Determination of the stability constant of Cobalt (II) – Piroxicam complex by spectrophotometery

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ABSTRACT

In this work, a new spectrophotometric method for the determination of trace amount of Cobalt (II) ion was investigated and the stability constant of the related complex was evaluated 2.174×10^4. In the Cobalt (II)-piroxicam complex, the maximum absorbance wavelength is 570 nm and the linearity of calibration curve was investigated (5-10 ppm). The relative standard deviation for seven replicate experiments is 0.5292 percent. The accuracy is 0.15 percent and limit of detection is 1.19 ppm. The analytical sensitivity allows us to detect the concentration difference of 0.06 ppm with reliable level of confidence. The ligand to metal ratio was determined (1:1) by the continuous variation method. The above spectrophotometric method was optimized in terms of pH, temperature, time, ligand concentration and ionic strength. This method is tolerant against several external matters, which means high selectivity.

Keywords: Piroxicam; Spectrophotometery; Cobalt, Stability constant.

INTRODUCTION

Piroxicam{4-Hydroxy-2-methyl-N-(2-pyridyl-2H-1, 2} benzothiazine-3-carboxamide-1, 1 dioxide} belongs to the class of acidic, non -steroidal, anti inflammatory drugs. The structure of piroxicam is promising to form chelate complexes with metals. These complexes have lower toxicity and higher pharmacological affect due to the inhibition of complex formation by other biologically important compounds [1].

Several methods were applied for the analysis of piroxicam that include voltametery [2, 3], High performance liquid chromatography [4, 5] and spectrophotometric methods included ultraviolet, visible [6] and Flourometery [6]. Some other spectrophotometric methods were also applied for the quantitative determination of pure drug and some of its pharmaceutical derivatives [7]. The aim of this research is development of a suitable spectrophotometric method for the application of piroxicam in quantitative and qualitative determination of Cobalt (II) ion and estimating the thermodynamic stability constant of the complex.

For the standardization of this important ion in versatile products, it is necessary to develop a reliable analytical method. The spectrophotometric method due to the facility, high sensitivity, good accuracy and vast usage has a lot of benefits to other advanced analytical methods.

Different types of chelating agents such as phenol triFlouroacetine [8], 5-nitroso salycilaldehyde 4-phenyl-3-thio semi carbazone [9], Iso nirtoso 4-methyl 2-pantanone [10], Iso nirtoso malone dianilide [10], 3-(4-phenyl-2-pyridyl 1, 2, 4 triazyle [11], phenyl – azobenzo aldoxime [12], tetra azolyne violet [13], triFlouro acetyl acetone [14], Nitrochromo tropicacide [15], 2-nitroso 1-naphtole [16] and 2-(5-bromo-2-pyridyl azo) 2-para kezole [17] were reported for spectrophotometric determination of Cobalt up to now. But such methods have some problem in terms of pH [18], long color extending time [17] and interference with some ions [11, 16 and 17]. The selected method in this research is more reliable in terms of precision and accuracy compared to 6, 9, and 17 and possesses good selectivity against external reagents.

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EXPRIMENTAL

1. Apparatus

The spectrophotometer used is 350. (Camspect) that has following specifications:
- Double beam
- Monochoromator type with 1200 lines mm halographic grating
- Wavelength range between 190-1100 nm
- Spectral band pass 2 nm

2. Reagents and Materials

Piroxicam solution (10^{-2} M), for this purpose 3.313×10^{-1} gr of piroxicam powder (prepared from Razac Comp.) was dissolved in 100 ml dimethyl formamide (DMF) solvent.

Stock solution of Cobalt (II) ion (1000 ppm), for this purpose 4.038×10^{-1} gr of $CoCl_2.6H_2O$ (prepared from Merck Comp.) was dissolved in 100 ml of distilled water, then standardized through titration with the 10^{-2} M solution of Ethylene diamine tetraacetic acid (EDTA) [19].

Buffer solutions with the pH range of 8-9.5, for this purpose a suitable amount of triethanol amine viscose solution in the Erlenmeyer was titrated by nitric acid to produce buffers with considered pH values [20, 21].

The following solutions were also used:
Acetone (drying), Hydrochloric acid solution (washing the vessels), Kalium perchlorate (setting the ionic strength) and tartarate solution (%2).

3. General procedure

3-1. Initial qualitative study for the formation of Cobalt (II) – Piroxicam complex

Piroxicam solution in DMF produced purple color with $CoCl_2.6H_2O$ in alkaline medium and room temperature and the testing tube also was increased in temperature.

3-2. Quantitative study for the formation of Cobalt (II) – Piroxicam complex

4 ml of Cobalt (II) solution with definite concentration was added to the test tube and some amount of tartarate solution (%2) was also added, 1 ml of buffer (pH=9) was added and finally the drug solution in DMF (10^{-2} M) was applied. After 15 minutes the absorbance of this solution at 570 nm (The maximum complex absorbance peak) against the blank solution of $CoCl_2.6H_2O$ once and another time against the blank solution of Cobalt (II) ion plus drug was measured. For recording the absorbtional spectrum, wavelength range of 190-800 nm was used [22].

RESULTS AND DISCUSSION

1. Determination of the complex stability constant with Job method

In this method, solutions of cation and ligand with similar concentrations (10^{-3} M) were prepared and then the two reactants were mixed in different volumetric ratios provided that the total volume of samples is the same. The proper buffer solution was added and after 15 minutes the absorbances were measured at 570 nm.

