



**Potentiometric, Spectroscopic and Voltammetric
Studies on the Complex Formation of Iron(III),
Copper(II) and Nickel(II) with Substituted
Hydroxamic Acid Type Ligands**

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Abstract

In order to establish the biological importance of hydroxamic acids derivatives the acid dissociation constants (ionization constants) were determined by potentiometric and spectroscopic methods. The possible correlation of the experimental values with theoretical values was examined using Gaussian 98 suit. In potentiometric method the data were analyzed by three analytical procedures such as Bjerrum method, Irving and Rossotti method and Sarkar and Kruck method. It has been found that the pK_a values obtained by these three methods are in good agreement with each other. The modified limiting absorption method was used to calculate the ionization constants in spectroscopic method. In the case of N-substituted hydroxamic acids, the relative order of pK_a values in 1:1 ethanol is as follows:

N-(o-methoxy)phenylbenzohydroxamic acid > N-(o-methyl)phenylbenzohydroxamic acid > N-phenylbenzohydroxamic acid > N-(o-bromo)phenylbenzohydroxamic acid > N-(o-chloro)phenylbenzohydroxamic acid.

The distribution of iron(III), copper(II) and nickel(II) complex species formed at different pH values was investigated and the stability constants of the formed complex species have also been determined. The stability constant values obtained for the deprotonated complexes MA, MA₂ and MA₃ of Fe(III) system by the three procedures are found to be in good agreement with each other. Similarly, the deprotonated complexes MA and MA₂ of Cu(II) and Ni(II) system of all hydroxamic acids studied are closely agreed in all three procedures.

The results obtained for Fe(III)- N-substituted hydroxamic acid systems indicated that the deprotonated MA₃ complex is the major complex species in equilibrium in the physiological pH range, 6.8-7.3. The relative order of the stability constant values obtained is the same as that of the pK_a values of the hydroxamic acids. In the case of Ni(II) and Cu(II), N-substituted hydroxamic acid systems, the deprotonated MA₂ complex predominates at the physiological pH range.

The species distribution studies of 1-naphthalenemethyliminodiacetohydroxamic acid with Fe(III), Ni(II) and Cu(II) indicated that the deprotonated MA₂ complex predominates at the physiological pH range and relative order of the stability constant values obtained is as follows:

Fe(III)-1-naphthalenemethyliminodiacetohydroxamic acid complexes > Cu(II)-1-naphthalenemethyliminodiacetohydroxamic acid complexes > Ni(II)-1-naphthalenemethyliminodiacetohydroxamic acid complexes.

The absorption spectra of Fe(III) complexes of N-phenylbenzohydroxamic acid derivatives at different pH values indicate two isosbestic points which suggests the formation of three types of complexes, but the Fe(III)-1-naphthalenemethyliminodiacetohydroxamic acid has only one isosbestic point.

The absorption spectra of Cu(II) complexes of N-phenylbenzohydroxamic acid and the aminohydroxamic acid system at different pH values show a specific broad band in the wavelength range 630 - 695 nm. In general, the maximum of the broad spectrum occurs near the infrared region and it shifts towards the visible region with the increase of pH. The absorption spectra of Ni(II) complexes of N-phenylbenzohydroxamic acid and the aminohydroxamic acid system at different pH consist of two absorption bands.

The selective ionophoric properties of the hydroxamic acids derivatives towards Fe(III) was studied and compared with the complexes formed with Mn(II) ions. The 1-naphthalenemethyliminodiacetohydroxamic acid exhibited a prominent selectivity towards Fe(III) with two step 1:1 and 1:2 quenching mechanism whereas those of Mn(II) exhibited 1:1 quenching mechanism.

The possible application of these N-substituted hydroxamic acid as a modifier to carbon paste electrode for *in situ* determination of Cu(II) and Co(II) in an analyte solution was studied. N-(o-chloro)phenylbenzohydroxamic acid (CPBHA) modified carbon paste electrode was found to accumulate copper(II) and cobalt(II) preferentially from solutions of analyte and generates a good remarkable operational stability for adsorptive cathodic stripping voltammetric analysis.