

## Study of Metal-complexes of 5-Substituted Uracils†

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The Electrochromatographic method, i.e. novel ionophoretic technique, has been employed in quite modified way, after several improvements. The method is based upon the migration of a metal ion spot on the chromatographic paper strip soaked with ligand added background electrolyte, under electrical influence. Ionophoretic mobilities were recorded at different pH's of background electrolyte (containing ligand viz. 5-methyluracil/5-aminouracil/5-bromouracil) and a plot mobility vs. pH was drawn for information on the formation of metal-complex and calculation of equilibrium constant values for Hg(II) and Be(II) ions at  $I = 0.1$  & temp.  $35 \pm 0.1^\circ\text{C}$ .

### INTRODUCTION

The metal-complexes of pyrimidine nucleotides play an important role in bio-chemical processes viz. genetics and molecular biology<sup>1</sup>. In past decade, certain synthetic substituted uracils have got attention due to their role in many metabolic processes; most of them involved active participation of metal ions<sup>2,3</sup>. 5-Substituted uracils have shown its potentiality by acting as chemical mutagens and inhibitors in synthesis of nucleic acids and proteins; and hence may be used as carcinostatic and antiviral agents<sup>4</sup>. Studies on the complexes of uracil with various metal ions, are well documented<sup>5,6</sup>. The present note describes the complexing behaviour of 5-methyl uracil, 5-bromo uracil and 5-amino uracil with Be(II) and Hg(II).

Paper electrophoresis has been used by some worker in qualitative studies of complexes<sup>7</sup>. We have employed the electro-chromatographic technique for the study of stepwise and mixed complexes, in quite modified way after making it almost free from vitiating factors like temperature variation, capillary flow, electroosmosis and molecular sieving<sup>8</sup>.

### EXPERIMENTAL

(i) *Instrument*<sup>6,8</sup>: Systronic paper electrophoresis equipment No. 604 horizontal type (India), with two hollow rectangular water circulated plates and transparent PVC moulded lid. pH-measurements were made with Elico pH-meter.

(ii) *Chemicals*: Chemicals used were of AnalaR grade. Be(II) and Hg(II) perchlorates of  $5 \times 10^{-3}$  M concentration were prepared.

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**Spot detecting reagents:** H<sub>2</sub>S water for Hg(II) ions (Black colour); while Aluminon-ammonium acetate 0.1 (w/v) aqueous solution for Be(II) ions (Pink-red colour). During colorimetric detection of metal ion spot, suitable pH of strip was adjusted by using glacial acetic acid and fuming ammonia. The glucose spot (electroosmotic indicator) was detected by spraying aqueous silver nitrate in acetone and 2% ethanolic caustic soda; a black spot was observed.

In study of binary complexes, the background electrolyte was 0.1 M HClO<sub>4</sub> with the ligand 0.01 M, 5-bromo uracil, 5-amino uracil, 5-methyl uracil (Sigma grade) solutions.

### Procedure<sup>8</sup>

(30×1 cm<sup>2</sup>) Whatman No. 1 filter paper strips (in triplicate) were spotted in the middle with metal ion solution. Two extra strips were marked with glucose. The loaded strips were sandwiched between two insulated hollow water circulated metallic plates mounted in the electrophoresis equipment; the ends of paper strips were dipping in two side electrode chambers in the instrument. When the paper strips become saturated with the electrolyte-ligand solution, a constant voltage of 200 V was applied for 60 minutes (potential gradient through strip 7.57 V cm<sup>-1</sup>). Then strips were removed, dried, developed and distances of migrated spots from the point of application were noted. All the complexes have shown unidirectional motion. The distances recorded in triplicate for every ion spot did not differ beyond ±5% from the mean value. Mean value converted into mobility was plotted against pH. Observations, pH vs. Mobility, at different pH values of solution were recorded and plotted<sup>8</sup>.

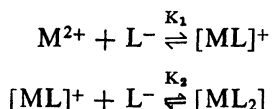
## RESULTS AND DISCUSSION

The plot of overall ionophoretic mobility of metal ion/complex, as a function of pH, shows the stepwise coordination behaviour from a non-complexed metal ion to ultimate complexed species in the experimental range.

There are three plateaus in the curves of both the cations<sup>6</sup>. A plateau is obviously an indication of a pH range where mobility of ion is practically constant, it evidences the overwhelming presence of only a particular complex species. The first plateau of positive mobility at lower pH range is due to non-complexed cation. In this pH range ligand is present as a noncomplexing species. Gradual increase of pH results in progressive decrease of mobility upto a second plateau which lies still in positive mobility region. It indicates formation of 1 : 1 complex of cationic nature, here the existing ligand's species is of anionic nature. Further increase of pH (till 10.00) gives third plateau in zero mobility, indicates the formation of electrically neutral complex (ML<sub>2</sub>). In third plateau

range, almost complete conversion of 1 : 1 complex species into ultimate 1 : 2 complex. A further increase in pH (upto 10.0) makes no change in mobility.

