PAPER ELECTROPHORESIS IN THE STUDY OF MIXED LIGAND COMPLEXES IN SOLUTION

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ABSTRACT

A method, involving the use of paper electrophoresis is described for the study of equilibria in mixed ligand 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). The concentration of one of the complexants NTA is kept constant, while that of second ligand (valine) is varied. A graph of log [valine] against mobility is used to obtain information on the formation of mixed ligand complex and to calculate the stability constants.

INTRODUCTION

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

Recently, a new method was reported to study the stepwise formation of complexes[3-6]. Although paper electrophoresis has been used to study metal complex systems with a single ligand, there is no systematic study of the formation of mixed ligand complexes using this technique. However Czakis-Sulikawska[7] studied the formation of the mixed halide complexes of mercury (II) using paper electrophoresis, but these were only qualitative in nature and did not throw any light either on the nature of the species or on their stabilities. This paper is an extension of paper electrophoresis technique and reports some results obtained with the mixed ligand system *viz.* $Cu(II)/UO_2$ (II)/Co (II)/Zn (II), nitrilotriacetate-valinate.

EXPERIMENTAL

Apparatus

Horizontal cum vertical type No.604 PE equipment (Systronics India) was used together with various accessories supplied with the instrument. In each case, electrophoresis was carried out for 60 min at 200 volt at 35°C. Whatman No.1 paper strips (30 × 1) cm were used. pH measurements were made with an Elico, model L_{1-10}, pH meter using glass electrodes.

Reagents

Metal perchlorates were prepared by appropriate methods and the final concentrations were kept at 5

$\times 10^{-3}$ M. A solution of 1-(2-pyridylazo)-2-naphthol (PAN) in ethanol (0.1 %) was used for detecting the metal ions. A saturated solution of silver nitrate in acetone was sprayed on the paper and subsequently fumed with ammonia to detect glucose in the spot. The background electrolyte consisted of a mixture containing 0.1 M perchloric acid, 10^{-3} M NTA and varying amounts of 0.01 M valine. It was maintained at pH 8.5 by the addition of sodium hydroxide solution.

Procedure

The mid point of each paper strip was marked and moistened with the background electrolyte. A spot of the metal solution was applied with 1 ml micro pipette on each strip with an additional one spotted with glucose. The strips were sandwiched between two insulated hollow plates. Water at 35°C was circulated into the plates. The plates were then mounted in electrophoresis equipment with the end of paper strips dipping in two tanks of the instrument. Each of the two electrode vessels was filled with 150 ml of the background electrolyte. The air-tight lid was closed and placed on 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 various metal ions and glucose were developed with reagents. The distance of the movement of spots was measured from the previously marked point. The movement of glucose was used as correction factor. The distance travelled towards the anode was taken as the negative whereas that towards cathode was positive. The mobilities were calculated by dividing movement by potential gradient (7.5 v/cm).

RESULTS AND DISCUSSION

The plot of mobility against log of concentration of

added valine, given in figure 1 shows a constant value for overall mobility in the beginning and then a transition terminating in another constant value for mobility. The mobility continuously decreases during the transition stage. The first constant values of mobilities -3.74×10^{-3}, -2.20×10^{-3}, -1.54×10^{-3} and -3.30×10^{-3} cm^2 volt^{-1} for Cu(II), UO$_2$ (II), Co(II) and Zn (II) respectively correspond to the mobilities of metal–NTA complexes (also observed[8] in the study of pure M–NTA complexes), whereas the second constant values of mobility viz. -8.8×10^{-3}, 7.26×10^{-3}, -6.60×10^{-3} and 8.14×10^{-3} cm^2.min^{-1} volt^{-1} for Cu(II), UO$_2$ (II), Co (II) and zn (II) respectively would correspond to mobility of the new complexes. This new complex cannot be 1:1 or 1:2 metal-valinate complexes, since mobilities of 1:1 complex of metal-valinate were 5.94×10^{-3}, 5.06×10^{-3}, 6.6×10^{-3} and 8.8×10^{-3} cm^2.min^{-1}.volt^{-1} in the case of Cu (II), UO$_2$ (II), Co (II) and Zn (II) respectively[8]. The mobility in the case of 1:2 metal-valinate complex was zero, which was observed in pure M-valinate complexes. Moreover as the mobility of the new complex is less than the mobility of pure M – NTA complex, it is inferred that some anionic species of valine (L) have added to M –NTA complex to form mixed complex. The pH of the system being 8.5, it is assumed that unprotonated anion of amino acid acted as second ligand species, and the interaction may be represented as:

$$M - NTA + L \xrightleftharpoons{K_{Mix}} M - NTA - L$$

where L is valine anion.

