common derivatives has led to their use in medicine[5]-[6] and chemical analysis[7]-[8] Thus knowing the stability of the complex decides its applicatory importance. Complexes are always possible, depending on the pH of the system. The actual complex-formation depends on the affinity of the metal ion towards the various ligands present, and the relative concentrations thereof. Kiso [9] has done a comprehensive study on paper electrophoretic migration of metal complexes. A number of methods have been employed for determination of stability constants of metal complexes [10]-[13]. B. B. Tewari [14] studied the quantitative indication of a complex formation comes from the estimation of the stability constants characterizing the equilibria corresponding to the successive addition of ligands. A search of literature indicated that no previous reports are available on stability constant determination by paper electrophoretic technique of aforesaid metal-alizarin complex. In view of this, an attempt was made to establish the optimum conditions for Zn(II), Cu(II), Ni(II) and Cr(III)-alizarin complex formation. In addition, the present paper describes a paper electrophoretic method for the determination of the stability constants of these complexes. For new metal complexes to form, which would be helpful for scientist and researchers in the field of medicine, biological fields, industries etc., the complexes must fulfil some requirements like water solubility, thermodynamic stability etc. In this context, stability constants are determined in given work and comparison is drawn between stability constant of alizarin with different metal cations. Traditionally, in order to study the complexation of ligand with metallic cations, potentiometry, paper electrophoresis, UV-Vis. And mass spectroscopy can be used. In this study, paper electrophoresis was chosen because of its simplicity, low cost, and availability in most laboratories. The factors affecting the mobility of ions like variation in temperature during the experiment, capillary flow on paper, electro osmosis and adsorption are the usual drawbacks of paper electrophoretic technique.

II. EXPERIMENTAL

Instruments:

An electrophoretic apparatus (systronics type 604, India) was used together with the various accessories supplied with the

instrument. The apparatus consisted of polyvinyl chloride of the cassette type and chromatogram could be run simultaneously on eight paper strips. The power unit capable of yielding a maximum of 300V. In each case electrophoresis was carried out for 1 hour at 220V and at 35^0C. Whatman no.1 paper strips were used with an applied voltage gradient of 9V Cm^{-1}. pH measurements were made with Elico digital pH meter having glass electrode assembly working on 220 volts/ 50 cycles stabilized AC main was used.

Chemicals:

Zn(II), Cu(II), Ni(II) and Cr(III) perchlorates were prepared by precipitating the corresponding carbonates from solutions of nitrate (Anala R grade) with the solution of sodium carbonate, washing the precipitates thoroughly with boiling water and dissolving in a suitable amount of perchloric acid. The resulting solutions were heated to boiling on a water bath and then filtered. The solutions were standardized and diluted with distilled water. As required Anala R/ BDH grade alizarin, NaOH, $HClO_4$, NTA and specific colour developing reagentswere used fordifferent metal ions of binary and ternary system sets for specific colour development. 1-(2-pyridylazo)-2 naphthol(PAN), 0.1% (w/v) in ethanol was used for detecting all the metal ions. A saturated aqueous solution (0.9ml) of silver nitrate was diluted with acetone to 20ml. Glucose was detected by spraying with this solution and then with 2% ethanolic sodium hydroxide, forming a black spot.

Background electrolyte

Stock solution of 5.0 M perchloric acid was prepared by its 70% solution (Anala R grade) 2.0m sodium hydroxide (Anala R grade), 0.5M alizarin (AnalaR grade) were prepared. Each solution was standardized as usual. The background electrolyte used in the study was 0.1M perchloric acid and 0.01M alizarin.

Procedure

The midpoint of each paper was marked and moistened with the background electrolyte. Excess electrolyte was allowed to drain off and papers were mounted on the plate of electrophoretic chamber. A spot of the metal solution was then applied at the marked point with the help of a fine glass capillary. For recording observations of particular metal ion two strips were spotted with the metal ion solution along with additional two spotted with glucose. The electrode compartment was filled with the equal volumes of the desired background electrolyte solutions. The lid of the chamber was then placed. It was left for 10 minutes to ensure wetting of strips. Subsequently a direct 220volts potential was applied between the electrodes. Electrophoresis was carried out for 60 minutes after which these strips were removed from the tanks with a glass rod and dried. The metal ion and glucose spots were detected by specific reagents. The leading and tailing edge were measured from the marked center point and the mean were taken. The distance moved by glucose was subtracted (in case the migration towards anode) toobtain correct path length. Migration towards anode and cathode

were designated by negative and positive signs respectively. The actual distance of the sample spot was measured after taking into account the distance travelled by the reference glucose spot. The distance recorded in the duplicated differed within ±5% and the average of two distances was noted. The mobility data were calculated and expressed in $10^3cm^2v^{-1}min^{-1}$. The mode of dissociation of pure alizarin is given in figure 2.

