

Spectrophotometric and Potentiometric Analysis of Calcichrome and Its Complex with Calcium Ion

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Abstract

It was confirmed in this research that the ligand calcichrome formed stable complex with calcium ion at pH of 8.5 which verified by UV/Vis and FTIR spectral analysis and the complexation occurred via hydroxyl groups.

The stoichiometric ratio of the formed complex was found to be 1:1 by mole ratio and continuous variation methods. Dry ashing method of the complex and flame emission photometric analysis offered a calcium percentage in calcium complex equal 4.5% with an error of 2.41% due to experimental errors.

Keyword: Calcichrome, Stoichiometry, Mole ration method, Continuous Variation method, Selective reagent.

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1. Introduction

Calcichrome was considered as a selective reagent for the determination of calcium [1]. This reagent was applied for estimation of the element calcium in different compounds by some researchers [2,4]. For instance, calcichrome has been used for determination of calcium in soil extracts [5].

Calcichrome was extensively studied as spectrophotometric reagent in determination of copper (I) and copper (II)[6], and determination of magnesium in highly alkaline solutions [7].

Calcichrome, creating a cavity through its folding, is even a better receptor for α , β and γ cyclodextrins in water (stability constants from 380 to 570 M^{-1})[8].

Although, calcichrome has also been studied by other authors, its structure has not been conclusively established, therefore the aim of this research is the verification of its structure and find out its applications in determination of calcium ions by different analytical techniques.

2. Experimental

Materials

Calcichrome solution

Solution of calcichrome ($1 \times 10^{-3} M$) was prepared by solubilizing (0.098 gram) of calcichrome in double distilled water to 100 ml by double distilled water. Series of solutions of various concentrations were obtained by dilution from this stock solution.

Standard calcium solutions

A standard calcium solution approximately to about ($1 \times 10^{-2} M$) of calcium was prepared by dissolving accurate weight of (1.47 g) of the salt calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) in double distilled water and the solution is completed to (1 L) by double distilled water. A series of standard solutions of different calcium concentrations were obtained from this stock solution by suitable dilution.

The stock solution was standardized by titration with standard EDTA solution prepared from disodium salt at $pH = 11$ using murexide indicator, where the color changed from red to bluish-violet. Murexide was prepared daily by dissolving (0.5 g) [9] of the dye in (100 ml) double distilled water.

Sodium hydroxide solution

It is obtained by dissolving about (1 gram) of solid NaOH in a cooled boiled water [9] and completed to the mark in volumetric flask (250 ml) and was standardized by (0.1 N) standard solution of oxalic acid using phenolphthalein as indicator.

Buffer solution (Ph 5.2)

These buffer solutions were obtained by mixing about (1 M) acetic acid with about (1 M) of sodium acetate solution in the suitable ratio and the pH was adjusted by addition drops of (0.1 M) HCl or (0.1 M) NaOH solutions[9].

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Instruments

- UV-Visible spectrophotometer (6405 Jenway)
- FTIR 8400 S. Shimadzu, Japan .
- Flame emission photometer (Jenway , U.K)
- A pH – Meter of Mettler – Toledo (China)
- A Glass electrode (combined model) from Mettler – Toledo (China)
- A double junction of calomel electrode of Mettler – Toledo (China)

Method of preparation and spectrophotometric

Measurements of the calcium – calcichrome complex solution :

A sample solution of calcium was mixed with (5 ml) of solution of calcichrome (4×10^{-4} M) and addition of (10 ml) of buffer solution (pH 5.2) and diluted to the mark of 250 ml volumetric flask . The absorbance of the mixture was taken at 535 nm against blank solution has been treated in the same procedure.

3. Results and Discussion

UV-Vis spectral analysis

Figures 1(a & b) depict the UV-Visible spectra of calcichrome and calcichrome complex with calcium respectively . Two absorption bands were obtained for calcichrome in buffer solution at 306 and 555 nm which were shifted into 300 and 539 nm . This shifting in uv-visible absorptions to lower wavelength is an indication to complex formation with calcium via the hydroxyl groups after loss of acidic hydrogen ions in the three hydroxyl groups . Most of oxygen electrons are participated in coordination bond formation with calcium ion and the remained electrons are highly localized and require higher energy for excitation ($n - \pi^*$) or ($\pi - \pi^*$) [10]. Therefore the absorption bands are shifted to lower wavelengths.