In the present electrophoretic study, a simple complex is transformed into mixed complex and hence the
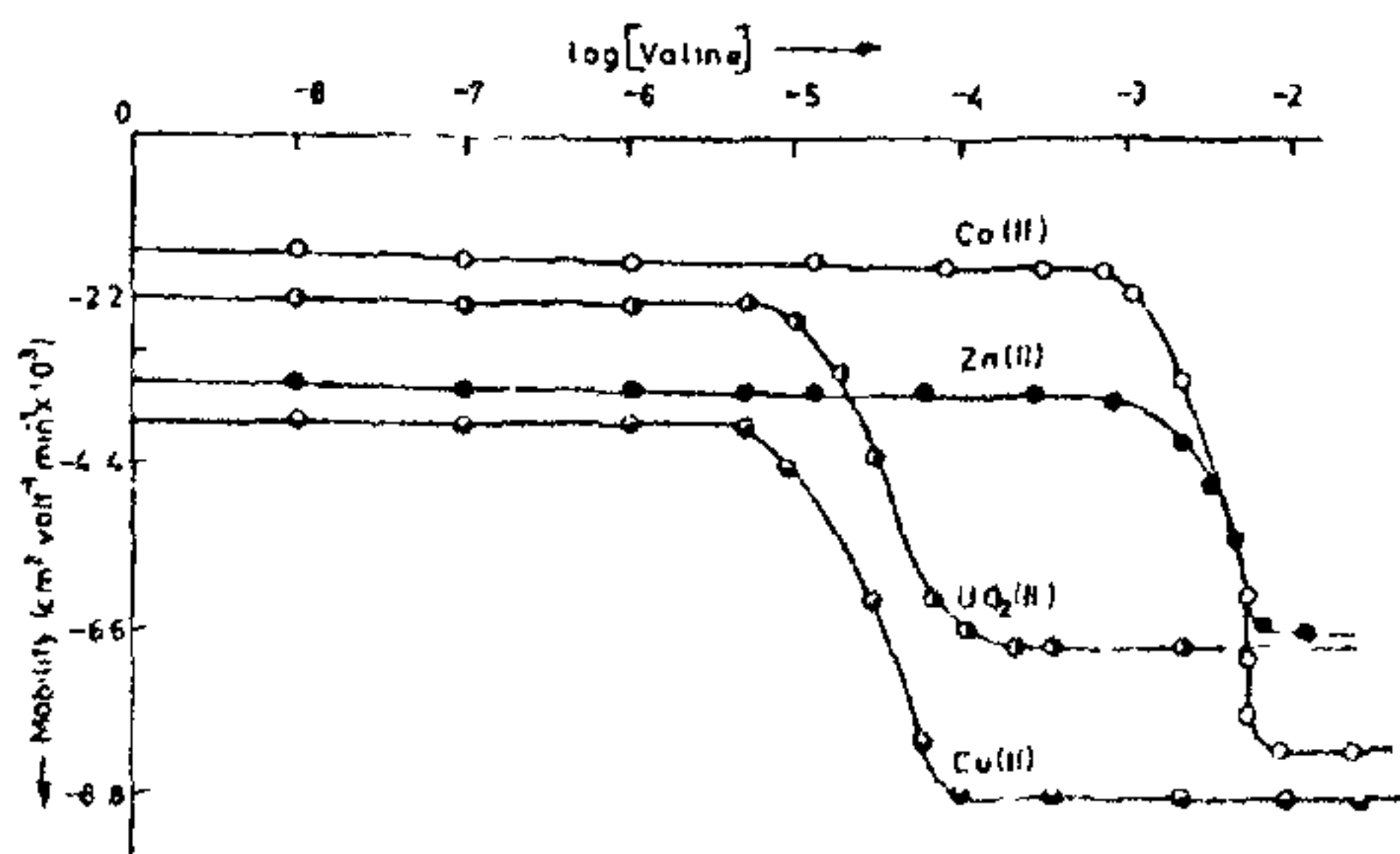

Figure 1. Mobility curves (M – NTA valine) system (Temperature: 35°C; Ionic strength 0.1)

Table 1 Stability constants for different metal – NTA – valine complexes at $\mu = 0.1$ and Temp. 35°C.

