

Electro Chromatographic Study of Some Metal Complexes in Solution [Cu(II)/Ni(II)/Co(II)/Zn(II)-8-Azaguanine-system]

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A modified electro chromatographic method has been developed for the study of 8-azaguanine complexes of some divalent metal ions viz., Cu(II), Ni(II), Co(II) and Zn(II). 1:1, 1:2 Complexes are formed with each metal ions. The stability constant were determined at ionic strength 0.1 M perchloric acid.

Key Words: Electro chromatography, Electrophoresis, 8-Azaguanine, Stability constants.

INTRODUCTION

Chromatography and electrophoresis are valuable and widely used techniques, work in solution for separation and isolation of bioactive species based on charge, size and molecular weight. Jokl¹ was the pioneer to employ paper electrophoresis for the assessment of metal ligand equilibria in solution, but the approach was qualitative and primitive. Paper electrophoresis as modified by Singh and Yadav²⁻⁶ gives vivid picturization of complex formation to find the equilibrium constants values in solution. The paper electro chromatography has the striking drawback in the sense that path of migrating ion is not uniform. There is no report available in literature in regard to electrophoretic studies in mixed electrolytic solution.

The modified method helps in studying stepwise formation of metal complexes and is almost free from the effect of several vitiating factors.

The present paper reports some observation on Cu²⁺, Ni²⁺, Co²⁺ and Zn²⁺-8-azaguanine (Fig. 1) complexes by solution electro chromatography.

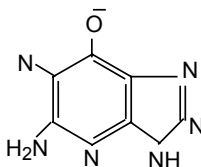


Fig. 1. Structure of azaguanine anion

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EXPERIMENTAL

An electrophoretic tube has been used for electrophoresis. The tube is 18.0 cm long and of 5 mm bore with a stopper in the middle and it fused perpendicularly at the ends with short wider tubes of 1.2 cm bore. Two 0.5×0.5 cm² platinum electrodes has been used for electrophoresis. These are connected with an electrophoresis voltage supply.

Carl Zeiss JENA colorimeter has been used for absorbance measurements. pH measurements were made with c/p 901 century digital pH meter having glass electrode assembly.

AR grade of perchloric acid, 8-azaguanine, metal ions [Cu(II), Ni(II), Co(II) and Zn(II)] and NaOH were used. Strength of 8-azaguanine was 2×10^{-2} M, strength of metal ions [Cu(II), Ni(II), Co(II) and Zn(II)] were 5×10^{-4} M.

Developing reagents for Cu(II), Ni(II), Co(II) and Zn(II): Ammonium thiocyanate solution for Cu(II), dimethyl glyoxime for Ni(II), stannous chloride solution, ammonium thiocyanate and acetone for Co(II), Zincon [5-(2-carboxy-phenyl)-1-(2-hydroxy 5-sulpho phenyl formazone)] for Zn(II)⁷ were used as developing reagents.

Procedure: A set of solution containing 5.0×10^{-4} M Cu(II), 0.1 M HClO₄ and 2.0×10^{-2} M 8-azaguanine at different pHs (by adding NaOH solution) was prepared. In the same way 5×10^{-4} M Ni(II) and Zn(II) solution was also prepared with same acids. A 10 mL of aliquot was taken in an electrophoretic tube and then thermostated at 30 °C. The tube is 18 cm long and 5 mm bore with a stopper in the middle and is fused perpendicularly at the ends with short wider tubes of 1.2 cm bore. The position of the tube is adjusted in such a way that the level of the solution in one wide end arm reaches a circular mark on it. This adjustment fixes the volume of the solution on both sides of the middle stopper. Two 0.5×0.5 cm² platinum electrodes were dipped in each arm and a potential difference at 50 V was applied between them. Electrolysis of the solution was allowed for 45 min after which the middle stopper of the tube was closed. The solution of anodic compartment was taken out in a 15 mL flask. The volume was made upto the mark in the flask and the absorbance of Cu(II), Ni(II), Co(II) and Zn(II) at suitable λ_{\max} with Spekol spectro colorimeter.

RESULTS AND DISCUSSION

Fig. 2 shows graphical representation of absorbance difference due to metal ion contents in the anodic compartment in unelectrolyzed and electrolyzed conditions at different pHs of the reaction mixture. Thus, the figure gives the change of overall mobility of the metal species with change in H⁺ in the reaction mixture. In each case three plateaus are obtained. The first plateau at low pHs corresponds to the region where metal ion is

uncomplexed. Further increase in pH brings about a progressive decrease in overall ionic mobility showing complexation with the 8-azaguanine anion. This decrease continues to a certain point in positive range of mobility after which the second plateau is obtained. Further increase of pH mobility decreases till the third plateau of zero mobility of 1:2 complex of divalent metal ion with 8-azaguanine anion is obtained.