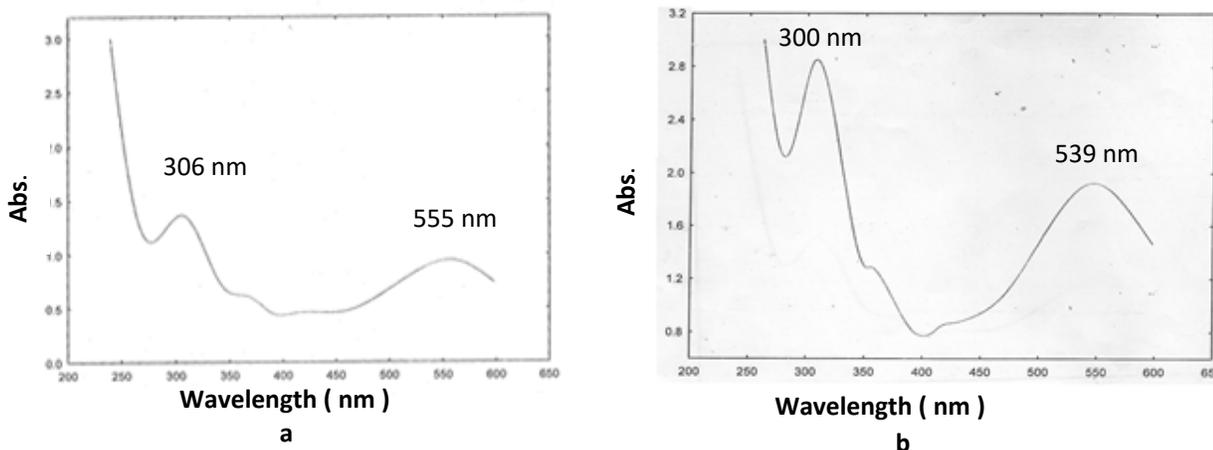


Figure (1): UV – Vis. Spectra of calcichrome (a) and its complex with calcium (b)