Metal ion	Calculated Value		Literature Value	
	$\log K_{Mix}$	$\log \beta_{Mix}$	$\log K_{Mix}$	Ref. No.
Cu (II)	5.25	18.01	5.10	9
UO$_2$ (II)	5.18	15.03	–	
Co (II)	3.25	13.63	–	–
Zn (II)	3.17	13.76	3.26	10

overall mobility is given by:

$$U = U_0 f_{M-NTA} + u_1 f_{M-NTA-L},$$

where u_0, u_1 and f_{M-NTA} $f_{M-NTA-L}$ are the mobilities and the mole fraction of M – NTA and M – NTA – L complex species respectively. Substituting the values of molefraction, the overall mobility can be given by the equation:

$$U = \frac{u_0 + u_1 K_{Mix}[L]}{1 + K_{Mix}[L]}$$

where u_0 and u_1 are mobilities of M – NTA complex and mixed complex (M – NTA – L) respectively. These mobilities are the mobilities on the two plateau regions of the curve. Using the principle of average mobility, K_{Mix} can be determined to be equal to $1/[L]$. Now for formation of M – NTA complex, the equilibrium

$$M + NTA \xrightleftharpoons{K} M\text{-}NTA$$

holds good. From these two equilibria,

$$[M - NTA - L] = K_{Mix}[M - NTA][L]$$
$$= K_{Mix}.K[M][NTA][L].$$

Obviously $K_{Mix}.K = \beta_{Mix}$ i.e. the overall stability constant of mixed complex. Since the values of log K are 12.76, 9.85, 10.38, 10.59 for Cu (II)/UO$_2$ (II)/Co (II)/Zn (II) – NTA complexes respectively, the values of β_{Mix} can be assessed if K and K_{Mix} are known. All these values are given in table 1.

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

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NEWS

A CONTEMPORARY TOUCH TO EPIDEMIOLOGY

... After studying an outbreak of *Salmonella muenchen* in Steubenville, Ohio, David N. Taylor and Emmett Schmidt (Ctrs. for Disease Control) announced their results in a press conference. " 'All the media were there—the local newspaper, the local radio, the local television, and the stringers for the wire services. I read our statement. I told them that the source of the outbreak wasn't water, it wasn't any eating place, it wasn't any food. I told them—and this is from our prepared statement—"Our most important lead suggests that a noncommercial product with an unknown distribution is the source of this salmonella. We have tested samples of marijuana associated with three different cases, and we have found the identical salmonella which has been isolated from the ill persons. This findings suggests that the marijuana currently in use in Jefferson County has become contaminated with salmonella and represents the primary vehicle of transmission for the illness" . . . . It was really very exciting. A big story. And not only locally. Both the wire services carried it. It wasn't so much that we had solved the mystery. It was the marijuana. That gave it a contemporary touch.' "

[Berton Rouechè in *New Yorker* 13 Aug 84, p. 76–85. Reproduced with permission from Press Digest, *Current Contents* ®, No 2, January 14, 1985, p. 15 (Published by the Institute for Scientific Information ®, Philadelphia, PA, USA.)]

WHY THE "BEST" TECHNOLOGY DOESN'T ALWAYS WIN

... "The technology that 'wins' a market does not necessarily have to be the 'best' or most efficient. In the case of the automobile, the steam (Rankine) cycle is thermodynamically more efficient than the gasoline (Otto) cycle. Given as much development as the gasoline engine has undergone over the last 90 years. It is quite possible that a steam engine could have been more economical. . . . It is [also] quite possible that gasoline was indeed innately superior. The matter has never been settled. But it is equally possible that a series of small events at the turn of the century gave gasoline a temporary lead that subsequently proved unassailable. . . . Steam continued viable as an automotive power source until in 1914 there was an outbreak of hoof-and-mouth disease in North America. This led to the withdrawal of horse troughs—which is where steam cars could fill with water. It took the Stanley brothers about three years to develop a condenser and boiler system that did not need to be filled every thirty or forty miles. But by then it was too late."

[W. Brian Arthur (Stanford U.) in *Options* (2): 10–13, 1984 (Internatl. Inst. for Applied Systems Analysis) Reproduced with permission from Press Digest, *Current Contents*® No. 2, January 14, 1985, p. 16 (Published by the Institute for Scientific Information®, Philadelphia, PA, USA.)]