ISSN : 0974 - 746X Volume 7 Issue 3

Trade Science Inc.

Inorganic CHEMISTRY

An Indian Journal

Full Paper

ICAIJ, 7(3), 2012 [99-103]

Solution electrophoresis technique in the study of biologically important Fe(III)/ Ni(II) - Norvaline binary complex

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Received: 17th March, 2012 ; Accepted: 17th April, 2012

ABSTRACT

A new method solution electrophoresis, involving the use of a ionophoretic technique is described for the study of Fe(III) and Ni(II) biologically important binary complexes with norvaline in solution. The stability constants of ML and ML_2 complexes of Fe(III) – norvaline and Ni(II) – norvaline system have been found to be (9.15 ± 0.05, 7.65 ± 0.04) and (5.48 ± 0.02, 4.55 ± 0.03) (logarithm stability constant values), respectively at 25 ^{0}C and ionic strength (μ) = 0.1 M ($HClO_4$).

KEYWORDS

Binary complex;
Overall mobility;
Stability constants;
Solution electrophoresis technique.

INTRODUCTION

The stabilities of binary complexes are known to play an important role in a number of metabolic and toxicological functions. Norvaline is an amino acid ($C_5H_{11}NO_2$) isomeric with valine, and is commonly made synthetically. It has several significances in biological systems[1–16]. The importance of metal ions to vital functions in living systems and for the well being of living organisms is now well established. Fe(III) and Ni(II) are well known for their biomedical applications and toxicity[17-21]. The present modified method is almost free from a number of defects[22] of common ionophoretic technique such as diffusion, ionic strength and temperature during ionophoresis obviously vitiate the ionophoretic mobility of a particular ion. The technique is very convenient in use.

Recent publications[23-25] described a new method for the study of binary complexes by using paper ionophoretic technique. The present work is an extension of the technique, and reports an observation on the determination of the stability constant values of binary complexes of iron(III)/ nickel(II) – norvaline. A simple ionophoretic tube has been designed which after standardization yields remarkable results. Ionophoresis

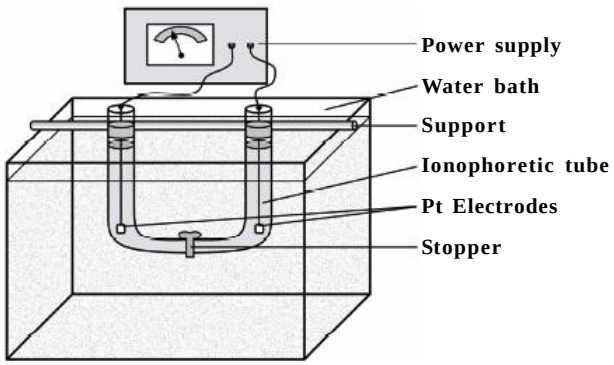


Figure 1: Electrophoresis setup

set- up is shown in Figure 1.

EXPERIMENTAL

Instruments

Ionophoresis equipment from Systronic (Naroda, India) model 604 was used. It has a built in power supply (a.c.- d.c.) that is fed directly to an ionophoretic tube (18 cm long and 0.5 cm bore) with a stopper in the middle and fused perpendicularly at the ends with short wider tubes of 1.2 cm bore. This tube is kept in a thermostatic water bath at 25 ^{0}C. pH measurements were made with century CP 901 digital pH meter using a glass electrode. Absorbance was measured with SPECTROCHEM MK II (PEI) spectrocolorimeter. A SICO made constant temperature water bath has been used to ensure uniform temperature.

Chemicals

Fe(III) and Ni(II) perchlorate solutions were prepared by precipitating the corresponding carbonates from solution of chlorides (AnalaR grade) with the solution of sodium carbonate, washing the precipitates thoroughly with boiling water and dissolving in a suitable amount of perchloric acid. The resulting solutions were heated to boiling on a water bath and then filtered. The solutions were standardized and diluted with distilled water as required. AnalaR grade ascorbic acid, NaOH, $HClO_4$ and developing reagent (for Fe(III) 20 % solution of ammonium thiocyanate, for Ni(II) bromine water, concentrated ammonia solution, 1% solution of dimethylglyoxime reagent) for specific colour development were used for different metal ions of binary system sets.

Electrolytic Solutions

For binary systems 15 ml of a solution each containing 1×10^{-3} M Ni(II), 0.1 M $HClO_4$, and 1×10^{-2} M norvaline was prepared at different pH values (by adding a NaOH solution). In the case of Fe(III), 1×10^{-4} M Fe(III), 0.1 M $HClO_4$, and 1×10^{-3} M norvaline were used.

