

SHORT COMMUNICATION

ELECTROPHORETIC STUDIES ON BIOLOGICALLY IMPORTANT COPPER(II), MANGANESE(II) AND URANYL(II) BINARY COMPLEXES

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ABSTRACT. Paper electrophoresis is used for the study of equilibria in binary complex systems in solution. The stability constants of ML and ML₂ complex species of some metal ions copper(II), manganese(II) and uranyl(II) with α -aminobutenoic acid and hydroxyproline were determined at an ionic strength of 0.1 M and 35 °C. The stability constants of ML and ML₂ complex species of metal(II)- α -aminobutenoic acid and metal(II)-hydroxyproline were found to be [(7.70 \pm 0.03, 6.38 \pm 0.11), (3.19 \pm 0.02, 2.07 \pm 0.09), (7.32 \pm 0.05, 5.49 \pm 0.12)] and [(8.23 \pm 0.05, 7.05 \pm 0.03), (3.74 \pm 0.06, 3.15 \pm 0.09), (7.39 \pm 0.11, 6.67 \pm 0.02)] for copper(II), manganese(II) and uranyl(II) complexes, respectively.

KEY WORDS: Ionophoretic technique, Copper(II) complex, Manganese(II) complex, Uranyl(II) complex, α -Aminobutenoic acid, Hydroxyproline, Stability constants

INTRODUCTION

Kiso [1] has done comprehensive study on paper electrophoretic migration of metal complexes. The paper ionophoretic technique usually suffers from a number of defects. Temperature during electrophoresis, capillary flow on the paper, electro-osmosis and adsorption affect the mobility of charged species [2]. The technique is modified to control these defects. The present modified technique is almost (95 %) free from these vitiating factors. The technique is very convenient in use. It gives results in fair agreement with the accepted literature values.

Communications [3-5] from our laboratory described a new method for the study of binary complexes. This work has been taken up as a part of our program to investigate the interaction of α -aminobutenoic acid and hydroxyproline with metal ions. In the present investigation binary complexes of copper(II), manganese(II) and uranyl(II) with α -aminobutenoic acid and hydroxyproline have been studied.

EXPERIMENTAL

Apparatus

A Systronic (Naroda, India) Model 604 electrophoresis system was used. In order to maintain the temperature constant, two hollow metallic plates coated with thin plastic paper on the outer surface were used for sandwiching paper strips and thermostated water (35 °C) was circulated through these plates. pH measurements were made with an Elico (Hyderabad, India) Model L₁₋₁₀ pH meter using a glass electrode.

Chemicals

Copper, manganese and uranyl perchlorate solutions were prepared by preliminary precipitation of metal carbonates from 0.1 M solution of sodium carbonate (Analytical Reagent grade, BDH, UK). The precipitate was thoroughly washed with boiling water and treated with calculated

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amounts of 1 % perchloric acid (AnalaR, BDH, UK). The resulting mixture was heated to boiling on a water bath and then filtered. Metal contents of the filtrates were determined by standard methods [6] and the final concentration was kept at 5.0×10^{-3} M.

Metal spots were detected on the paper using a 0.1 % solution of 1-(2-pyridylazo)-2-naphthol (PAN) (E. Merck, Darmstadt, Germany). A saturated aqueous solution (0.9 mL) of silver nitrate was diluted with acetone to 20 mL. Glucose, as a black spot, was detected by spraying with this solution and then with 2 % ethanolic sodium hydroxide.

Background electrolytes (BGEs)

Stock solutions of 9.0 M perchloric acid, 2.0 M sodium hydroxide, 0.5 M α -aminobutenoic acid and 0.5 M hydroxyproline were prepared from analytical reagents grade chemicals (BDH, UK). The BGEs used in the study of metal complexes were 0.1 M perchloric acid, 0.01 M α -aminobutenoic acid and 0.01 M hydroxyproline.

