BINARY & TERNARY COMPLEXS OF THYMINE AND NITRILOTRIACETATE BY PAPER ELECTROPHORETIC METHOD

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The binary equilibria M(II)- thymine, and M(II)-NTA and the ternary equilibria M(II)-NTA-thymine have been studied using the paper electrophoresis method. The log K values of the mixed complexes of Hg (II) Be (II) and Cu (II) are 5.47, 5.36 and 4.36 respectively at μ = 0.1 and 35°C

Metal-complexes of purine & pyramidine bases play a dominant role in many biological systems. Thymine constitute the backbone base of the DNA molecule. As a part of our programme to investigate the interaction of purine & pyramidine with metal ions, this work has been taken up.

Paper electrophoresis (PE) was applied to the study of stepwise metal complexes in solution, [1] and mixed ligand complexes [2].

In the present investigation Hg(II),Be(II), Cu(II) complexes of thymine & mixed ligand complexes of NTA with thymine as secondary ligand have been studied.

EXPERIMENTAL

Apparatus

The description of the electrophoeretic equipment & the thermostatic arangement are as described [3].

PH measurements were made with Elico model L 1-10 pH meter (AC 220 V/50 cycles) using glass electrode.

Chemicals

Hg(II), Be(II) & Cu(II) perchlorate were prepared by precipitating the corresponding carbonates with sodium carbonate from solutions of nitrates, washing the precipitate thoroughly with boiling water, treating with suitable amount of 1% perchloric acid. The resulting mixtures were heated to boiling on a water bath and then filtered. The metal contents of filtrates were determined as usual and final concentration was kept at 5.0 mM.

Hydrogen sulphide water was used for detecting Hg(II) ions (black colour) while 0.1% of 1-(2-pyridylazo)-2-naphthol (PAN) in ethanol was used for detecting Cu(II) ions (Red colour). Aluminon-ammonium actate 0.1 (w/v) solution in water was used for detecting Be(II) ions (pink-red colour). During colourimetric detection of metal ion spot, suitable pH of the strip was maintained by using Glacial acetic & ammonia. Glucose spot (Electroosmatic indicator) was detected by spraying aqueous silver nitrate in acetone and 2% ethanolic caustic soda: a black spot was observed.

Background Electrolyte

Stock solution of 9.0 M perchloric acid, 2.0 M Sodium hydroxide and 0.5 M thymine were prepared from AnalaR samples (BDH), nitrilotriacetic acid (E. Merck Dramstadt F.R.G.) was used to prepare 0.01 M solution. Each solution was standardized as usual. The background electrolyte for electrophoretic experiments in binary complexes consists of 0.1 M perchloric acid and 10 mM thymine/1 mM NTA. In study of ternary complexes, it consists of 0.1 M sodium perchlorate, 1.0 mM NTA and varying amount of 10 mM thymine it was maintained at pH 8.5 by addition of sodium hydroxide. Electrophoretic experiments are carried out as described earlier [2,3] using 200 volts power source and the length of the paper ship between the tanks being 26.5 cms. The current is passed for 1 hr in each experiment.

A plot of mobility vs pH is presented in case of Hg(II), Cu(II) and Be(II) with the individual ligands and presented in Fig. 1 & 2. A plot of mobility against log [thymine] was made, which are shown in Fig.3.

RESULTS

Metal-Thymine Binary Systems

The plot of overall electrophoretic mobility

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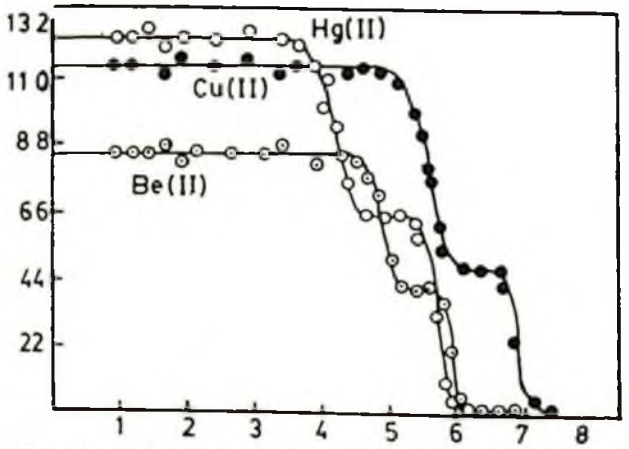


Fig. 1 Mobility Curve of [M(II) Thymine] System [Temperature 35° C Ionic Strength 0.1]

