Electrophoretic Method for the Study of Mixed Complexes Metal - Nitrilotriacetate - Iso-leucinate Systems

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Binary equilibria of metal(II) - iso-leucinate, Metal(II) NTA and also mixed complex formation have been studied using paper electrophoresis. The log K values of Metal - NTA - iso-leucinate complexes have been found to be 5.65, 5.53, 5.43, 3.83 and 3.53 for Cu (II), UO_2(II), Be(II), Co (II) and Mn (II) complexes respectively at μ 0.1 and 35°C.

Paper electrophoresis has been used to determine the stability constants of the complex species [1,2], for the study of the stepwise complex formation [3] and of mixed complexes [4]. The present work is an extension of the technique and reports our observation on the mixed system.

EXPERIMENTAL

Apparatus

Electrophoresis equipment (systronics model, 604 INDIA) used is the same as described earlier [4]. The electric current running through paper strips generates heat which causes evaporation of background electrolyte leading to serious error. In order to eliminate it, two hollow metallic plates coated outwardly with thin plastics have been used for sandwiching paper strips and thermostated water (35°C) is circulated through them. pH measurements were made with Elico model L1-10 pH meter using glass electrode.

Chemicals

Cu(II), UO_2(II), Be(II), Co(II) & Mn(II) perchlorates were prepared by precipitating the corresponding carbonates from solutions of nitrates, washing the precipitates thoroughly with boiling water and treating with a suitable amount of 1% perchloric acid. The resulting mixture was heated to boiling on a waterbath and then filtered. The metal contents of the filtrates were determined as usual and final concentration was kept at 5.0 mM.

1-(2-Pyridylazo)-2- naphthol (PAN), 0.1%(W/V) in ethanol was used for detecting the Cu(II), UO_2 (II), Co(II) & Mn(II) ions and aluminon-ammonium acetate mixture in water was used for detecting the Be(II) ion. Glucose spot was detected as usual by Silver nitrate and 2% ethanolic sodium-hydroxide.

Stock solution of 9.0 M perchloric acid 2.0 M sodium hydroxide and 0.5 M iso-leucine were prepared from AnalaR samples. 0.01 M nitrilotriaocetic acid was prepared from a E Merk sample. Each solution was standardized as usual. The background electrolytes were prepared from these stock solutions.

General Procedure

For Binary Complexes

The background electrolyte was 0.1 M $HClO_4$ with either 1.0×10^{-2} M iso-leucine or 1.0×10^{-3} M M NTA. The electrolyte was filled into tanks, thermostat water was circulated, the paper strips were spotted and mobility measured in the background electrolyte as described earlier. The electrophoretic migration of metal spot on paper was observed at different pH of background electrolyte. Dividing movement by potential gradient yields mobility. These are plotted as a function of pH.

For Ternary Complexes

The background electrolyte consists of 0.1 M perchlorate 0.1×10^{-3} M NTA with 1×10^{-2} M iso-leucine. The pH was maintained at pH 8.5 - by addition of NaOH. The mobility of metal spots was determined as described earlier [4].

For subsequent observation, the iso-leucinate solution, maintained at pH 8.5, was added progressively and ionophoretic mobility was recorded again. A plot of mobility against log iso-leucine was made.

RESULT AND DISCUSSION

Metal - iso-leucinate - Binary System

The plot of overall electrophoretic mobility of metal spot against pH gives a curve with a number of plateaus shown in figure 1. A plateau is obviously an indication of a pH range where speed