Procedure

The level of the hollow base plate in the instrument was made horizontal using a spirit level and 150 mL of 0.1 M perchloric acid was placed in each tank of the electrophoretic apparatus. The levels of the two tank solutions were made equal by siphoning them through a bent tube. These precautions were taken to prevent any gravitational or hydrodynamic flow. Paper strips (Whatman No. 1) of 30 x 1 cm in size were soaked in the background electrolyte and the excess of electrolyte solution was blotted gently within the folds of dry filter paper sheets. Duplicate strips were then spotted in the centre with metal ion solution using a micropipette before being placed on the base plate and sandwiched under the upper hollow metallic plate with the end of strips allowed for 15 min to remain as such. After 15 min the ends of the strips were completely dipped in ligand solution. A 240 V potential difference was then applied between the tank solutions to initiate electrophoresis.

The electrolysis was carried out for 60 min, while water maintained at 35 °C by a thermostat was circulated through the hollow plates. After this the strips were taken out by means of glass rod, dried on a horizontal platform and spots detected. The observation was repeated for different pH values of the background electrolyte (variation in pH was made by addition of caustic soda solution). The distance recorded in the duplicates differed within ± 5 % and the average distance in duplicates was noted for calculation. The distance travelled towards the anode was assumed to be negative and that towards the cathode positive. The actual distance of the sample spot was measured after taking into account the distance travelled by the reference glucose spot. The potential gradient through the strip was found to be 7.5 V/cm, calculated by dividing the movement by the potential gradient and time yield mobility (Figures 1 and 2).

RESULTS AND DISCUSSION

Metal(II)- α -aminobutenoic acid system

The plot of overall electrophoretic mobility of the metal spot against pH is shown in Figure 1. The first plateau in the beginning corresponds to a region in which metal ions are uncomplexed. It is obvious that protonated ionic species of the α -aminobutenoic acid, which are found in low pH ranges, are non-complexing. The second plateau in each case with positive mobility indicates the formation of a 1:1 complex of cationic nature, the ligand being the α -aminobutenoic acid anion. Further increase in pH also gives rise to a third plateau with zero mobility with anionic species of α -aminobutenoic acid indicates formation of 1:2 metal

complexes of neutral nature. The prominent ligating properties of the unprotonated anionic species of α -aminobutenoic acid ruling out any such property to zwitterions [7]. The complexation of metal ions with the α -aminobutenoic anion $[L^-]$ may be represented as:



where M^{2+} is Cu^{2+} , Mn^{2+} and UO_2^{2+} metal ions; $[L^-]$ is α -aminobutenoic acid anion, K_1 and K_2 are the first and second stability constants, respectively. The spot is moving under the influence of electric field and the overall mobility U is given by equation [8]

$$U = \frac{u_0 + u_1 K_1 [L^-] + u_2 K_1 K_2 [L^-]^2}{1 + K_1 [L^-] + K_1 K_2 [L^-]^2} \quad (3)$$

where u_0 , u_1 and u_2 are the mobilities of the uncomplexed metal ions, 1:1 and 1:2 metal complexes, respectively.

