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Synthesis of Erichrome Black T-Zn^{2+} complex by electrochemical method, Characterization and Kinetic study of the formation of complex

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Abstract

Synthesis of (Erichrome Black T) EBT – Zn^{2+} complex by electrochemical method has been carried out. The reaction was carried out in the presence of platinum electrode as cathode and zinc electrode as anode. The rate constant for the disappearance of EBT to form EBT-Zn^{2+} complex was calculated by first order plot. The effect of current and concentration of EBT indicates increase of current increases the rate of formation and EBT concentration decreases the rate of formation of EBT-Zn^{2+} complex. The thermodynamic parameters for the formation of EBT-Zn^{2+} complex were determined. The reaction mechanism for the formation of EBT-Zn^{2+} complex was proposed. The complex has been characterized by spectral data including IR, UV-Vis and LC-MS techniques.

Keywords: Erichrome Black T; anodic oxidation; platinum electrode; Zinc electrode;

Introduction

Erichrome Black T is an azo compound, carcinogenic in nature. It is mainly used as an indicator in complexometric titrations to determine the total hardness of water due to elements like calcium, zinc, magnesium and other metal ions. It is well known that EBT has chelating properties. Therefore, EBT has been widely used for the determination of calcium, magnesium, manganese, zinc, zirconium, nickel, copper, thulium and cobalt [1−6]. Literature survey shows the extensive polarographic, spectroscopic and colorimetric studies on some metal complexes with EBT [4−14]. The review of the literature indicates that EBT-Zn^{2+}complex were not synthesized by electrochemical method and the kinetics for the formation of the complex has not been studied [1−16]. Hence we have developed the electrochemical method for the synthesis of EBT-Zn^{2+} complex with Zinc electrode as anode and platinum electrode as cathode. The kinetics for the formation of EBT-Zn^{2+} complex was studied.

Experimental

A solution of EBT (MERCK) [4×10^{-5}M] was prepared. The experimental set up is as shown in the figure (1). It consists of reaction chamber and a voltage power supply. The electrode system consists of a Pt electrode as cathode and a zinc wire electrode as anode. The experiment was carried out for different intervals of time with constant stirring. The kinetic runs were carried out to study the effect of [EBT] and current at constant temperature.

A positive voltage was applied by using battery eliminator (NEULITE INDIA) and current output of 1mA-5mA using rheostat (INSIF INDIA). The experiments were performed with 20ml of EBT solution. The change in optical density for the formation of complex was followed by spectrophotometer (ELICO SL 171).

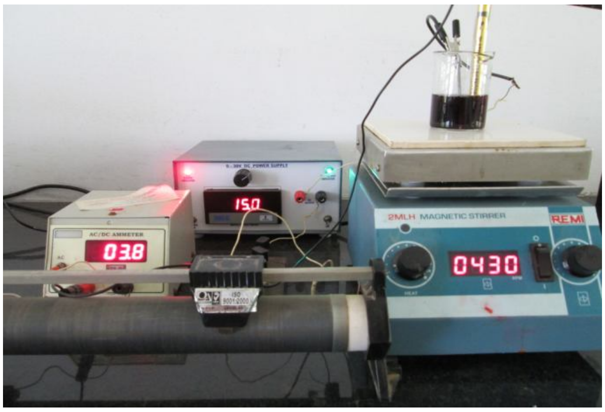


Figure 1. Experimental set up for the synthesis of EBT-Zn^{2+} complex by electrochemical method.