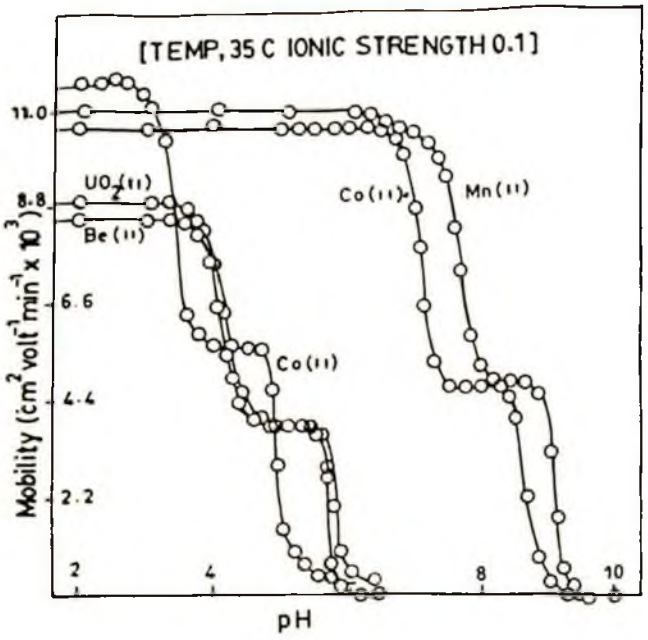


Fig. 1 Mobility Curve [II]-Iso-leucine System

is practically contant. This is possible only where one particular complex is overwhelmingly formed. Thus every plateau indicates the pH range where one particular complex species, is present. The first one at low pH value corresponds to region in which metal ion is uncomplexed. Here isoleucine is in its protonated form and its complexing ability in quite small. At higher pH value the mobility of the metal ion spot progressively decreases; and hence complexation of metal ion should be taking place with other ionic species of iso-leucine whose concentration increases progressively with increase of pH. The second plateau, in each case with positive mobility, indicates the formation of 1:1 complex of cationic nature. Further increase in pH gives rise to the third plateau with zero mobility in each case which again indicates formation of electrically neutral 1:2 metal complex. This is possible only when two anionic species of isoleucine combine with one bivalent metal ion. The anionic species of iso-leucine acid is known to have better liganding power than the zwitter ion [5,6]. Further increase of pH has no effect on the mobility of metal ions.

The mobility is expressed as

$$U = \frac{U_0 + U_1 K_1 [L^-] + U_2 K_1 K_2 [L^-]^2}{1 + K_1 [L^-] + K_1 K_2 [L^-]^2}$$

Where U_0 , U_1 and U_2 are mobilities of uncomplexed metal ion, 1:1 metal-complex and 1:2 complex respectively.

This equation has been used for calculating stability constants of the complexes of metal ions with iso-leucinate anion. For calculating first stability constant K_1, the region between first and second plateau is pertinent. The overall mobility 'U' will be equal to the arithmetic mean of mobility of uncomplexed metal ion, U_0 and that of first complex U_1 at a pH where $K_1 = 1/[L^-]$. With the help of dissociation constants of iso-leucine (log K_1 = 2.65 and log K_2 = 9.62) the concentration of iso-leucinate anion $[L^-]$ is determined for the pH, from which K_1 can be calculated. The stability constant K_2 of second complex can be calculated by taking into consideration the region between second and third plateau of mobility curve. The calculated values are given in Table 1.

Metal-NTA-Binary Systems

The observation on overall mobility of metal spots in presence of NTA at different pH values are represented in Figure 2. It is evident from

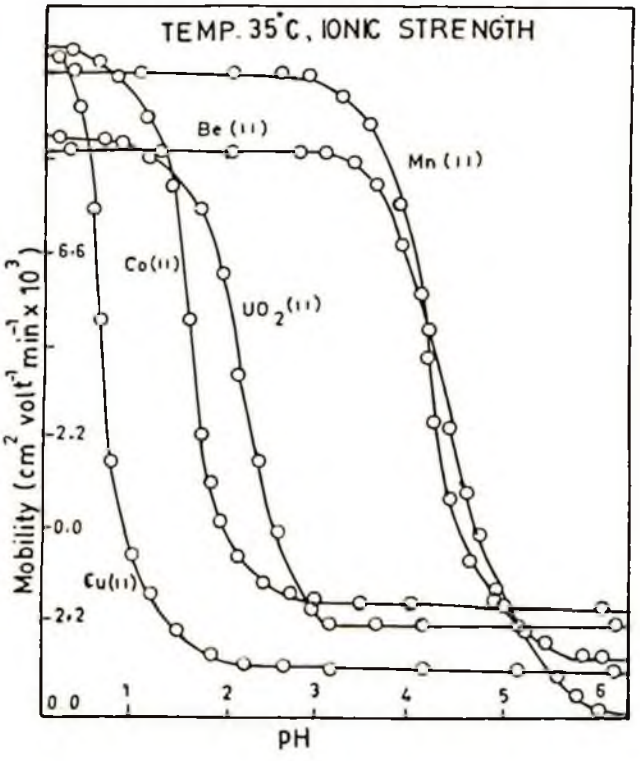


Fig. 2 Mobility Curve [M-(II) NTA] System

figure that with all five metal ions, two plateau are obtained. The mobility of last plateau lies in negative region showing negatively charged nature of complex. Hence only one NTA anion is assumed to combine with one bivalent metal ion to give 1:1 M-NTA complex which is in conformity with earlier finding [8 -10]. The stability constants of complex with NTA are calculated in a manner described in preceding paragraph. The calculated values are given in Table 1.