The above observations may be expressed as following equilibria:



The metal spot on the chromatogram is thus a conglomeration of  $M^0$ ,  $ML^+$  and  $ML_2$  species (dynamic equilibria  $M^{2+} + L^{-} \rightleftharpoons ML^+$ , and  $ML^+ + L^{-} \rightleftharpoons ML_2$  give a single spot, not separate bands of differently charged species).

For the species (spot) moving under the influence of the electric field, the overall mobility is given by eqn. (1),

$$U = u_n f_n \quad (\text{Ref. 7}) \quad (1)$$

where  $u_n$  and  $f_n$  are mobility and mole fraction of a particular complex species. This equation is transformed into the following form on taking into consideration, different equilibria (for two step complexation process).

$$U = \frac{u_0 + u_1 k_1 [L^{-}] + u_2 k_2 k_1 [L^{-}]^2}{1 + k_1 [L^{-}] + k_2 k_1 [L^{-}]^2} \quad (2)$$

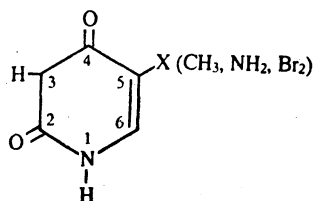
where  $u_0$ ,  $u_1$  and  $u_2$  are mobilities of  $M^0$ ,  $ML$  and  $ML_2$  species. This equation has been used for the calculation of equilibrium constant (stability constt) of the complex. Using the dissociation (protonation) constants of ligands (electrophoretically obtained values; methyl-uracil  $10^{9.68}$ ; bromo-uracil  $10^{7.47}$ ; uracil  $10^{9.33}$ ; amino-uracil  $10^{9.50}$ ), the concentration of the ligating species  $L^{-}$  was calculated at a particular pH:  $k_1$ ,  $k_2$  for the complexes were calculated as described earlier<sup>6,8</sup>. The results are given in Table 1.

Uracil and 5-substituted uracils are pyrimidine base containing two heterocyclic nitrogen atoms at 1, 3 positions and two phenolic-OH groups at 2- and 4-position. Uracils show keto-enol tautomerism more at  $N_{(3)}$  than  $N_{(1)}$ . Theoretically these have two ionisable protons but they have been observed to yield only one, other constant<sup>9</sup>. As regards the site of deprotonation, there has been a controversy, however a number of workers<sup>10</sup> have lately given evidence for deprotonation preferably from  $N_{(3)}$  to  $C_{(4)}$ .

The basicities of the ligands were found to be in order, 5-bromo-uracil < uracil < 5-aminouracil < 5-methyluracil. This can be explained taking into account the inductive-effect (electron attracting). The increased protonation constants of 5-methyl uracil and 5-amino uracil compared to uracil is explained on the basis of electron-releasing effect of methyl (inductive) and amino (resonance) groups. Though there are three possible

TABLE I  
EQUILIBRIUM CONSTANTS OF BINARY  
COMPLEXES

(ionic strength 0.1; temp.  $35 \pm 0.1^\circ\text{C}$ )



Metal ion $\rightarrow$ Ligand	Hg(II)			Be(II)		
	Expt. values		Lite. values	Expt. values		Lite. values
	log $K_1$ (a)	log $\beta_2$ (b)	log $K_{ML}^M$ (c)	log $K_1$ (d)	log $\beta_2$ (e)	log $K_{ML}^M$ (f)
(1) 5-Methyl Uracil	7.36	14.02	5.45*	6.90	13.34	7.81
(2) 5-Amino Uracil	7.14	13.44	5.42*	6.82	13.00	7.47
(3) 5-Bromo Uracil	5.80	10.55	3.40*	5.67	10.42	5.65
(4) Uracil†	7.00	13.00	5.04*	6.51	12.35	7.41
			(5)			(5)
			$K_1, 7.30;$ $\beta_2, 13.59$			$K_1, 6.52;$ $\beta_2, 12.02$

†Already published (ref. 6), \* $K_{ML}^M$  (at temp.  $31 \pm 0.1^\circ\text{C}$ ;  $\mu = 0.1$  M KCl (ref. 11).

sites on the 5-substituted uracils for complexation<sup>11</sup>; (i) chelation between 5-substituent and 4-carbonyl, (ii) complexing on  $N_{(1)}$ , and (iii) complexation at  $N_{(3)}$ , but most plausible site which involve in coordination is  $N_{(3)}$ . A perusal on Table 1, reveals that stability values of metal complexes with different ligands are according to basicity order of ligands.

A comparison of stability values of Hg(II) and Be(II) complexes show that Hg(II) complexes are more stable than those of Be(II), but difference in log k values of Hg(II) and Be(II) lies within one unit for all values in all the ligands. The lesser difference in log k values of Be(II) and Hg(II) is due to comparatively higher stability of Be(II) complexes than expected, which may be owing to smaller effective ionic radii and hard acid nature of Be(II) ion.

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