Results and Discussion

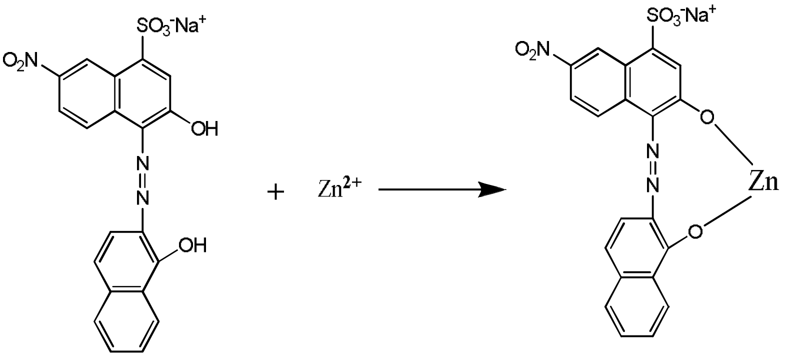
Synthesis and reaction mechanism of EBT-Zn^{2+} complex by electrochemical method.

A solution of EBT [4×10^{-5}M] was prepared. A requisite amount of EBT solution was taken in an electrochemical cell. The electrolysis reaction was carried out in presence of platinum electrode as cathode and zinc electrode as anode. The reaction was carried out for three hours with continuous stirring. During electrolysis the zinc ions were liberated from zinc electrode and the liberated zinc ions react with EBT and formation of a wine red colored complex takes place. The reaction mechanism proposed in scheme-I.

Reaction At anode:

$$Zn \longrightarrow Zn^{2+} + 2e^- \qquad (i)$$

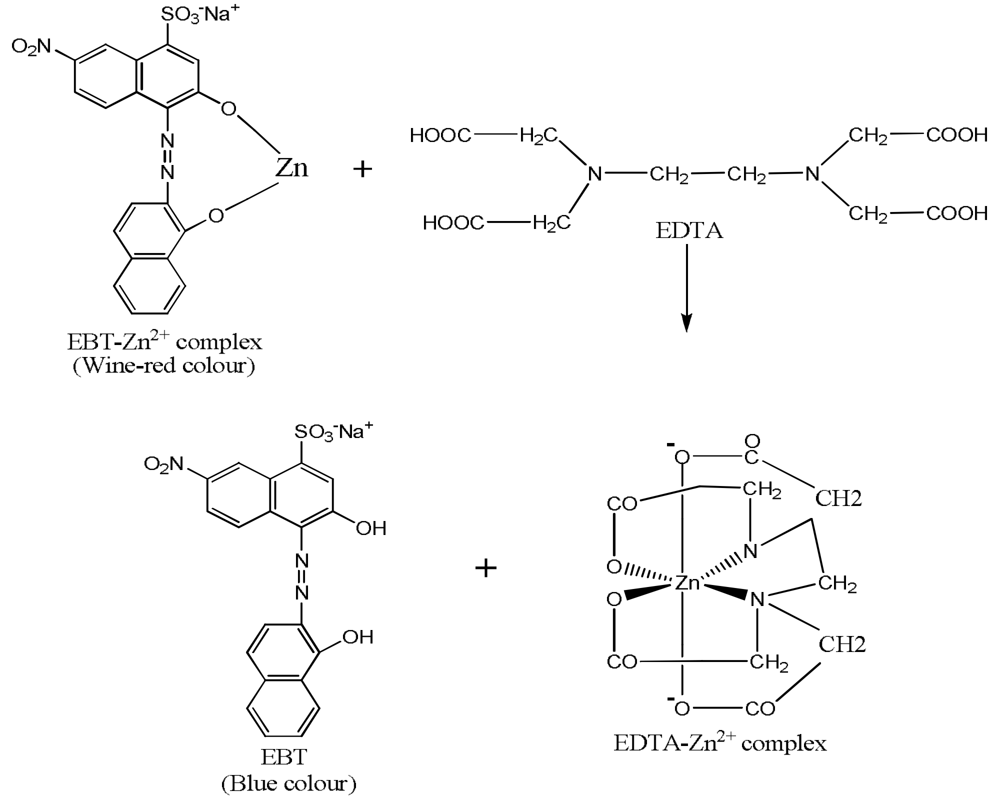
Reaction in solution:



EBT (Blue colour) EBT-Zn^{2+} complex (Wine-red colour) (ii)

SCHEME-I

The formation of product EBT-Zn^{2+} was confirmed by reaction with EDTA. The wine red colored EBT-Zn^{2+} reacts with EDTA form EDTA-Zn^{2+} complex and blue colored EBT reproduced. The reaction mechanism proposed in scheme-II.