III. RESULTS AND DISCUSSION

Several workers [15] - [16] have been employed graphical methods for determination of stability constants of metal complexes using ionic mobility data. Theionophoretic mobility of the metal spot against pH gives a curve with a number of plateaus as is shown in Figure 1. A constant speed over a range of pH is possible only when a particular complex species is overwhelmingly formed. Two plateaus with all the four metal ions are observed. The first plateau in each case corresponds to a region of pH where metal ions are un-complexed. In this low pH protonated form of alizarin is maximum. Further increase in pH from this region onwards which naturally leads to increase in ligating alizarin anion concentration and brings about a progressive decrease in overall ionic mobility of the metal ion species. This decrease indicates formation of complex of the metal ion with the ligand. This is the second plateau which corresponds to a pH region in which 1:1 binary complex of cationic nature is formed.A further increase of pH has no effect on the mobility of metal ions, which indicates no further interaction between the metalions and ligands. It is significant that these studies give clear evidence of the complexation of the anionic species of alizarin with metal ions forming binary complexes of 1:1 in composition

In view of the above observation the complexation of metal ions with these ligands may be represented as

$$M + L \underset{}{\overset{K1}{\rightleftharpoons}} ML$$
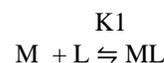
The metal ion moving under the influence of electrical field, the overall mobility is given by the equation.

$$u= \sum u_n f_n$$

Where, u_n and f_n are mobility and mole fraction, respectively of a particular complex species. This equation is transformed into the following form. On taking into consideration of different equilibria.

$$u= \frac{u_0+u_1K_1[L]+u_2K_1K_2 [L]^2+........}{1+K_1[L]+K_1K_2[L]^2 +...........}$$

Where K's(K_1K_2) are the stability constants of complexes and [L] is concentration of alizarin. U's (U_0, U_1, U_2) are the ionic mobilities of different species of the metal ions, which can be accessed from the plateaus of the Fig1. In the region between first and second plateau, the system contains, mixture of free

metal ion and 1:1 complex. The existence of 1:2 complex can be excluded and hence the third term in the numerator and the denominator of the above equation can be neglected. U would be equal to $(u_0+u_{1/2})$ provided $K_1[L]=1$.

The pH corresponding to the average value of U_0 and U_1 is found from the fig.1 and with the knowledge of the dissociation constant of alizarin (pKa 6.94), the concentration of alizarin ion at this pH is calculated. Its reciprocal gives the stability constant K_1 of the 1:1 complex

The concentration of chelating alizarin anion [L] is determined a

$$[L] = \frac{[L]_{tot}}{1+[H]/K_1 + [H]^2 K_1 K_2}$$

Where $[L]_{tot}$ is the total concentration of the ligand alizarin (0.01M) and K_1 and K_2 are first and second dissociation constants of the alizarin respectively.

The stability constants of metal complexes can be very easily calculated by this technique. The present paper technique is limited to charged species, and the precision of the method is not as accurate as other physicochemical methods. However, uncertainty in the results is (±5%). It is not felt that itcan replace the other methods, yet it is an alternate approach used.
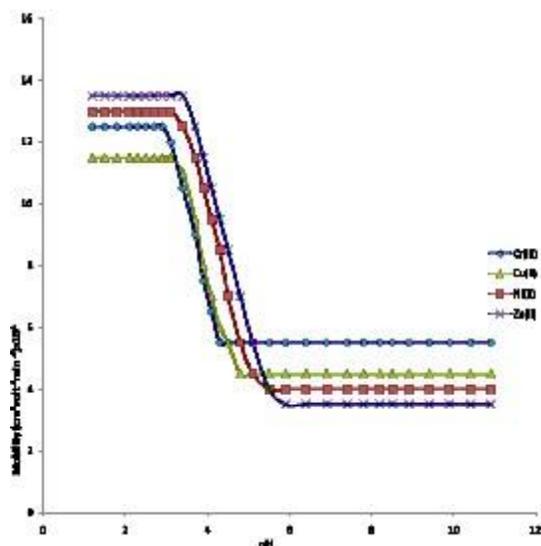

Fig. 1Mobility curves for metal(II)/metal(III)– alizarin systems --◆----. = Cr(III) -alizarn; ▲----=Cu(II)-alizarin;----■---= Ni(II) –alizarin;--x--=Zn(II)-alizarin. The paper strips were spotted with 0.1 µl of sample solution and glucose (for making osmotic correction)
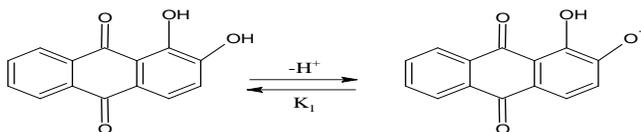

Figure 2. Mode of dissociation of pure alizarin. Ionic strength: 0.01 M. Temperature: 35 °C.

STABILITY CONSTANT OF M - ALIZARIN COMPLEXES
Temp. 35^0C Ionic Strength – 0.1M (HClO$_4$

S.No.	Metal ions	Calculated Values log K$_1$	Literature values log K$_1$
1	Cr(III)	5.1405	-
2	Cu(II)	4.8407	5.1[17]
3	Ni(II)	4.4415	4.1[17]
4	Zn(II)	4.1433	-

From the table (1) it can be surely deduced that the order of stability constant of various metal ions are as follows:

Cr $^{+++}$> Cu^{++}> Ni^{++}> Zn^{++}
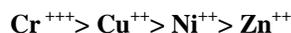
This is in agreement with general order of the stability of the complexes of these metal ions which is established before by which is in accordance with the Irving Williams[17] and Grinberg and Yatsimiki [18] order for stability constant of the transition metal complexes.

IV. CONCLUSION

Metal complex dye is an important term in textile industry, thus in order to form new metal-dye complex it will be very helpful to have information about their important chemical properties. One of these properties is the stability constant of the metal ligand complex. Thus given conclusion represents new and reassessed stability data that are applicable to a wide range of chemical and biological applications including metal ion detection, quantification and affinity studies of alizarin with Zn(II), Cu(II), Ni(II) and Cr(III) metal ions in a wide pH range. The accuracy of the predicted values of stability constant is equivalent to the experimental uncertainties.

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