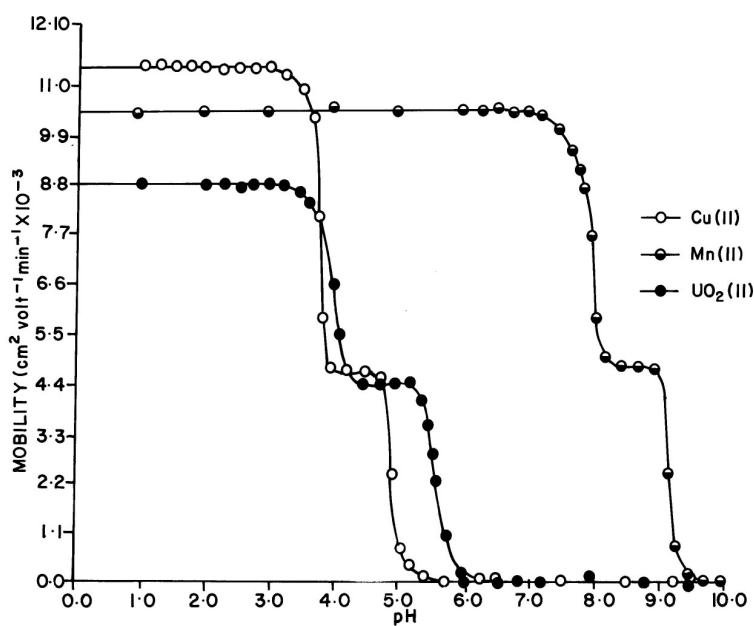


Figure 1. Mobility curves for the metal(II)- α -aminobutenoic acid: $-\circ-$ Cu(II)- α -aminobutenoic acid, $-\circ-$ = Mn(II)- α -aminobutenoic acid, $-\bullet-$ = UO_2 (II)- α -aminobutenoic acid. Concentration of Cu(II), Mn(II) and UO_2 (II) = 0.005 M. Ionic strength = 0.1 M, temperature = 35 °C.

For the calculation of the first stability constant, K_1 , the region between first and second plateau is pertinent. The overall mobility U will be equal to the arithmetic mean of the mobility of uncomplexed metal ion, u_0 and that of first complex, u_1 at a pH where $K_1 = 1/[L^-]$. With the help of dissociation constants of pure α -aminobutenoic acid [$K_{a1} = 2.45$, $K_{a2} = 9.25$ (paper electrophoretically obtained value)] the concentration of ligating, $[L^-]$, is calculated by

$$[L^-] = \frac{[L_T]}{1 + [H]/K_{a2} + [H]^2/K_{a1} \cdot K_{a2}} \quad (4)$$

where $[L_T]$ is total concentration of ligand α -aminobutenoic acid; K_{a1} and K_{a2} are the first and second dissociation constants of the pure α -aminobutenoic acid, respectively.

The second stability constant, K_2 , of 1:2 complex can be calculated by taking into consideration the region between the second and third plateau of mobility curve. The calculated values of K_1 and K_2 are given in Table 1.

Table 1. Stability constants of binary complexes of copper(II), manganese(II) and uranyl(II) with α -aminobutenoic acid and hydroxyproline.

Metal ions	Complexes	Log stability constant values		
		Calculated	Literature	
Cu ⁺⁺	CuL ⁺	K ₁	7.70 ± 0.03	7.82 [9]
	CuL ₂	K ₂	6.38 ± 0.11	6.54 [9]
	CuL ⁺	K ₁	8.23 ± 0.05	8.38 [9]
	CuL ₂	K ₂	7.05 ± 0.03	7.04 [9]
Mn ⁺⁺	MnL ⁺	K ₁	3.19 ± 0.02	-
	MnL ₂	K ₂	2.07 ± 0.09	-
	MnL ⁺	K ₁	3.74 ± 0.06	-
	MnL ₂	K ₂	3.15 ± 0.09	-
UO ₂ ⁺⁺	UO ₂ L ⁺	K ₁	7.32 ± 0.05	-
	UO ₂ L ₂	K ₂	5.49 ± 0.12	-
	UO ₂ L ⁺	K ₁	7.39 ± 0.11	7.52 [9]
	UO ₂ L ₂	K ₂	6.67 ± 0.02	-

Ionic strength = 0.1 M; temperature = 35 °C; α -aminobutenoic acid anion = [CH₂=CH-CH(NH₂)COO⁻]; hydroxyproline anion = [CH₂CH(OH)CH₂(NH)COO⁻]; $K_1 = [ML]/[M][L]$; $K_2 = [ML_2]/[ML][L]$; M = metal cations (Cu⁺⁺, Mn⁺⁺, UO₂⁺⁺); L = ligand (α -aminobutenoic acid); L⁺ = ligand (hydroxyproline).