Procedure

10 mL of electrolytic solution as mentioned for binary system is taken in an ionophoretic tube and then thermostated at 25 °C. The position of the tube was adjusted in such a way that the level of the solution in one wide end arm reached a circular mark on it. This adjustment fixed the volume of the solution on both sides of the middle stopper. Two platinum electrodes were dipped in each arm cup and a 50 V potential difference was applied between them. Ionophoresis of the solution was allowed for 45 minutes, after which the middle stopper of the tube is closed. The solution of the anodic compartment was taken out in a 15 mL flask. The Ni(II) content was converted to nickel dimethylglyoximate[26] and absorbance was taken at 445nm. Similarly the Fe(III) content of the anodic compartment was converted to iron thiocyanate[26] complex and absorbance was measured at 480 nm against a reagent blank. The observations were repeated for different pH values of different background electrolyte (variation in pH is made by the addition of caustic soda solution). The plot of the absorbance difference vs. pH is shown in Figure 2.

As for the possibility of hydroxy compound formation, we had considered this aspect in our earlier studies. For this we performed the study of binary complex formation at two different concentration of ligand giving complexing species at two different pH values. In that study we find two different plateaus but almost same stability constant. If it would have been a hydroxyl complex only one plateau at fixed pH value must have been formed irrespective of different concentration of ligand (norvaline here) used. This clearly indicates that at very low concentration of metal (i.e. Fe(III) = 10^{-4} M) no hydroxy compound are formed. Hence the possibility of hydroxy compound formation at very low concentrations of metal ions is ignored in these studies.

RESULTS AND DISCUSSION

Chemical literature[27-30] confirms that anionic species of amino acids are the sole ligating species for metal ions. The electrophoretic mobility of the metal spot against pH gives a curve with number of plateus is shown in Figure 2. A constant speed over a range of pH is possible only when a particular complex species is overwhelmingly formed. Thus, every plateau is indicative of formation of a certain complex species. The first one in the beginning corresponds to a region in which metal ions are uncomplexed. In this region of low pH, concentration of unprotonated species of norvaline [CH_3

CH_2 CH_2 CH (NH_3^+) COOH] is maximum and this species is non-complexing, beyond this range, metal ions have progressively decreasing mobility, complexation of metal ions should be taking place with anionic species of norvaline, whose concentration increases progressively with increase of pH. Figure 2 shows three plateaus in both Fe(III) and Ni(II), hence both metal ions form two complexes with norvaline anion. Prominent chelating properties have also been assigned to unprotonated anionic species of norvaline, ruling out any such property to the zwitterions[31-33]. Figure 2 discloses that Fe(III) and Ni(II) metal ions form their first complex movement towards negative electrode.

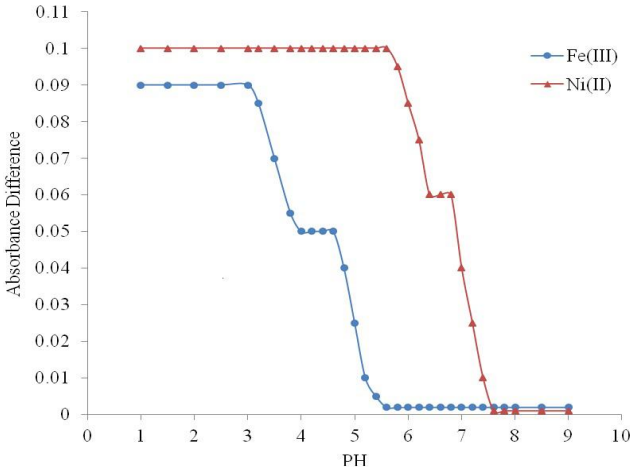


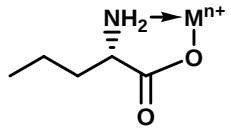
Figure 2 : Mobility curves for the metal -norvaline complexes.

Hence one anionic species of norvaline [CH_3 CH_2 CH_2 CH (NH_2) COO^-], must have combined with Fe(III) and Ni(II) metal ions to give 1:1 [Fe {$CH_3CH_2CH_2CH$ (NH_2) COO}]$^{++}$ and [Ni {CH_3 CH_2 CH_2 CH (NH_2) COO}]$^+$, complex cations, respectively. The third plateau in each case is due to 1:2 metal – ligand complex. Hence, two anionic species of norvaline [CH_3 CH_2 CH_2 CH (NH_2) COO^-], must have combined with Fe(III) and Ni(II) to give 1:2 [Fe {CH_3 CH_2 CH_2 CH (NH_2) COO}$_2$]$^+$, and [Ni {CH_3 CH_2 CH_2 CH (NH_2) COO}$_2$], metal complexes, respectively. Proposed molecular structures[35] of binary complexes are given below.