TABLE 1

STABILITY CONSTANTS OF SOME BINARY AND TERNARY COMPLEXES OF Cu(II), UO_2(II), Be (II) Co(II) & Mn(II)

Ionic strength = 0.1 : Temperature = 35°C

NTA anion A : Iso-leucinate anion L

Metal ion		log K of			
		ML	ML_2	MA	MAL
Cu(II)	a	8.34	6.92	12.74	5.65
	b	8.40[11]	7.00[11]	12.94[11]	--
		8.50[11]	6.90[11]	13.60[13]	--
		8.40[12]	7.00[12]	12.75[13]	--
UO_2(II)	a	7.83	5.87	9.77	5.53
	b	--	--	9.50[11]	--
				7.88[13]	--
				9.50[13]	--
Be(II)	a	7.83	5.92	7.25	5.43
	b			7.11[11]	
Co(II)	a	4.62	3.02	10.32	3.83
	b	--	--	10.38[11,13]	
Mn(II)	a	3.92	2.52	7.55	3.53
	b	--	--	--	--

a. Present Study ; b. Literature Value.

Metal - NTA - iso-leucine - Ternary Systems

It is observed from the mobility curve of M(II)-iso-leucine and M-nitrilotriacetic acid binary systems, that binary complexes, M-iso-leucinate and M-nitrilotriacetate are formed at a pH lower than 8.5. Thus it would be proper to study the tranformtion of M-NTA complex into M-NTA-iso-leucinate complex at pH 8.5 in order to avoid any side interaction.

The plot of mobility against logrithm of concentration of added iso-leucine gives curves (Figure 3) containing two plateaus. The mobility in the range of first plateau corresponds to mobilities of 1:1 M-NTA complexes. The mobility in this range is also in agreement with mobility of 1:1 M-NTA complex as evident in the study of binary M-NTA system. The mobility of last plateau is negative; so it indicates the formation of a negatively charged complex. The mobility in this last plateau does not tally with the mobility of 1:1 and 1:2 metal iso-leucinate complex (observed in our study of binary sustem). It is inferred that the moiety in last plateau is due to co-ordination of iso-leucinate anion to 1:1 M-NTA moiety resulting in the formation 1:1:1 mixed complex (M-NTA-iso-leucinate) as.

$$M\text{-}NTA^{-} + L^{-} \underset{\leftarrow}{\overset{K'}{\rightleftharpoons}} [M\text{-}NTA\text{-}\ L]^{2-}$$

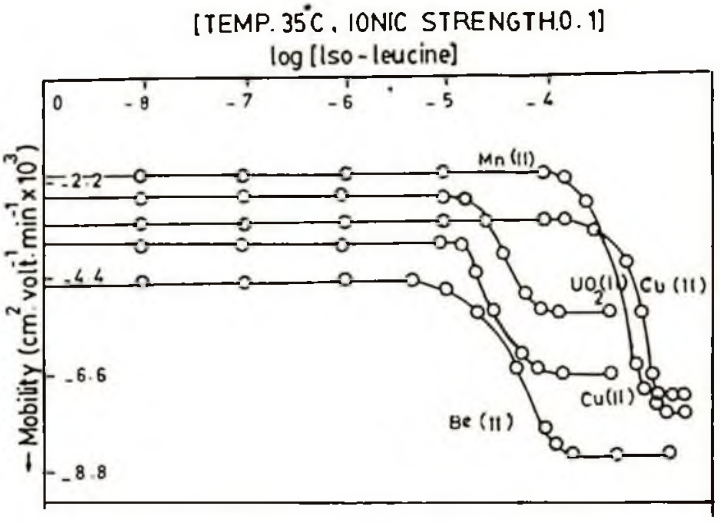


Fig. 3 Mobility Curve [M-NTA-Iso-leucine] System

In the present electropheretic study, the transformation of a simple complex into mixed complex takes place, hence the overall mobility is given by

$$U = U_0 \cdot f_{M\text{-}NTA} + U_1 f_{M\text{-}NTA\text{-}L}$$

Where u's and f's are the mobilities and the mole fractions of the complexes respectively. Substituting the values of mole fractions, the overall mobility is given by equation.

$$U = \frac{U_0 + U_1 K' [L^-]}{1 + K' [L^-]}$$

U_0 and U_1 are the mobilities in the regions of the two plateaus of the Curve. From the figure, concentration of iso-leucinate at which overall mobility is mean of the mobilities of two plateaus is determined. The concentration of anionic species of iso-leucine at pH 8.5 for this iso-leucine concentration is calculated K' is obviously equal to 1 , $[L^-]$. All these calculated values of K' are given in Table 1.

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