Metal(II) – hydroxyproline system

Mobility curves in the presence of hydroxyproline at different pH are shown in Figure 2. The mobility curves in all three metal ions copper(II), manganese(II) and uranyl(II) show three plateaus. The first due to uncomplexed ion, second due to 1:1 complex and third due to 1:2 complex. First and second plateau with positive mobility indicate cationic nature of charged species while third plateau with zero mobility indicates its neutral nature. The dissociation constants of pure hydroxyproline [$K_{a1} = 1.80$; $K_{a2} = 9.46$] were determined by same paper ionophoretic technique. The first stability constant, K_1 , and second stability constant, K_2 , of metal(II)-hydroxyproline complexes were determined by similar method as reported for metal(II)- α -aminobutenoic acid. The complexity constants obtained are given in Table 1.

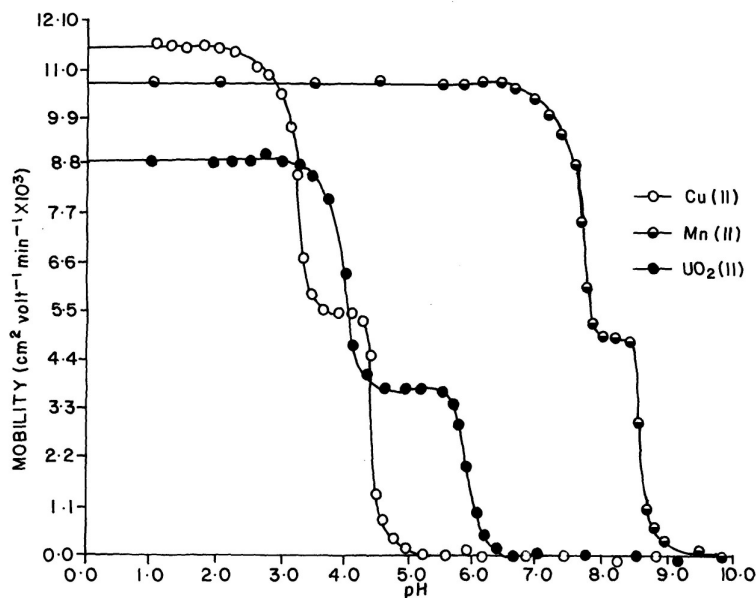


Figure 2. Mobility curve for the metal(II)-hydroxyproline system: \circ = Cu(II)-hydroxyproline, \bullet = Mn(II)-hydroxyproline, \bullet = UO₂(II)-hydroxyproline. Ionic strength = 0.1 M, temperature = 35 °C. The paper strips were spotted with 0.1 μ L of sample solutions and glucose (for making osmotic corrections).

It is observed from Table 1 that values of first and second stability constant follow the order: copper(II) > uranyl(II) > manganese(II) with both amino acids complexes. The stability constant values of metal(II)-hydroxyproline complexes are found to be higher in comparison to metal(II)- α -aminobutenoic acid. The strong bonding by hydroxyproline with metal ions may be due to presence of hydroxyl group and ring structure in it. The Cu(II)-hydroxyproline complex and Mn(II)- α -aminobutenoic acid complexes are found to have maximum and minimum stability constants, respectively. Highest stability constant values of copper(II)-hydroxyproline complex indicate strong bonding between copper(II) ion and hydroxyproline, while lowest stability constant values of manganese(II)- α -aminobutenoic acid complex indicated weak bonding between manganese(II) ion and α -aminobutenoic acid.

CONCLUSIONS

The modified ionophoretic technique has proved to be useful in deciding whether a complex system is formed or not, and if it is formed its stability constants can also be determined. It can also be concluded from these studies that copper(II), manganese(II) and uranyl(II) metal ions are significant for biological systems but as such they are toxic. The α -aminobutenoic acid and hydroxyproline may be used to reduce the levels of these metal ions in living systems.

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