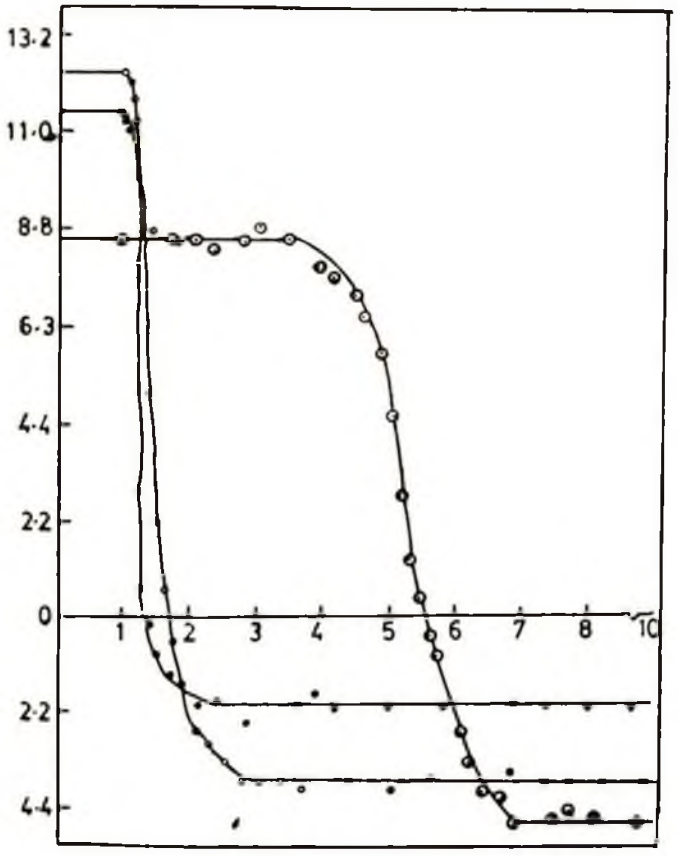


Fig. 2 Mobility-Curve [M(II) - NTA] System (Temp. 35° C Ionic Strength 0.1)

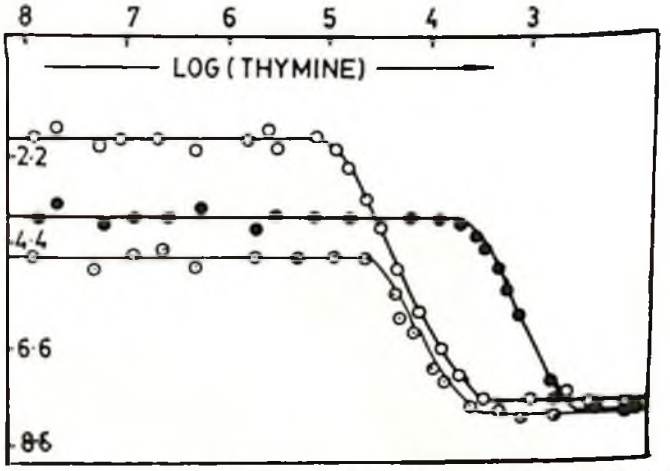


Fig. 3 Mobility-Curve M(II) NTA-Thymine System pH 8.5 Temp. 35°C ionic Strength 0.1

of metal spot against pH gives a curve with a number of plateaus shown in Fig. 1. The complexity constants are calculated as described earlier[1]. The first plateau in the beginning corresponds to a region in which metal ions are uncomplexed. It lies in low pH region where concentration of neutral species of thymine is obviously maximum, hence it is concluded that this neutral species of thymine is non-complexing. The second plateau in each case with positive mobility indicates the formation of 1:1 complex of catinic nature, the ligand being the anionic species of thiamine (L^-). Further increase in pH gives rise to a third plateau with zero mobility in each case which indicates formation of electrically neutral metal complex from anionic species of thymine (L^-) with one bivalent metal ion. It is well known that unprotonated anionic species of thiamine is a good ligand [4]. Further increase of pH has no effect on the mobility of metal ions.

Using the dissociation constant of thymine (Electrophoretically obtained value, log K = 9.81, the concentration of thymine anion $[L^-]$ is determined at the pH between first and second step, from which K_1 can be calculated ($K_1 = 1/[L^-]$). The stability constants K_2 of second complex can be calculated by taking into consideration the region between second and third plateau of the mobility curve. These calculated values are given in Table 1.

Metal-NTA Binary Systems

The observations on overall mobility of metal spots in presence of NTA at different pH

values are represented in Fig 2. As it is evident from the figure that with all the three metal ions two plateaus are obtained, the mobility of the second plateaus lies in the negative region, showing negatively charged nature of the complexes. Only one NTA anion is assumed to combine with one bivalent metal ion to give 1:1 M-NTA-complex which is in confirmity with finding of others [5]. The stability constants of complexes with NTA are calculated in a manner described in preceding paragraphs (by using electrophoretically obtained dissociation constant values (log K_1 = 1.80, log K_2 = 2.45 log K_3 = 9.65). The calculated values are given in Table 1.