EBT-Zn^{2+} complex (Wine-red colour)

EDTA

EBT (Blue colour)

EDTA-Zn^{2+} complex

SCHEME-II

Effect of EBT on the rate:

The reaction was performed in the presence of EBT (4×10^{-5}M) with constant current (5mA). The change in concentration of the EBT was recorded by change in color using spectrophotometer. The kinetic runs were carried out at different intervals of time for different [EBT] solution. The first order rate constant values were obtained by plotting log%T versus time, which are given in (Table-1, Figure-2). The reaction rate decreased with increase in [EBT]. At higher concentration of the dye, a formation of thin film of dye on the surface of the electrode takes place. This decreases the rate of flow of current across the electrode-solution interface which decreases rate of formation of OH radicals and other oxidizing species. Hence the rate of oxidation of EBT decreases at higher concentration of the EBT.

Table 1 Effect of [EBT] on the rate of formation of the complex.

10^{-5} M[EBT]	10^{-4} k sec^{-1}
5.0	3.07
4.5	2.60
4.0	3.40
3.5	3.46
3.0	3.49

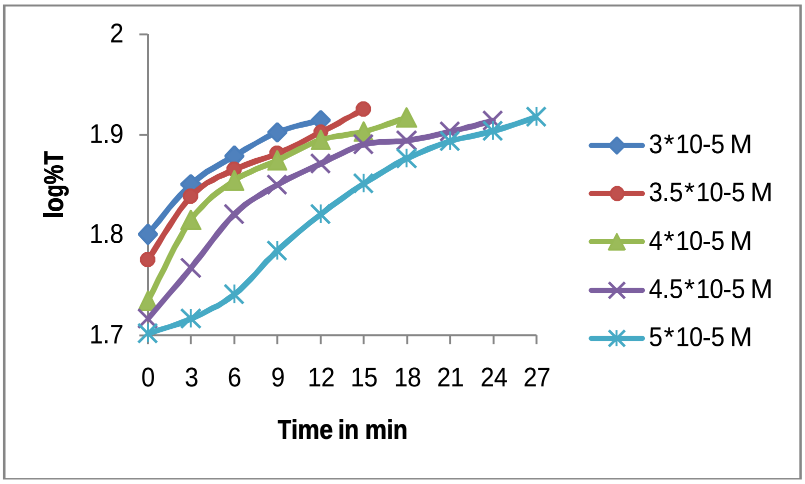


Figure 2. Effect of concentration of EBT on the rate of formation of the complex.

Effect of current on the rate:

At fixed [EBT] the rate of reaction increased with increase in applied current. The current was varied from 1mA-5mA. (Table-2, Figure-3). The increase of current increases the concentration of oxidizing intermediates and OH radicals, which increases the rate of formation.

Table 2 Effect of current on the rate of formation of complex.

