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PAPER ELECTROPHORESIS IN THE STUDY OF MIXED-LIGAND COMPLEXES IN SOLUTION

THE SYSTEMS COPPER(II) AND NICKEL(II)-OXALATE-NITRILOTRIACETATE

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SUMMARY

A new method, involving the use of paper electrophoresis, is described for the study of the equilibria in mixed-ligand complex systems in solution. The method is based on the migration of a spot of a 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 (A) is kept constant, while that of the second ligand (L) is varied. A graph of $-\log [L]$ against mobility is used to obtain information on the formation of the mixed-ligand complex, and to calculate the stability constant. Using this technique, the values of the overall stability constants β_{MAL} of the complex metal(II)-oxalate-nitrilotriacetate, $[MAL]^{3-}$, have been found to be $10^{9.8}$ and $10^{8.9}$ for copper(II) and nickel(II) complexes, respectively.

INTRODUCTION

Paper electrophoresis (PE) has been applied to the study of metal complexes in solution, attempts having been made to determine the stability constants of the complex species¹⁻⁵. 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 since complex formation is widely used in effecting separations of metal ions, and further refinements in instrumentation may lead to its use in the study of metal-ligand equilibria in solution.

In a recent communication⁶ from these laboratories, a new method was reported for the study of the stepwise formation of complexes formed between copper(II) and nickel(II) ions and oxalic acid, and the method has been extended to complexes involving malonic, succinic, malic, maleic and nitrilotriacetic acids⁷. 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-

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ligand complexes using this technique. However, Czakis-Sulikowska⁸ made some observations on the formation of 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. This paper reports some of the results obtained with the systems: (i) copper(II)-oxalate-nitrilotriacetate; and (ii) nickel(II)-oxalate-nitrilotriacetate.

EXPERIMENTAL

Instruments

Horizontal Type No. 3276 PE equipment (LKB, Stockholm, Sweden) was used, together with the various accessories supplied with the instrument. The apparatus was of the cassette type, and chromatograms could be run simultaneously on six paper strips. The power unit was capable of yielding a maximum of 400 V d.c. In each case, electrophoresis was carried out for 150 min at 250 V and at 25°. Whatman No. 1 paper strips (46.5 × 1.9 cm) were used with an applied voltage gradient of 2.82 V/cm².

pH measurements were made with an Elico Model L 1-10 pH meter using a glass-calomel electrode assembly.

Chemicals

Copper(II) and nickel(II) perchlorates were prepared by precipitating the corresponding carbonates from solutions of the nitrates with sodium bicarbonate, washing the precipitates thoroughly with boiling water and treating with a suitable amount of 1% perchloric acid. The resulting mixtures were heated to boiling on a water-bath and then filtered. The metal contents of the filtrates were determined chelometrically in each case and the final concentrations were kept at $5.0 \cdot 10^{-3}$ M.

1-(2-Pyridylazo)-2-naphthol (PAN), 0.1% (w/v) in ethanol, was used for detecting the copper and nickel ions. A saturated aqueous solution (0.9 ml) of silver nitrate was diluted with acetone to 20 ml. Glucose was detected by spraying with this solution, and then with 2% ethanolic sodium hydroxide, when a black spot was formed.

Background electrolyte

Stock solutions of 2.0 M perchloric acid, 2.0 M sodium hydroxide and 0.5 M oxalic acid were prepared from AnalaR samples (BDH, Poole, Great Britain); 0.01 M nitrilotriacetic acid (NTA) was prepared from a sample obtained from E. Merck (Darmstadt, G.F.R.). Each solution was standardized as usual. The background electrolyte consisted of a mixture containing 0.1 M perchloric acid, $2.0 \cdot 10^{-3}$ M oxalic acid and varying amounts of 0.01 M NTA; it was maintained at pH 8.5 by addition of sodium hydroxide solution.

Procedure

The midpoint of each paper strip was marked and moistened with the background electrolyte. Excess of electrolyte was allowed to drain off and the papers were mounted on the cassette. A spot of the metal solution was then applied at the marked point by use of a 1.0- μ l micropipette. In each set, six strips were mounted including two strips which were spotted with glucose. Each of the two electrode vessels was

filled with 700 ml of the background electrolyte. The cassette was closed and placed on the electrode vessels. The electrophoretic migration of the metal spot on the paper was observed for various compositions of the background electrolyte. After electrophoresis, the spots of Cu(II), Ni(II) and glucose were developed with the reagents. The distances of the leading and tailing edges from the marked centre were measured; the metal ions moved towards the anode in each case (and the distances are therefore positive), whereas glucose moved towards the cathode. The diameters of the spots were *ca.* 1 cm. The mean of the two distances was noted and the distance travelled by glucose under identical conditions was added in order to obtain the corrected path length. The mobilities were then calculated and expressed in $\text{cm} \cdot \text{V}^{-1} \cdot \text{sec}^{-1}$.

RESULTS

In the experiments the background electrolyte contained 0.1 M perchloric acid; the concentration of oxalic acid was held constant at $2.0 \cdot 10^{-3}$ M, whereas that of NTA was varied between $1.0 \cdot 10^{-10}$ and $2.0 \cdot 10^{-3}$ M. The mobilities were plotted against the logarithms of the concentrations of NTA (Fig. 1). The graphs for copper(II) and nickel(II) each had two plateaus. The first plateau corresponds to the formation of $[\text{M}(\text{C}_2\text{O}_4)_2]^{2-}$ and the second to the formation of the mixed-ligand species $[\text{M}(\text{C}_2\text{O}_4)(\text{NTA})]^{3-}$. The second plateau gave mobilities of $2.24 \cdot 10^{-6}$ and $1.48 \cdot 10^{-6}$ $\text{cm} \cdot \text{V}^{-1} \cdot \text{sec}^{-1}$ for copper(II) and nickel(II), respectively, at $[\text{NTA}] = 2.00 \cdot 10^{-4} - 2.00 \cdot 10^{-3}$ M. In the presence of only NTA, the mobilities of $[\text{Cu}(\text{NTA})]^{-}$ and $[\text{Ni}(\text{NTA})]^{-}$ are $1.13 \cdot 10^{-6}$ and $0.95 \cdot 10^{-6}$ $\text{cm} \cdot \text{V}^{-1} \cdot \text{sec}^{-1}$, respectively⁷. It has already been observed that NTA only forms a 1:1 complex. These observations indicate that mixed-ligand species are formed in the present systems.