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FTIR

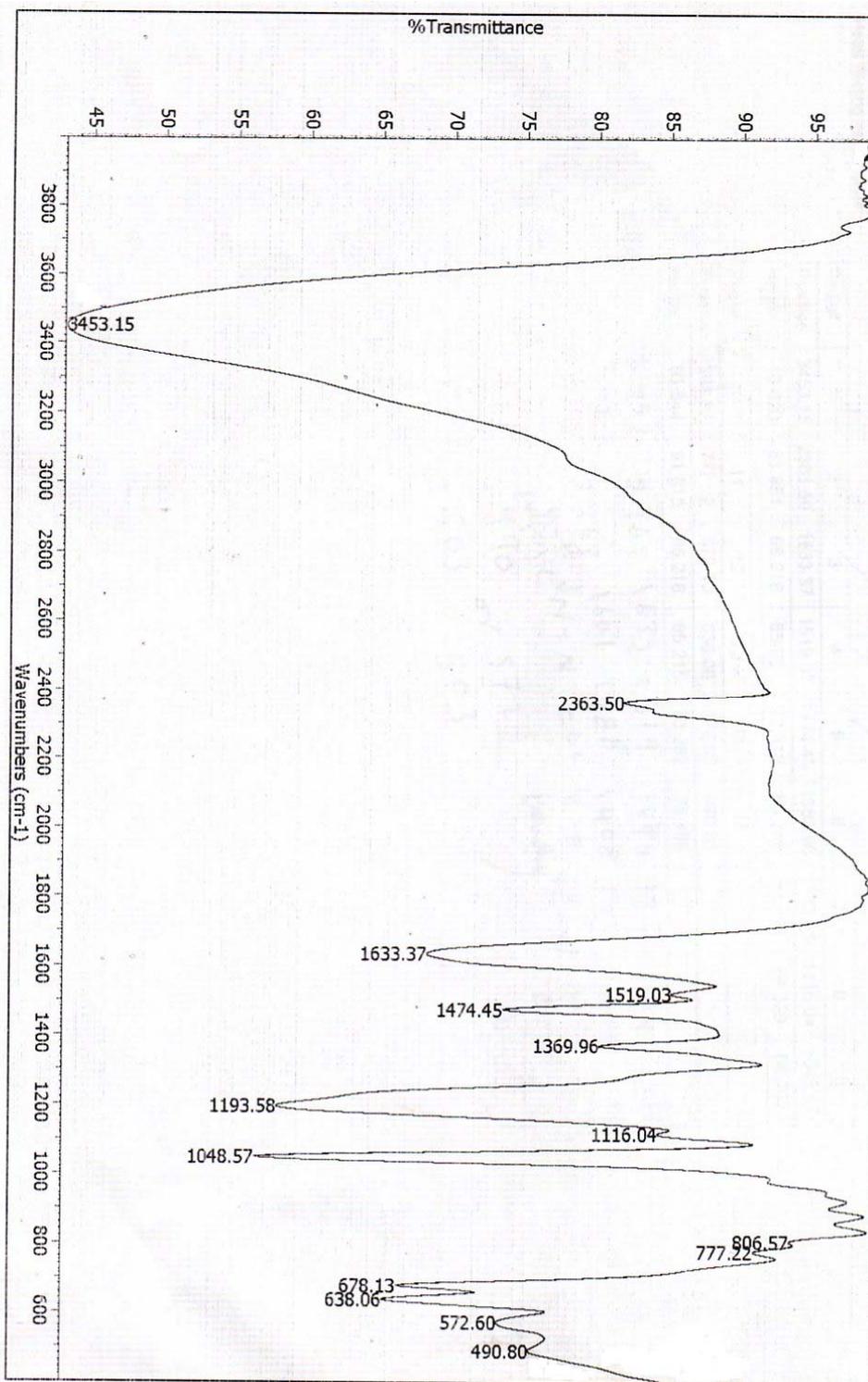
Figures (2 & 3) show the FTIR absorption spectral peaks for calcichrome and its complex with calcium ions [11]. It is obvious from the result in Figures (2 and 3) that the OH groups in calcichrome were engaged in the complex formation therefore the wave number of ν O-H was shifted from 3453 cm^{-1} into 3427 cm^{-1} in addition to δ O-H from 1194 cm^{-1} into 1162 cm^{-1} . At the same time, there was shifting of ν N=N from 1633 to 1601 cm^{-1} indicating that the participating of azo groups also in the complex formation. While ν O-H of sulfonic group remained at the same wave number (2363 cm^{-1}) in addition to ν C-S and ν S=O which also remained approximately the same. This IR information give practical confirmation for the complex formation (Figures 2 and 3).

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Figure (2):FTIR spectrum of calchichrome .