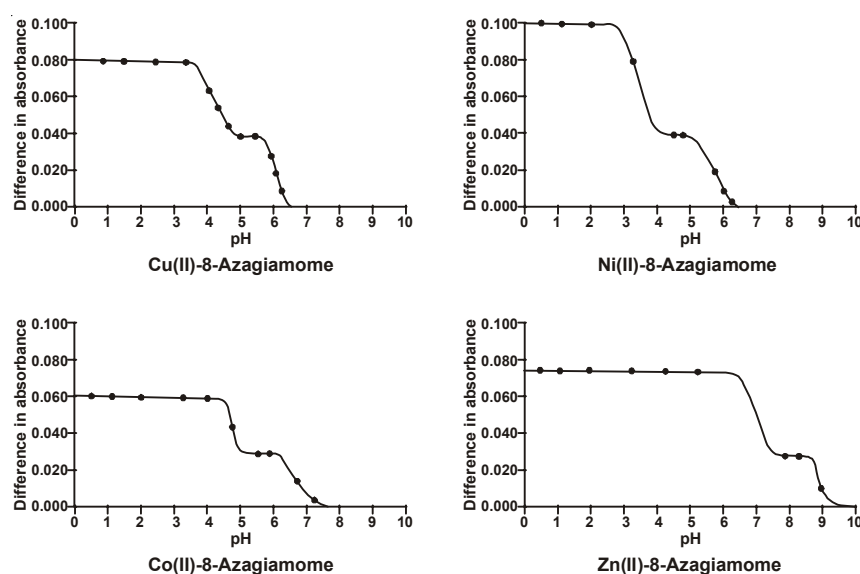


Fig. 2. Absorbance curve [M(II)-8-Azaguanine-system]
(Temp. 30 °C; Ionic strength 0.1)

During the process of electrolysis different ions move in one direction or the other direction. Hence the environment of any ionic entity remains unchanged in bulk of the reaction mixture. As such the distribution of the metal ion in free as well as in complexed form remains intact in the bulk during the migration. No doubt the speed of various ionic entities of metal ions will be different but the condition of fixed composition at all time during migration rules out separation of the species in the bulk. Overall effect of this overriding condition is that metal ion will move with a speed which is composite of weighted speeds of free and complexed metal ions. The weighting factor should be actual fraction of the total metal ion constituted by a particular species. Hence the overall mobility U should be given by the following expression eqn. 1.

$$U = u_1f_1 + u_2f_2 + u_3f_3 \quad (1)$$

where u_1, u_2, u_3 and f_1, f_2, f_3 are ionic mobilities and mole fractions of metal ion which is free of differently complexed with ligand.

A number of factors obviously vitiate the electrophoretic mobility of a particular ion *e.g.*, non uniformity of the tube, diffusion, ionic strength, temperature, *etc.* If the tube is not uniform the potential gradient will be different at different places, where the tube is narrower the potential gradient will be high as compared to that of the broader zones. It would certainly be inversely proportional to the cross-sectional area for unit time would be the same regardless of the non uniformity of the tube.

The eqn. 1 for overall mobility and the mobility *vs.* pH in Fig. 2 are relevant for the assessment of the composition and stability constant of the complexes formed in the interaction of the divalent metal ions with the anion of 8-azaguanine. As mentioned above formation of two complexes first with mono negative 8-azaguanine anion (Fig. 2). In the beginning at low pH values, the metal ions are uncomplexed and with increase of pH the second plateau, indicative of the formation of metal-mono positive 8-azaguanine complexes appears. Though the eqn. 1 is general but this can be justifiably modified for the transition range between the first and second plateau as:

$$U = u_1f_1 + u_2f_2 \quad (1)$$

where u, u_1 and u_2 are overall mobility of uncomplexed metal ion with that of mono negative 8-azaguanine metal complex ions. The first and second plateau comes to u_1 and u_2 . In the transition range mole fraction, f_1 and f_2 of the uncomplexed and complexed metal ions, respectively must be additively equal to unity *i.e.*, $f_1 + f_2 = 1$. It is now easy to conclude that overall mobility $U = u_1 + u_2/2$ at the stage where $f_1 = f_2 = 1/2$ *i.e.*, where half the metal ion are in uncomplexed state and the remaining half is in mono negative 8-azaguanine complex form. The stability constant of the mono negative 8-azaguanine complex:

$$K_1 = \frac{[1:1 \text{ 8-Azaguanine complex}]}{[H + 1][8\text{-Azaguanine anion}]}$$

It can be now easily calculated since at the relevant pH at which the overall mobility is average of the u_1 and u_2 . Then $K_1 = \frac{1}{[8\text{-Azaguanine}]}$. The knowledge of the different deprotonation constants of 8-azaguanine ($\log K_1 = 3.42$, $\log K_2 = 10.48$)⁸ helps in calculation of the mono negative 8-azaguanine anion at the relevant pH. The calculated stability constants of the mono negative 8-azaguanine complexes in case of Cu(II), Ni(II), Co(II) and Zn(II) are elucidated in the Table-1.

TABLE-1
STABILITY CONSTANTS OF 8-AZAGUANINE COMPLEXES
Temp. = 30 °C; Ionic strength = 0.1

Metal ion	Calculated value		
	$\log K_{ML}^M$	$\log K_{ML_2}^{ML}$	$\log \beta_{ML_2}$
Cu(II)	9.75	5.65	15.4
Ni(II)	5.74	3.92	9.66
Co(II)	5.65	3.68	9.33
Zn(II)	5.45	4.31	9.76

The concept of average mobility in transition region between second and third plateaus help in calculation of stability constant of the 1:2 second complex. The reason has mentioned earlier. Beyond this further increase in pH do not change the path of the curve ruling out any possibility of formation of hydroxy complex.

It is to be noted that the method under taken in this paper is novel so the actual purpose is to find out that it is suitable for the study of stability constants.

In conclusion, it is to be stressed that the electrophoretic technique used in these study is simple and handy for the study of complexation reaction. It give vivid picturization of complex formation whose stability constant can be very easily determined.

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