Current in mA	10^{-4} k sec^{-1}
1	0.30
2	2.30
3	2.33
4	3.40
5	3.40

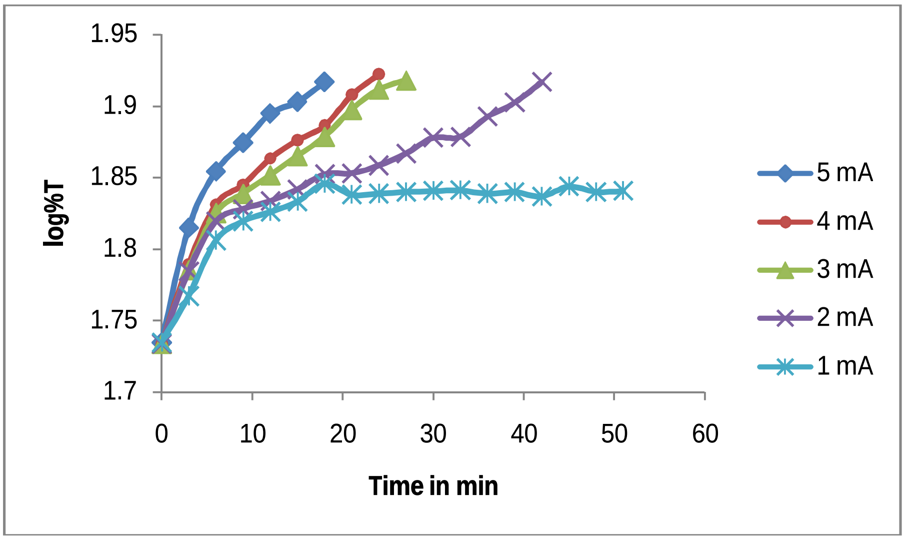


Figure 3 Effect of current on the rate of formation of complex.

Effect of temperature:

It is clear that increase in the reaction temperature increases the rate of formation of EBT-Zn^{2+} complex. It is observed that the rate of formation of complex is not with usual significance at low temperature. However the rate of reaction is significantly influenced at higher temperature (Table-3, Figure-4). The thermodynamic parameters for the formation of the complex are given in table-4.

Table 3 Effect of Temperature on the rate of formation of complex.

Temperature in K	10^{-4} k sec^{-1}
298	3.40
308	3.40
323	4.60

Table 4 Thermodynamic parameters for the formation of EBT-Zn^{2+} complex.

Temperature in K	ΔH	ΔS	ΔG
298	10.7339 kJ/mol	-3235.520 J/K	974.91 kJ/mol
308	10.6508 kJ/mol	-2957.147 J/K	921.452 kJ/mol
323	10.5260 kJ/mol	-2494.630 J/K	818.977 kJ/mol

UV-Visible spectra:

Figure 4 (A and B) represents UV-Visible spectra of EBT alone and EBT-Zn^{2+} complex. The synthesized complex by electrochemical method is compared with complex obtained by complexometric reaction of EBT and Zinc chloride solution. The broad visible color absorption spectra at 573nm observed in both the cases indicates the presence of EBT-Zn^{2+} complex, which was absent in EBT spectra.

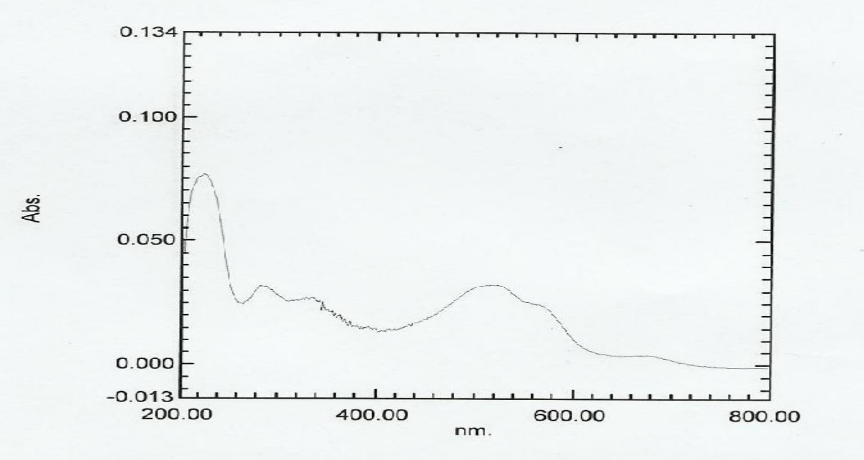


Figure 4(A) UV-Visible spectra of EBT.