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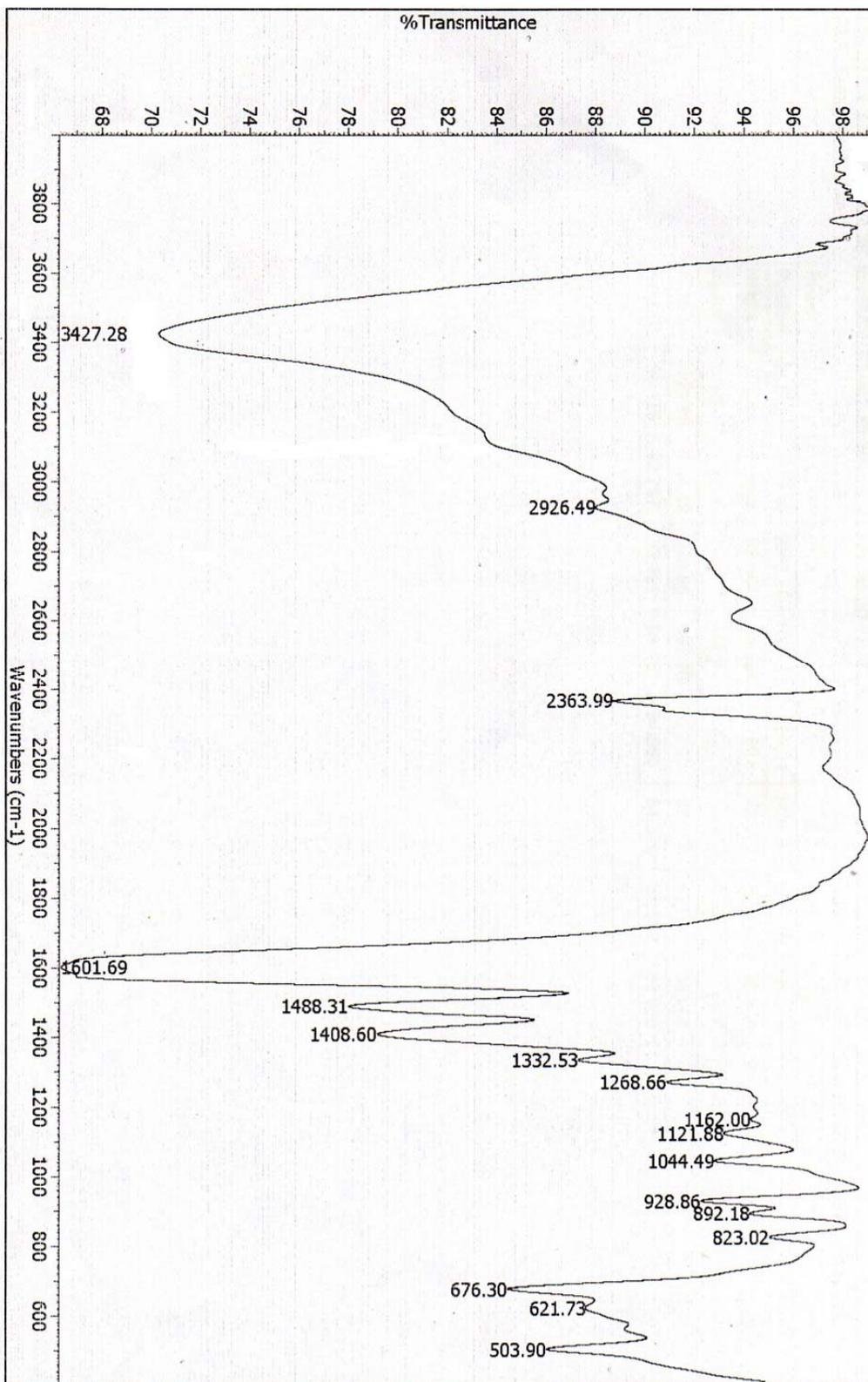


Figure (3): FTIR spectrum of calchichrome complex with calcium .

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Stoichiometric ratio of calcium to calcichrome

Two methods were attempted to get the composition of calcichrome calcium complex: The first method was Job's method (the continuous variation method) and the second method of mole ratio were attempted at the same time at pH=5.2 to confirm the stoichiometric ratio of calcium [M] to the ligand [L] calcichrome . Absorption measurements were done at λ_{max} of 539 nm. Both methods revealed that calcium forms (1 to 1) λ_{max} with (L) Figures (4 and 5) .

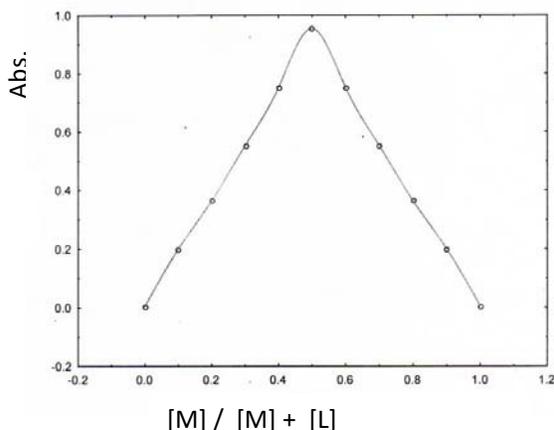


Figure (4): Continuous variation method plot for determination the composition of calcium calcichrome complex

