Paper Electrophoretic Studies of Iron(III) and Chromium(III) Complexes with Penicillamine

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The main biochemical aspects of D-penicillamine has been reviewed by Jocelyn [1]; the mercapto group in this compound takes part in many chemical and complexation reactions. Sorensen [2] has demonstrated the anti-inflammatory activity of copper-D-penicillamine. Great biological imortance is attached to the study of metal-sulphur bonds formed in such processes - primarily in the non-haeme iron proteins [3] and the blue copper proteins [4].

Our laboratory has published a number of papers [5-7] on single ligand complex system. The present work is an extension of the technique and reports our observation on binary complex system viz. Fe(III)/Cr(III)-penicillamine.

EXPERIMENTAL

The apparatus and procedure are as described earlier [5-7]. Iron(III) and chromium(III) metal perchlorate were prepared by precipitating metal corbonates by adding a solution of sodium carbonate (AnalaR grade) to a 0.1 M solution of sulphates of Fe(III)/ Cr(III). This was followed by washing the precipitate. Solutions were prepared by dissolving this pure carbonate in required amount of perchloric acid [5]. Stock solutions of 9.0 M perchloric acid, 2.0 M sodium hydroxide and 0.5 M penicillamine were preapred from A.R. grade chemicals (BDH, England).

The background electrolytes used in the study of binary complexes contained 0.1 M perchloric acid and 1.0 x 10^{-2} M penicillamine and adjusted to different pH values. The electrophoretic cell showing sandwiched paper strips is shown in Fig.1. Paper strips showing the spots after electrophoressis is shown in Fig.2. Iron spot on the paper was detected using potassium ferrocyanide

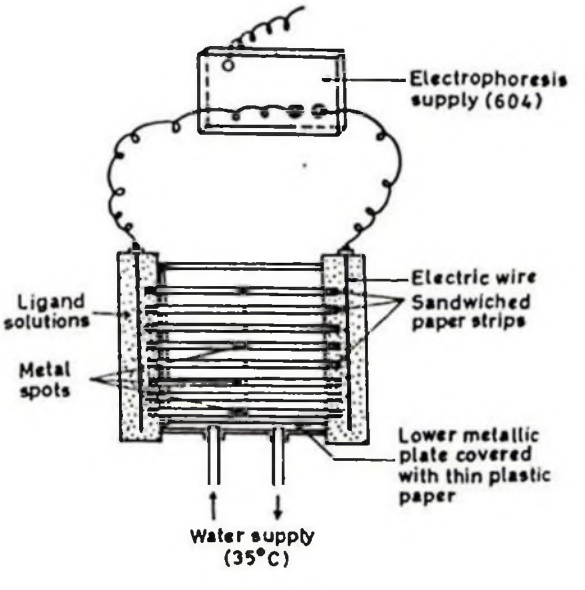


Fig. 1 Electrophoresis cell showing sandwiched paper strips.

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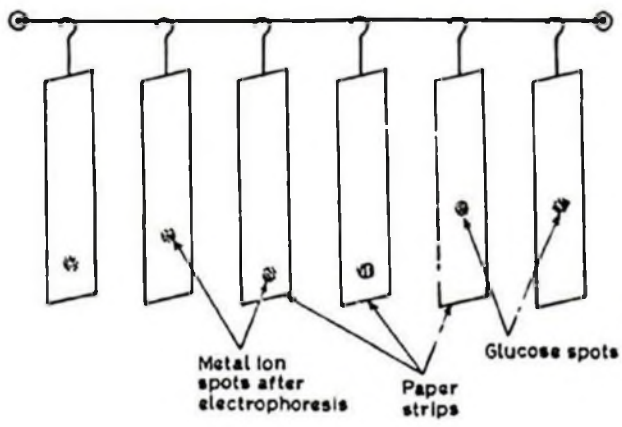


Fig. 2 Paper strips showing position of metal ion spots after electrophoresis.

solution (BDH) and Cr(III) spots were detectd using 1-(2-Pyridilazo)-2-naphthol (PAN) solution (E, Merck). A saturated aqueous solution (0.9 ml) of silver nitrate was diluted with acetone to 20 ml. Glucose spot was detected by spraying this solution followed by 2% ethanolic sodium hydroxide.