The curve of absorbance against the molar ratio of Cobalt (II) ion was obtained. For the confidence, the procedure was repeated by the different concentration of reactants (5×10^{-4} M) and the related curve was again obtained. By using the continuous variation curve for the Cobalt (II) – piroxicam and applying the Job method, logk=4.325 [23, 24]. This value shows good stability of the formed complex.

The estimation of stability constant by continuous variation method is shown in Figure 1.

2. Optimization of the procedure

By performing a series of experiments, optimized pH, time, temperature and ligand concentration were 9, 15 minutes, 25 °C and 10^{-2} M, respectively. It was known that the ionic strength of medium has not any significant affect on the absorbance of complex [22].

3. Investigation of spectral interferences

Studying the absorbance spectra, it was known that the piroxicam solution in DMF shows a strong absorbance band at 320 nm and the Cobalt (II) solution does not show any absorbance peaks around 570 nm (maximum complex absorbance wavelength). DMF solvent possesses an absorbance peak at 268 nm. So, the observed absorbance peak at 570 nm is related to Cobalt (II) - piroxicam complex and there are no spectral interferences.

4. Investigation of chemical interferences

For doing this, versatile salts and ions were added to Cobalt (II) solution (20 μg/ml) and the concentration of Cobalt at 570 nm was determined through its absorbance [22]. Tolerance limit (concentration difference that causes %3 error in determining Cobalt ion) of different ions were as follows:

F^-, Br^-, Cl^-: high, EDTA: 0.5 mg, tartarate: 160 mg, oxalate: 40 mg, Acetate: 15 mg, Mg: 160 mg, Fe: 15 mg, Cu: 10 mg, Ni: 20 mg, Cr: 120 mg and Pb: 80 mg.

As it is observed, among anions, chloride, bromide and iodide up to high amounts did not have any interference. Acetate is an interferent to a little extent. For omitting the Copper interference, we can mask it by a Natrium thiosulfate solution (%1). For iron interference, citric acid solution or tartarate can be used. For EDTA, the solution can be boiled with nitric acid. So, the method possesses a high selectivity.

5. Calibration, limit of detection, sensitivity, accuracy and precision

A liner calibration curve in the range of 5-16 ppm with regression coefficient of 0.9995 was obtained. The limit of detection (the concentration of a sample that produces a single which equals intercept of calibration curve plus three times of standard deviation) was 1.19 ppm. Analytical sensitivity (the ratio of calibration slope to the signal standard deviation in a definite concentration of analyte which here is 2.018×10^{-4} M) is 15.93 ppm^{-1}. So, the detection of concentration difference of 0.06 ppm (analytical

sensitivity $^{-1}$) is possible. The relative standard deviation (RSD) for 7 replicate experiments at the absorbance of 0.434 (minimum instrumental error) is 0.5292 percent. The accuracy (relative error) is 0.15 percent [25, 26]. So, the method possesses good accuracy, precision, sensitivity and has suitable limit of detection. In Figure 2. the calibration curve with linear range of 5-16 ppm for Cobalt (II) – piroxicam complex is shown.

CONCLUSION

The spectrophotometric method that in fact is a type of spectroscopic analysis based on the absorbance of ultraviolet and visible light is one of the most suitable methods in quantitative analysis. The illustrated method possesses a high sensitivity, good accuracy, high precision, suitable limit of detection and facility.

In this method it was understood that piroxicam can serve as a suitable ligand for determining trace amount of Cobalt (II) ion and in this way, the thermodynamic stability constant of formed complex can be evaluated. The obtained results showed that the Cobalt (II) – piroxicam complex has a good thermodynamic stability.

CAPTIONS FOR FIGURE
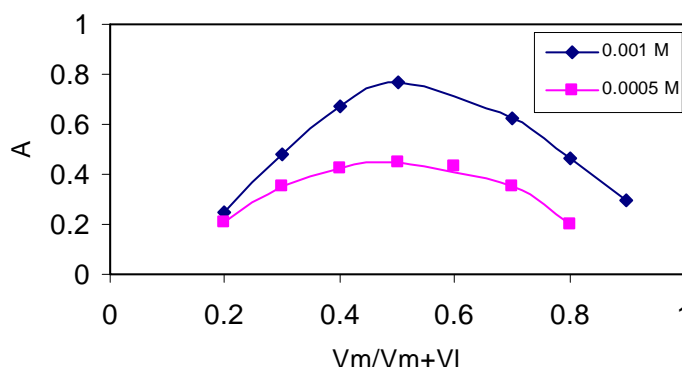
Fig.1. Continuous variation curve for Cobalt (II) – piroxicam complex in two different concentrations.
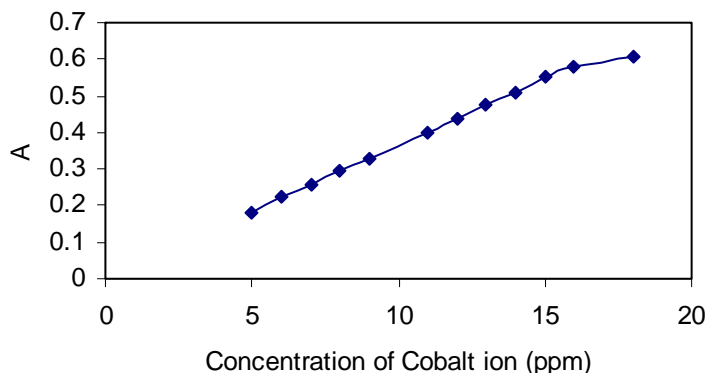
Fig.2. Calibration curve for Cobalt (II) – piroxicam complex.

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