Paper Electrophoresis in the Study of Mixed-Ligand Complexes in Solution

The System Cu(II), Zn(II), and Co(II)-Glutarate-Nitrilotriacetate

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A new method. Involving the use of paper electrophoresis, is described for the study of the equilibria in mixed complex systems in solution. The method is based on the migration of a spot of metal ion, with the complexants added in the background electrolyte (0.1 M perchloric acid) at a fixed pH. The concentration of one of the complexants (L) is kept constant, while that of the second ligand (NTA) is varied. A graph of −log (TNA) against mobility is used to obtain information on the formation of the mixed complex and to calculate the stability constant. Using this technique, the values of the overall stability constants βMLx NTA of the complex metal (II) −glutarate−nitrilotri−acetate, have been found to be $10^{9.7}$, $10^{9.10}$, $10^{7.10}$ for Copper (II), Zinc (II) and Cobalt (II) complexes respectively.

PAPER electrophoresis (PE) has baen applied to study metal complexex in solution, and attempts have been made to determine the stability constants of the complex species[1-2]. This technique is limited to charged species, and the precision of the method is not as high as that of other physicochemical methods. Nevertheless, it is of interest in the study of metal ligand systems in solution.

In a recent communication[3-4] from these laboratories a new method was reported for the study of the stepwise formation of complexes. Although the use of PE for the study of metal complex systems with a single ligand seems to be well established, there is no systematic study of the formation of mixed ligand complexes using this technique. However, Czakis-Sulikawska[5] made some observations on the formation of the mixed halide complexes of mercury (II) using PE, but the studies were only qualitative and did not throw light either on the nature of the species or on their stabilities. A publication[6] of these laboratories deals with a new method for the study of mixed complexes.

This paper is an extension of the technique and some of the results obtained with the mixed systems viz. Copper (II), Zinc (II) and Cobalt (II) – glutaric acid – hitrilotriacetate.

EXPERIMENTAL

Instruments : Electrophoresis equipmeet (Systronics, model 604 India) has been used. It has a built-in power supply (AC–DC) which is directly fed to a paper electrophoresis tank. The potential in each experiment was kept at 240 volts and electrophoresis carried out for 60 minutes, temp. 35°C.

Whatman No. 1 paper strips 26.5 × 1.5 cm were used pH measurements were made (Elico, model L_{I-10}) using glass-calomel electrodes.

Chemicals : Metal perchlorates were prepared by the precipitation of metal carbonates from their nitrates with sodium bicarbonate, which were throughly washed with boiling water and treated with calculated amounts of 1% perchloric acid. These were heated and filtered. The metal contents of the filtrates were determined and the final concentrations were kept at 5.0×10^{-3}M.

1-(2-Pyridylazo)-2-naplhthol (PAN), 0.1% (w/v) in ethanol was used for detecting the metal ions. A saturated solution of silver nirate in acetone was sprayed on the paper and subsequently fumed with NH_3 to detect glucose in the spot.

Background electrolyte : Stock solutions of 2.0 M perchloric acid, 2.0M sodium hydroxide and 0.1 M glutatic acid were prepared from BHD AnalaR samples. 0.01 M NTA was prepared from a sample obtained from E.Merck (Darmstadt, G.F.R.). Each solution was standardized as usual. The back ground electrolyte consisted of a mixture containing 0.1M perchloric acid, 5.0×10^{-3} M glutaric acid and varying amounts of 0.01M NTA; it was maintaned at pH 8.5 by addition of sod um hydroxide solution.

Procedure : Paper strips (26.5 × 1.5 cm) are marked in the middle point to which metal spots are applied with a micropipette. They are mounted on the tank lengthwise and to prevent kinking a plastic plate is placed beneath the stips. Another strip marked with glucose spot is also placed on the tank in the same fashion as described above. The air tight lid is closed and when the strips become wet by the backgroud electrolyte, 240 volts, dc is applied for 60 minutes. After that strips are removed from the tank and dried. Spots are detected by spraying appropriate reagents. Distance moved by spots are measured from the previously marked point. Movement of glucose is used as a correction factor. Distance travelled towards the anode is negative and distance towards cathode is positive. Dividing the movement by potential gradient, mobilities are obtained.

RESULTS

In preliminary experiments[8] using the new technique, it has been observed that glutaric acid forms Cu $(CH_2)_3$ C_2O_4, Zn $(CH_2)_3$ COOH COO^+ and CO $(CH_2)_3$ COOH COO^+ complexes in the pH range 3.0–10.0 where as NTA forms $(Cu\ NTA)^-$, $(Zn\ NTA)^-$ and $(Co\ NTA)^-$ complexes in the pH range 1.5–10.0. In the present experiments, the supporting electrolyte contained 0.1M perchloric acid, the concentration of glutaric acid was held constant at 5.0×10^{-3}M where as that of NTA was varied between 1.0×10^{-7} and 5.0×10^{-3}M. The pH of the supporting electrolyte was maintained at 8.5 by adding appropriate amount of caustic soda. This pH 8.5 is important since both ligands form 1 : 1 complex individually with the 3 metal ions. The mobilities were plotted against the logarithms of the concentrations of NTA (Fig. 1). The graphs for Cu (II), Zn (II) and Co (II) each had two plateaus. The first plateau corresponds to the formation of simple complexes Cu L, Zn HL^+, Co HL^+ and the second to the formation of the mixed-ligand species $\{Cu\ (L)\ NTA\}^{-3}$, $\{Zn\ (HL)\ NTA\}^{2-}$ and $\{Co\ (HL)\ NTA\}^{2-}$. The second plateau gave a constant value of mobilities of –3.65, –3.00 and –4.80 $Cm^2\ volt^{-1}\ min^{-1}\ X10^3$ for Cu (II), Zn (II) and Co(II) respectively at NTA 5.0×10^{-3}M. In the presence of only NTA 1 : 1 complexes are formed in the pH range 1.5–10.0. The mobilities of these complex ions $\{Cu\ (NTA)\}^-$, $\{Zn\ (NTA)\}^-$ and $\{Co\ (NTA)\}^-$ are –230, –5.10, –2.90$cm^2\ volt^{-1}\ min^{-1}\ X10^3$ respectively[7].