Metal-NTA-Thymine Ternary Systems

It is observed from the mobility curves of M-thymine and M-NTA binary systems that binary complexes, (M-thymine and M-nitrilotriacetate) are formed at a pH lower than 8.5. Thus it would be proper to study the transformation of M-NTA complex into M-NTA-thymine complex at pH 8.5 in order to avoid any side interaction. So the study of this system has been made at pH 8.5

Tne plot of mobility against logarithm of concentration of added thymine gives a curve (Fig.3) containing two plateaus. The mobility in the range of first pleateau is in agreement with mobility of 1:1 M-NTA-complex and corresponds to the mobility of 1:1 M-NTA complexes. The mobility of the last plateau is more negative than that of first plateau. It indicates, the formation of more negatively charged complex. Further since the mobility in the last plateau does not tally with the mobility of 1:1 and 1:2 metal thymine complex it is inferred that the moiety in last plateau is due to coordination of thymine anion to 1:1 M-NTA moiety resulting in the formation of 1:1:1 mixed complex (M-NAT-thymine) as:

$$M\text{-}NTA^{-} + L^{-} \rightleftharpoons M\text{-}NTA\text{-}L^{2-}$$

In the present electrophoretic study, transformation of a simple complex into mixed complex takes place; the overall mobility is given by:

$$U = U_o f_{M\text{-}NTA} + U_1 f_{M\text{-}NTA\text{-}L}$$

where u_o, u_1 and $f_{M\text{-}NTA}$; $f_{M\text{-}NTA\text{-}L}$ are mobilities and mole fraction of $M\text{-}NTA^{-}$, and $M\text{-}NTA\text{-}L^{2-}$ complexes respectively. Substituting the values of mole fractions, the overall mobility is given by the equation:

$$U = \frac{u_o + u_1 K' [L^{-}]}{1 + K' [L^{-}]}$$

TABLE 1

STABILITY CONSTANTS OF BINARY AND TERNARY COMPLEXES OF Hg(II), Be(II) & Cu(II)

(Ionic Strength 0.1 N : Temp. 35° C)

NTA anion = $N\text{-}(CH_2COO)_3^{3-}$ Thymine anion = $L^{-} = (C_5H_5N_2O_2)^{-}$

Metal ion	log stability constant - experimental					log stability constant - literature				
	(a)	(b)	(c)	(d)	(e)	(a)	(b)	(c)	(d)	(e)
Hg(II)	5.47 ±0.05	13.30 ± 0.07	18.77 ± 0.12	7.21 ±0.06	13.21 ± 0.11	-	14.6 [6]	-	7.93 [4] ±0.04	14.70 [4] ± 0.06
Be(II)	5.36 ±0.06	7.10 ±0.06	12.46 ± 0.12	6.80 ±0.05	12.60 ± 0.10	-	7.11 [6,7]	-	7.01 [4] ±0.03	13.21 [4] ± 0.05
Cu(II)	4.36 ±0.04	12.71 ± 0.06	17.06 ± 0.10	6.11 ±0.04	10.92 ± 0.09	-	12.94 [6] 13.60 [8] 13.30 [8] 12.75 [8]	-	5.80 [4] ±0.01	- -

a) log $K^{MNTA}_{M\text{-}NTA\text{-}L}$ b) log $K^{M}_{M\text{-}NTA}$ c) log $\beta_{M\text{-}NTA\text{-}L}$ d) log K^{M}_{ML} e) log β_2 of ML_2

u_0 and u_1 are the mobilities in the regions of the two plateaus of the curve. From the figure, concentration of thymine at which overall mobility is mean of the mobilities of two plateaus is determined. Concentration of thymine anion at pH 8.5 (for this thymine concentration) is calculated. K' is obviously equal to $1/[L^-]$. All these calculated values of K'are given in Table 1.

DISCUSSION

A perusal of table 1 reveals that the order of stability constants, viz. Hg(II) > BE(II) > Cu(II) is same for M(II)- thymine and M(II)-NTA-thymine complexes while in M(II)-NTA binary complexes, Hg(II) shows superior co-ordinating tendency followed by Cu(II) and Be(II). It might be by virtue of different dentacity and nature of thymine and NTA ligands.

It is meaningful to compare column (a) with (d) which gives an idea of the affinity of anionic thymine for metal ion. It is seen that the order in the complexity constants with different metals with thiamine is the same but it is smaller when it combines to form binary complex in comparison. The comparison of $\log K^{M}_{M(Thy)}$ and $\log K^{M}_{M(Thy)_2}$ also eludidates the same view.

The values of $\log {}^{M\text{-}thy}_{M\text{-}thy\text{-}NTA}$ (11.56, 5.66 & 10.95) for the M(II)-thy-NTA ternary complex of Hg(II), Be(II) and Cu(II) can be computed from the expression:

$$\log K^{ML}_{ML\text{-}NTA} = \log \beta_{M\text{-}NTA\text{-}L} - \log K^{M}_{M\text{-}L}$$

gives a measure of the tendeny of NTA coordinating with binary (1:1) complex of the metal with thymine (ML). Comparison of $\log K^{M}_{M\text{-}NTA}$ and $\log K^{M}_{M\text{-}thy}$ shows better coordinating capacity of NTA over thymine.

Our experimental values resemble with the available liteature values, the slight difference may be due to change in temperature, ionic-strength and experimental conditions.

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