RESULTS AND DISCUSSION

Metal(III)-Penicillamine Binary System.

The plot of ionophoretic mobility of a metal spot *vs* a pH gives a curve with a number of plateaus as shown in Fig.3. A plateau is obviously an indication of a pH range, where the speed is virtually constant and indicates the formation of a single complex species. The first plateau (at low pH) corresponds to a region in which metal ions are

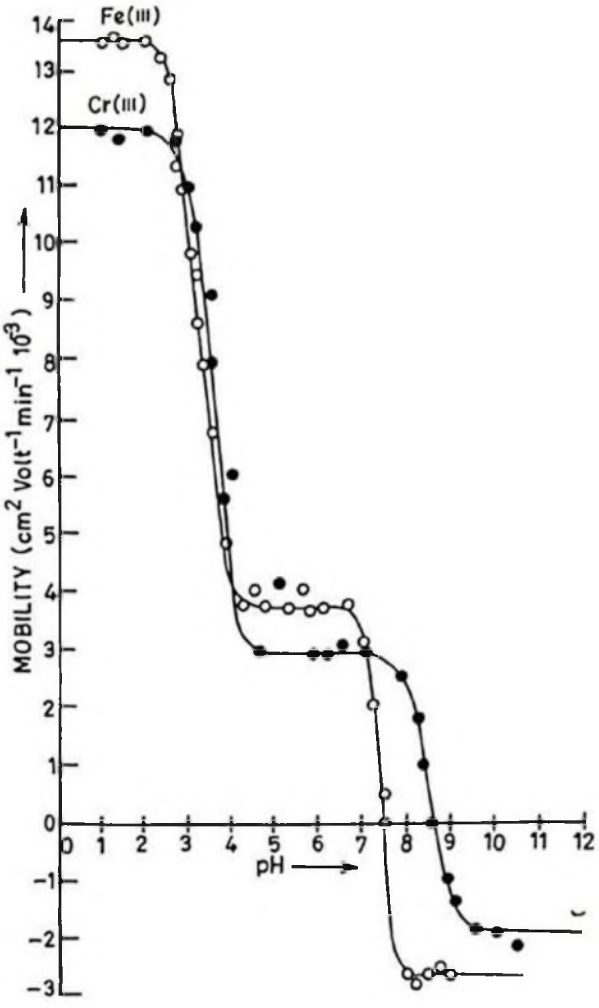


Fig. 3 Mobility curves [Fe(III)/Cr(III) penicillamine] system
(Ionic strength 0.1 M, Temp. 35°C)

uncomplexed. The second plateau (with positive mobility) corresponds to 1:1 complexes of cationic nature. The third plateau in negative region indicates the anionic nature of the second metal complex. Further increase in pH has no effect on the mobility of metal ions. The unprotonated anionic species but not the zwitterion of penicillamine is known to have ligating properties [8].

In view of these observations, the complexation of metal ions with the penicillamine anion [L^{2-}] may be represented as:

$$M^{3+} + L^{2-} \xrightleftharpoons{K_1} ML^{+} \quad ...(1)$$

$$ML^{+} + L^{2-} \xrightleftharpoons{K_2} ML_2^{-} \quad ...(2)$$

where,
M^{3+} is iron(III)/chromium(III) metal cation.
L^{2-} is ligand (penicillamine anion),
ML^{+}, ML_2^{-} are 1:1 & 1:2 metal complexes,
K_1, K_2 are first and second stability constant of complexes.