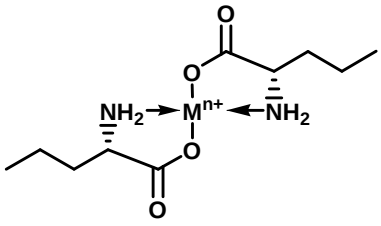
Where M^{n+} = Fe^{3+}, Ni^{2+} and Nva = Norvaline in scheme 1.

Further increase of pH has no effect on the mobility of metal ions, which indicates no further interaction between metal ions and ligands. The complexation of metal ions with norvaline anion may be represented as:

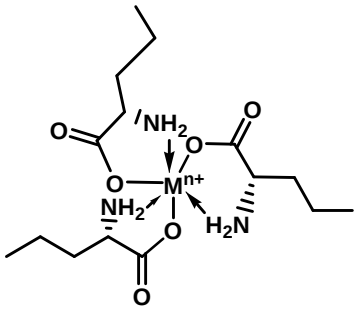
$$M^{2+} + L^- \underset{}{\overset{K_1}{\rightleftharpoons}} ML^+ \qquad (1)$$



M^{n+} Nva



M^{n+} Nva_2



M^{n+} Nva_3

Scheme 1: Molecular structures of binary complexes.

$$ML^+ + L^- \underset{}{\overset{K_2}{\rightleftharpoons}} ML_2 \qquad (2)$$

here M^{2+} = metal cations; [L^-] = norvaline anion; K_1 and K_2 are the first and second stability constants respectively.

The overall mobility U is a composite parameter contributed by different ionic species of the metal ion and is given by following equation (3).

$$U = \frac{u_0 + u_1K_1[L^-] + u_2K_1K_2[L^-]^2 + ...}{1 + K_1[L^-] + K_1K_2[L^-]^2 + ...} \qquad (3)$$

here u_0, u_1, u_2 mobilities of the uncomplexed metal ions, 1:1 and 1:2 metal complexes, respectively. The protonation constants of pure norvaline (pKa_1 = 2.31, pKa_2 = 9.65)[34] were determined by same solution ionophoretic technique. The mode of deprotonation of pure norvaline can be represented in scheme 2.

Using protonation constants of pure norvaline the concentration of norvaline anion [L^-] is determined for the pH value(s) of interest, from which K_1, can be calculated. The concentration of complexing norvaline anion [L^-] is calculated with the help of equation.

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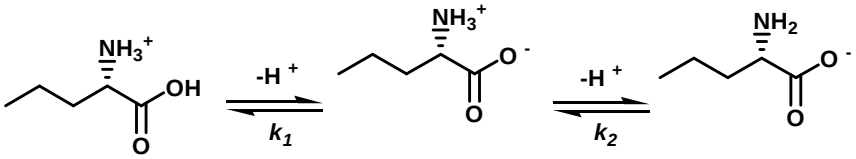
$$[L^-] = \frac{[L_T]}{1 + [H]/k_2 + [H]^2/k_1.k_2} \quad (4)$$

here $[L_T]$ = total concentration of ligand norvaline [0.001 Mol L^{-1}], k_1 and k_2 = first and second protonation constant of pure norvaline, respectively.



Scheme 2 : Deprotonation of pure norvaline

For calculating first stability constant, K_1, the region between first and second plateau is pertinent. The overall mobility will be equal to the arithmetic mean of the mobility of uncomplex, u_0, and that of first complex, u_1, at a pH value where $K_1 = 1 / [CH_3\ CH_2\ CH_2\ CH(NH_2)\ COO^-]$. The second stability constant K_2, of 1:2 complex can be calculated by taking into consideration, the region between second and third plateau of mobility curve. The calculated value of K_1 and K_2 are given in TABLE 1.

TABLE 1: Stability constants of binary complexes of Fe(III) and Ni(II) with norvaline.

Metal Ions	Complexes	Stability Constants	Logarithm stability constant values
Fe^{+++}	ML^+	K_1	9.15 ± 0.05
	ML_2	K_2	7.65 ± 0.04
Ni^{++}	ML^+	K_1	5.48 ± 0.02 5.42[34]
	ML_2	K_2	4.55 ± 0.03 4.45[34]

CONCLUSION

It can be concluded that Fe(III) and Ni(II) are significant for biological systems but as such they are toxic, the norvaline may be used to reduce the level of these metal ions in the biological systems. The present solution electrophoretic technique is very helpful in finding whether complex system is formed or not, if formed its stability constants can also be determined. ML_2 complexes are found to have low stability constant value and less stable in comparison to ML complexes. Stability constants of metal complexes can be very easily calculated through this technique, so the present solution electrophoretic technique has significant advantages over the other physiochemical methods reported in chemical literature for the determination of stability constants of metal complexes.

ACKNOWLEDGEMENTS

Authors are thankful to Head, Department of Chemistry, University of Allahabad, for providing research facilities and U.G.C, New Delhi for financial assistance.

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