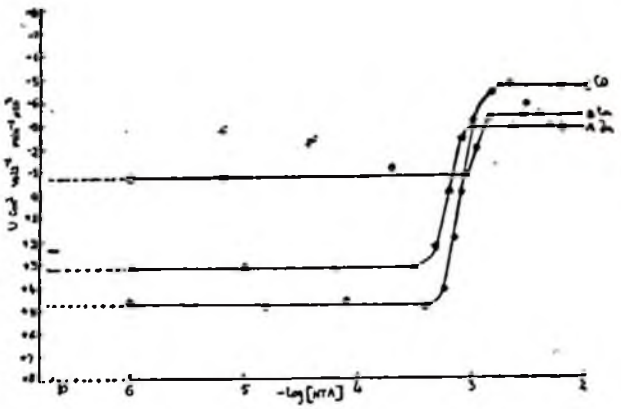


Fig. 1. Metal-Glutaric acid-Nitrilotri Acetate System -Log NTA Vs mobility

A. Zn (II) – Glutaric acid – Nitrilotri Acetate System

B. Cu (II) – Adipic acid – Nitrilotri Acetate System

C. Co (II) – Adipic acid – Nitrilotri Acetate System

[L = HL^- or L^{2-}
where $HL^- = (CH_2)_3\ COOH\ COO^-$,
$L^{2-} = (CH_2)_3\ C_2O_4^{2-}$]

The observations indicate that mixed-ligand species are formed in the present systems.

DISCUSSION

In the presence of an excess of glutarate ion, the positive metal ion is complexed to form

$$M^{n+} + x(L^{-a}) \rightleftharpoons \{ML_x\}^{-ax+n} \quad (1)$$

When increasing amounts of NTA^{3-} are gradually added, addition of NTA^{3-} takes place as—

$$\{ML_x\}^{-ax+n} + NTA^{3-} \rightleftharpoons \{ML_xNTA\}^{-ax+n-3} \quad (2)$$

The gross stability constant of the simple and the mixed complex can be represented by the equations.

$$\beta ML_x = \frac{[\{ML_x\}^{-ax+n}]}{[M^{n+}]\ [L^{-a}]} \quad (3)$$

$$K_{ML_xNTA} = \frac{[\{ML_xNTA\}^{-ax+n-3}]}{[\{ML_x\}^{-ax+n}]\ [NTA^{3-}]} \quad (4)$$

Since there is no third plateau, no further interaction with NTA^{3-} is possible. Thus we get the following equation.

$$\beta_{ML_xNTA} = \frac{[\{ML_xNTA\}^{-\alpha x+n-3}]}{[M^{n+}]\,[L^{-\alpha}]^x\,[NTA^{3-}]} = \beta_{ML_x} K_{ML_xNTA} \quad (5)$$

In the electrophoretic study reported here, the concentration(L) is fixed and $[NTA^{3-}]$ is varying, hence the overall mobility is given by

$$U = U_1 f_{ML_x} + U_2 f_{ML_xNTA} \quad (6)$$

Where u_1, u_2 and f_{ML_x}, $f_{ML_x\,NTA}$ are the mobilities and the mole fractions of the $\{ML_x\}^{-\alpha x+n}$ and $\{ML_xNTA\}^{-\alpha x+n-3}$ species respectiveiy.

It is obvious from the Fig. 1 that only one mixed complex is formed with each ligand. so the change of mobility from the first plateau to the second plateau can be represented by the equation

$$U \quad \frac{u_1 + u_2 K_{ML_xNTA}\,[NTA^{3-}]}{1 + K_{ML_xNTA}\,[NTA^{3-}]} \quad (7)$$

From this equation, taking the average mobility at a point corresponding to $K_{ML_xNTA}\,[NTA^{3-}] = 1$, the valves of log K_{ML_xNTA} were calculated to be 2,95, 3.20, 3.10 for $\{Cu\ (L)\ NTA\}^{-3}$. $\{Zn\ (HL)\ NTA\}^{-2}$ and $\{Co\ (HL)\ NTA\}^{-2}$ respectively. Since the values of log β_{ML_x} are 3.90, 2.90 and 2.70 for Cu (II), Zn (II) and Co (II)- glutarate complexes respectively[8], log β_{ML_xNTA} is therefore 6.85, 6.10, 5,80 for the mixed-complexes of Cu (II), Zn (II) and Co (II).

Since these mixed complexes are being reported for the first time, no comparision can be made for the values of stability constants.

The simple electrophoretic technique has thus been helpful in deciding as to whether a mixed complex system is formed or not and if it is formed its stability constant can also be determined,

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