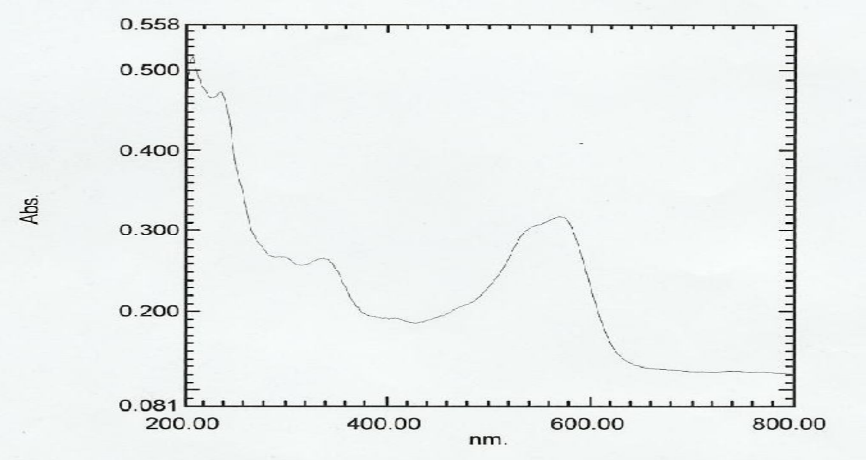


Figure 4(B) UV-Visible spectra of EBT-Zn^{2+} complex synthesized by electrochemical method.

LC-MS spectra (Liquid Chromatography-Mass Spectroscopy)

Figure 5(A to D) represents the LC-MS spectra of EBT and EBT-Zn^{2+} complex synthesized by electrochemical method. The peak at 525 shows the formation of the EBT-Zn^{2+} complex, which is obtained by electrochemical method.

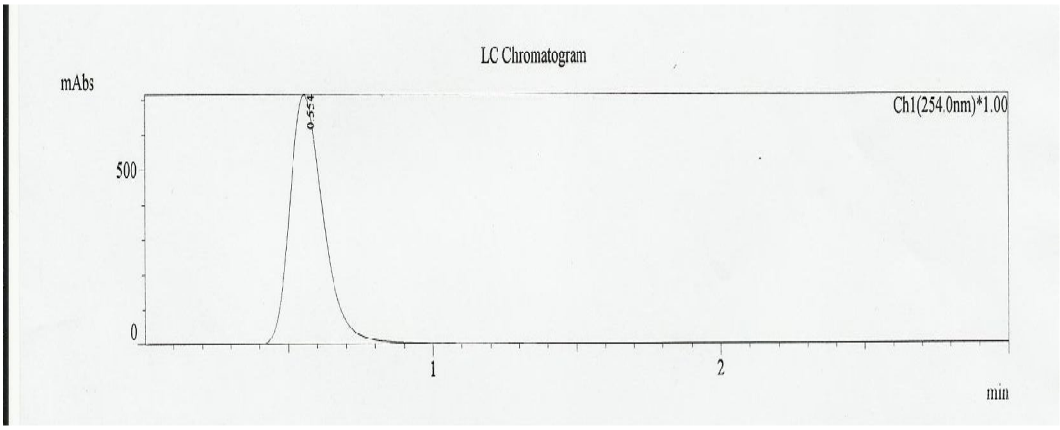


Figure 5(A) chromatogram for EBT.