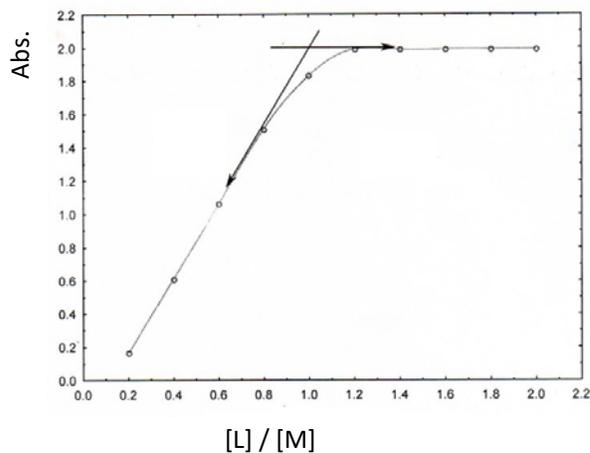


Figure (5): Mole ratio method plot for stoichiometric composition of calcium calcichrome complex .

Determination the percentage of calcium in calcium calcichrome complex:

The method involved dry aching of (0.05 g) of the formed complex in a muffle furnace at 550 c°. The residue was cooled and accurately weighed. The residual ash was dissolved in nitric acid (1:1) and the solution was completed to 50 ml by distilled water .The flame emission photomet was calibrated by serial standard solutions of 1,5,10,15,25,30,50 and 80 ppm of calcium and the concentration of calcium in calcium calcichrome complex was picked up from calibration curve as shown in Figure(6). The percentage of calcium in calcium calcichrome complex was found 4.5% with an error of 2.41% which may be ascribed to experimental error where the actual value = 4.61% .

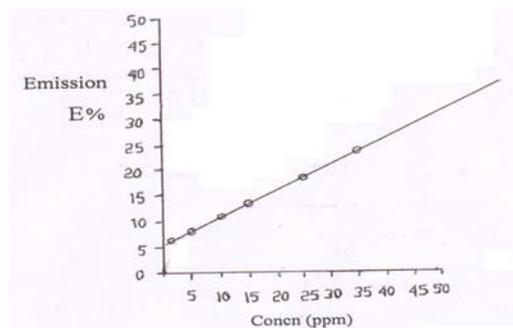


Figure (6): calibration curve of atomic emission spectrometry for determination of Ca in Ca calcichrome complex .

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Potentiometric titration of calcichrome and its calcium complex with standardized sodium hydroxide solution :

The potentiometric titration of calcichrome and its calcium complex were accomplished in order to find out the mechanism of the reaction between calcichrome and calcium where their concentrations equal 5×10^{-4} mol/L . The ionic strength was fixed at 0.1 using potassium nitrate solution and the reaction was followed at 25 C° with (0.1 M) standardized sodium hydroxide solutions . The results were formulated at figure (7) where the curves 1 and 2 depicted the titration curves of calcichrome and its 1:1 calcium complex respectively .

It is clear from figure (7) that calcichrome dissociates to release five protons up to about pH 5 (point a) and the sixth proton is released at approximately pH 8.5 (point ,b) which liberated also in the complexation calcichrome containing six sulphonic groups which are completely ionised at lower pH region . Therefore , the groups that sharing in the complex formation with calcium ion are the hydroxyl groups at higher pH and the ionization of calcichrome is considered as shown in equation (1) [12]:

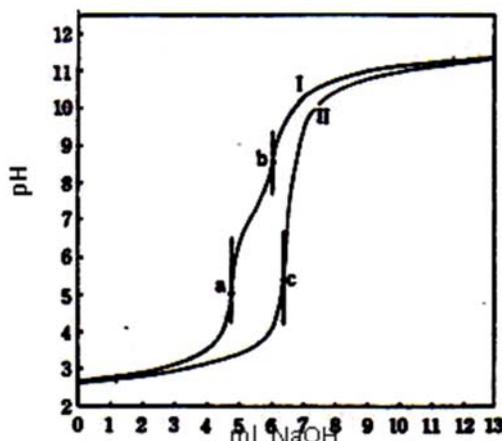
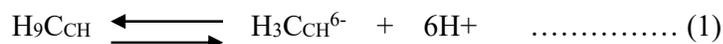


Figure (7): Potentiometric titration curves of Calcichrom and its calcium complex.

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