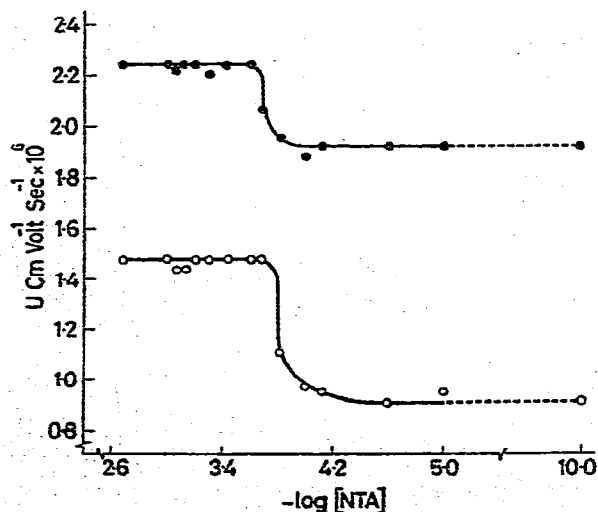
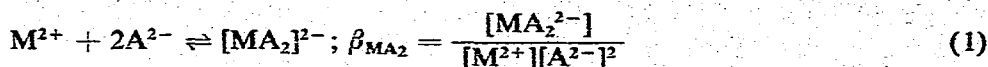


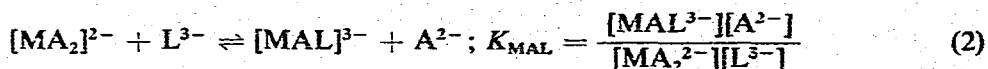
Fig. 1. Variation of the mobility with $-\log [\text{NTA}]$ for the complexes of copper(II) (●) and nickel(II) (○).

DISCUSSION

In the presence of an excess of oxalate ions (A^{2-}), the positive metal ion is complexed to form $[MA_2]^{2-}$:



When increasing amounts of NTA (L^{3-}) are gradually added, displacement of oxalate occurs as:



Further reaction between $[MAL]^{3-}$ and L^{3-} is not possible since $[ML_2]^{4-}$ is not formed, as evidenced by two (and not three) plateaus in the mobility graphs (Fig. 1). Thus we obtain eqn. 3.

$$\beta_{MAL} = \frac{[MAL^{3-}]}{[M^{2+}][A^{2-}][L^{3-}]} = \beta_{MA_2} \cdot K_{MAL} \quad (3)$$

In the electrophoretic study reported here, the concentration $[A^{2-}]$ is fixed and $[L^{3-}]$ is varying; hence the overall mobility is given by

$$U = u_1 \cdot f_{MA_2} + u_2 \cdot f_{MAL} \quad (4)$$

where u_1 , u_2 and f_{MA_2} , f_{MAL} are the mobilities and the mole fractions of the $[MA_2]^{2-}$ and $[MAL]^{3-}$ species, respectively. The presence of two plateaus corresponds to the formation of the species $[MA_2]^{2-}$ and $[MAL]^{3-}$, respectively. Substituting the values of mole fractions f_{MA_2} by $(1 + K_{MAL} \cdot [L^{3-}][A^{2-}]^{-1})^{-1}$ and f_{MAL} by $K_{MAL} \cdot [L^{3-}][A^{2-}]^{-1} (1 + K_{MAL} \cdot [L^{3-}][A^{2-}]^{-1})^{-1}$ in eqn. 4, and simplifying, we obtain

$$U = \frac{u_1 + u_2 \cdot K_{MAL} \cdot [L^{3-}][A^{2-}]^{-1}}{1 + K_{MAL} \cdot [L^{3-}][A^{2-}]^{-1}} \quad (5)$$

From this equation, taking the average mobility at a point corresponding to $K_{MAL} \cdot [L^{3-}][A^{2-}]^{-1} = 1$, the values of $\log K_{MAL}$ were calculated to be 2.2 for $[CuAL]^{3-}$ and 2.4 for $[NiAL]^{3-}$. Since the values of $\log \beta_{MA_2}$ are 7.6 and 6.5 for copper(II)- and nickel(II)-oxalate complexes, respectively⁷, $\log \beta_{MAL}$ is therefore 9.8 for the mixed complex of copper(II) and 8.9 for that of nickel(II) (from eqn. 3).

Jackobs and Margerum⁹ investigated the system $[NiL]^- + A^{2-} \rightleftharpoons [NiAL]^{3-}$ and obtained a value of $K_{NiAL} = 10^{2.11}$ for this equilibrium. Now $\beta_{NiAL} = K_{NiAL} \cdot K_{NiL}$ and the values of $\log K_{NiL}$ reported in the literature for the NTA complex of nickel(II) vary from 10.5 to 11.5 (refs. 2 and 10-12). Thus $\log \beta_{NiAL} \approx 13$, which is greater than the value of 8.9 reported here. However, Jackobs and Margerum⁹ admit that they could not use the tangent method directly in the region where the mixed-ligand complex is formed, and since they had to use an extrapolation method their values may not be reliable.

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