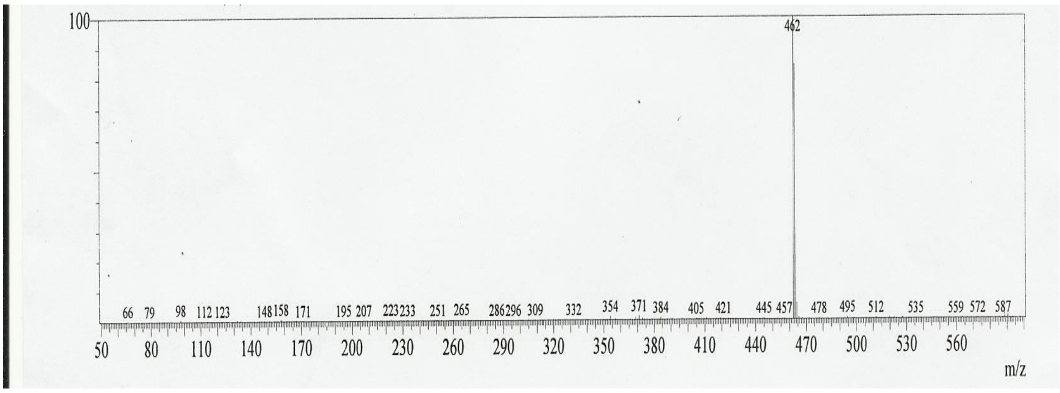


Figure 5(B) LC-MS of EBT.

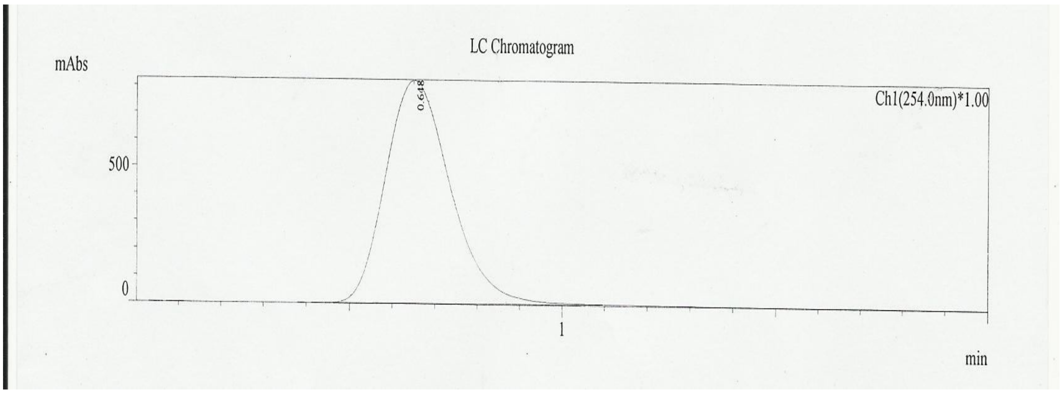


Figure 5(C) chromatogram for EBT-Zn^{2+} complex.

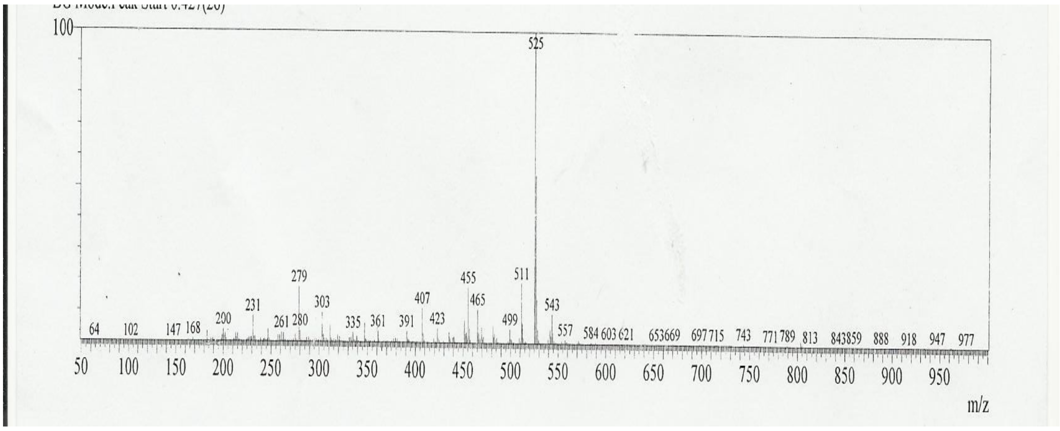


Figure 5(D). LC-MS of EBT-Zn^{2+} complex.