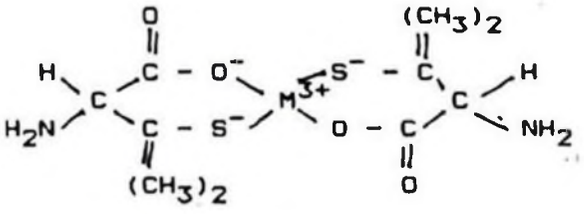
The pH corresponding to the mean mobility between the first and second plateau is read out from graph. Concentration of penicillamine anion at this pH is calculated using acid dissociation constant of penicillamine. K_1 is the reciprocal of this concentration. Similarly at the pH corresponding to the mean of the mobility between the second and third plateau, K_2 is calculated. Calculaed values of constants are given in Table 1.

Table 1

Stability Constants of Fe(III) and Cr(III) Binary Complexes with Penicillamine
(Ionic strength = 0.1 M) ;(Temperature = 35°C)

Metal ion	log K_1	log K_2
Fe(III)	13.90	19.53
Cr(III)	13.51	17.66

In ML_2^{-} complexes, two penicillamine molecules are bonded to metal ion. The structure of complexes was considered to be planer, with CS and COO^{-} functions coordinated to central metal ion. The probable strucutre of the ML_2^{-} complexes is given as below



It can be concluded from these studies that Fe(III) and Cr(III) metal ions play a dominant role in biochemical processes. The penicillamine may be used to reduce the levels of Fe(III) and Cr(III) in biological systems.

ACKNOWLEDGEMENT

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TERMS USED IN METAL FINISHING PRACTICE

ACTIVATION: Elimination of Passive Conduction or Removal of Oxide Film on the Surface.

ADDITION AGENT: Material Added to the Plating Bath for Modifying the Characteristic of the Deposit. The addition Agent may be Organic, Metallic Salts and Compounds.

ADHESION: The Attractive Force that exists between the Electrodeposit and its Surface.

ALLOY: A Substance having Metallic Properties composed of 2 or more Elements of which at least one is a Metal.

ALLOY PLATING: Co-deposition of 2 or more Metals.

AMPERE: Current which will deposit Silver at the rate of 0.0011180 G/Sec.

BATH VOLTAGE: The total Voltage between Cathode and Anode in a Plating Bath due to Electrolysis.

BATH EFFICIENCY: The Efficiency of the Bath is Measured by the Weight of Metal Deposited per unit current passed per unit time.

CATHODE CURRENT DENSITY: The Current Consumed by Cathode Per Unit Area. Usually Expressed in A/dm2 (dm2 = 100 cm2).

COLOUR: Generally in Horological industries we follow Swiss Nihs Standard specified as 1N, 2N, 3N, 4N & 5N.

CONDUCTING SALT: A compound added to the solution in order to increase its Electrical Conductivity.

COVERING POWER: Ability of the Bath to cover with a coating as fast as possible.

DUCTILITY: Is the ability of the coating to withstand repeated bending without any cracking.

ELECTROPOLISHING: The Improvement in Surface Finish of a Metal by making it Anodic in a Appropriate Solution.

FARADAYS LAWS: 1) The amount of Chemical change produced by an Electric Current is proportional to the Quantity of Electricity.

2) The amount of different substances Liberated by a given Quality of Electricity are proportional to their Chemical Equivalent weights.

ONE FARADAY: 96,490 Coulomb: i.e., 96,490 Amperee second.

GOLD CONCENTRATION: Usaually specified by the supplier of proprietory baths as optimum in grams per liter as Metal to get the correct colour, plating rate and other characteristics.

HARDNESS: Is a measure of the resistance of the deposit to withstand penetration.

HYDROGEN EMBRITTLEMENT: Brittleness caused on the deposit due to the inclusion of Hydrogen along with the deposit.

INSOLUBLE ANODE: An Anode which is insoluble in the plating Bath under conditions during Electrolysis.

LEVELLING: As the ability to cover any surface imperfections like Scratches, Dents and Pits.

MICRON: One thousandth of the Millimeter (.001 mm = 1 mm).

PEELING: The Detachment of a plated Metal Coating form the basis Metal.

PITTING: Dispersion Produced in a Metal Surface by Non-uniform Electrodeposition or by Corrosion.

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