IR Spectra:

Figure 6(A and B) represents IR spectra of EBT and EBT-Zn^{2+} complex synthesized by electrochemical method. The presence of absorption bands near 471cm^{-1} indicates the existence of Zn-O bond in EBT-Zn^{2+} complex, which was not obtained for IR spectra of EBT.

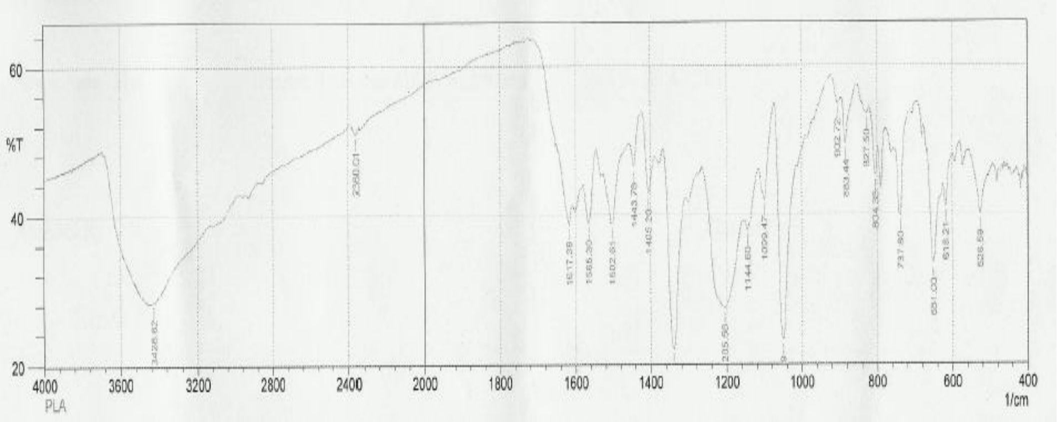


Figure 6(A) IR spectra of EBT.

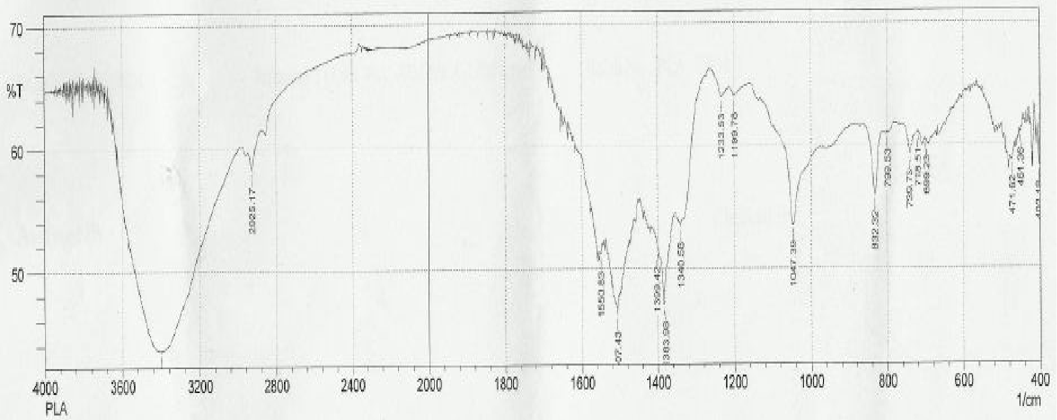


Figure 6(B) IR spectra of EBT-Zn^{2+} complex by electrochemical method.

Conclusion

EBT-Zn^{2+} complex were obtained by electrochemical method. The kinetics of formation of complex is controlled by the current and potential. The complex has application for determining the total hardness of water. The formation of the complex is confirmed by UV, IR, and LC-MS spectra.

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