A SPECTROSCOPIC INVESTIGATION OF THE COMPLEX OF TURMERIC DYE WITH COPPER(II) IN AQUEOUS SOLUTION

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Abstract

The structure of the complex formed between Cu(II) and curcumin in aqueous solution was investigated using UV-visible spectroscopy. The molar ratio method was applied to ascertain the stoichiometric composition of the complex in aqueous solution. The resulting stoichiometry for Cu(II) to curcumin was 1:2. A structure for $Cu(Cur)_2$ was proposed. Curcumin uses the β-diketone moiety as the binding site with copper(II) ion. In addition, IR spectra and diffuse reflectance UV-Vis spectra have been performed to support the experimental observations.

Keywords: Curcumin, spectrophotometry, complexation, copper

Introduction

The rhizome of turmeric, *Curcuma longa* Linn., is an important source of a natural yellow pigment. The compounds responsible for the yellow pigment are curcumin[1,7-bis-(4-hydroxy-3-methoxyphenyl)-1,6-heptadien-3,5-dione] (Cur) and 2 curcuminoids, demethoxycurcumin (DC) and bisdemethoxycurcumin (BDC) (Jayaprakasha *et al.*, 2002; Jayaprakasha *et al.*, 2005; Jiang *et al.*, 2006). Some studies on curcumin are based on the ionic structure where the keto-enol equilibrium (Figure 1) is present or when it is fully in keto form (Tønnesen *et al.*, 1982; Tønnesen, 1989; Wang *et al.*, 1997) with the resulting properties depending on the latter.

The water solubility of curcumin is relatively low, although it is soluble in alcoholic media. The β-diketo moiety of curcumin undergoes keto–enol tautomerism. Crystal studies (Tønnesen *et al.*, 1982; Tønnesen *et al.*, 1983; Karilsen *et al.*, 1988) have shown that the symmetric structure of curcumin leads to a statistically even distribution of the enol proton between the 2 oxygen atoms. The strong chelating ability of diketones has been widely investigated towards a great number of metal ions. In such conditions the curcumin molecule should bind with species which have a positive or partially positive charge, for example, a transition metal ion (Bates, 2000).

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Turmeric dyes have been used as a natural dye for centuries (Moeyes, 1993). Unfortunately, the use of natural yellow dyes is related to "poor fastness" due to their problematic issues in light fastness and wash fastness properties. Curcuminoids have particular disadvantages when dyeing onto silk fibroin, cotton and wool (Tsatsarosi *et al.*, 1998; Popoola, 2000; Yoshizumi, and Crews, 2003). The solution is usually to use metal ions as mordants (Tsatsaroni *et al.*, 1998).

Metal complex formation has been a well-known feature of textile dyeing from very early times, since it was recognized that the technical performance, including fastness to washing and light, of many natural dyes could be enhanced by treatment with certain metal ions, a process known as mordanting (Christie, 2001). In the northeast of Thailand, villagers usually use trial and error methods to find some mordants for silk dyeing (Moeyes, 1993). Alum and salt, iron oxide and copper sulphate are common examples.

Copper(II) sulphate pentahydrate ($CuSO_4{\cdot}5H_2O$) is widely used as a mordant for dyeing silk fibre with polyphenolic dyes to obtain bright colours and improve fastness to light and wash (Christie, 2001).

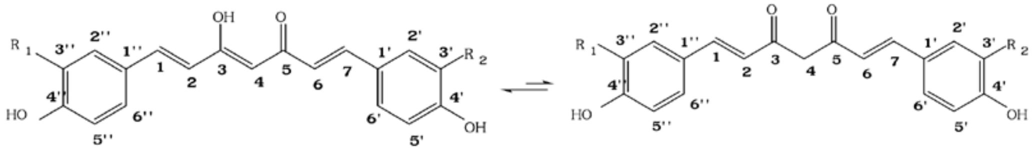
The complexes formation of curcumin with various metal ions have been investigated (Vajragupta et al., 2003; Borsari *et al.*, 2002; Barik, *et al.*, 2007). The stoichiometries of curcumin with some metal ions were also reported (Borsari *et al.*, 2002; Barik *et al.*, 2007). However, the complex formation of copper(II) with curcumin which is a major composition of curcuminoid dyes in aqueous solution has not yet been reported. The aim of this present work is to determine the stoichiometric composition of the curcumin – Cu(II) complex formed between curcumin and the Cu(II) ion in an aqueous solution. The complex formation between curcumin dyes and the Cu(II) ion were investigated by using the UV-Vis spectrophotometry method. These complexes can be directly applied to dyeing silk.

Materials and Method

All chemicals in this study, copper(II) nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$), copper(II) sulphate pentahydrate ($CuSO_4{\cdot}5H_2O$), sodium hydroxide (NaOH), ammonium acetate, acetic acid and ethanol were A.R. grade obtained from Merck, while 98% curcumin [458-37-7] in amber widemouthed reagent bottle was purchased from Across Organics.

Determination of the Mole Ratio for the Cu(II)-Curcumin Complex

The molar ratio method was used to determine the composition of this complex in aqueous solution from spectrophotometric spectra. For this method, fresh 5.0×10^{-3} M curcumin stock solution was prepared by dissolving 0.1842 g of curcumin in 100 mL 95% ethanol directly in the volumetric flask and kept it in an amber reagents bottle. A 5.0×10^{-3} M copper(II) nitrate stock solution was prepared in deionized water. A concentration of 2.5×10^{-5} M of curcumin in aqueous solution of 0.5% ethanol was prepared by pipetted 50 μL of 5.0×10^{-3} M curcumin stock solution



Compounds	R1	R2	MW
Cur	OCH_3	OCH_3	368
DC	OCH_3	H	338
BDC	H	H	307

Figure 1. The equilibrium of keto-enol formations of curcuminoid

into a 10 mL volumetric flask, and adjusted using deionized water. A concentration of 2.5×10^{-5} M of curcumin in aqueous solution was kept constant whereas the copper(II) nitrate stock solution was varied from 0 to 7.5×10^{-5} M. The pH was controlled using a buffer system consisting of 4% of 1.0 M ammonium acetate-acetic acid buffer pH 5.5 which was added to a mixture of copper(II) and curcumin dye. In order to reach the complexation equilibrium, the absorption spectra of the solution was recorded after standing for 20 min. An Agilent 8453 UV-Vis spectrophotometer was employed for measuring absorbance values using quartz cells of a path length of 1 cm.

Preparation of Cu(II)-Curcumin Solid Complex

The synthesis of the solid 1:2 complexes between copper(II) ion and curcumin was carried out by the addition of 10 mL MeOH to 0.25 mmol curcumin, after which 240 mL deionized water was added, followed by the drop-wise addition of copper(II) nitrate 0.125 mmol in aqueous solution, which was stirred for 2 h at room temperature. After standing overnight, a yellow green solution, a gelatinous residual product appeared. This was then isolated by vacuum filtration, washed with cold MeOH and dried overnight in a desiccator. The solid crude was then recrystalized in MeOH and acetic acid. The crystal was separated and washed with cold MeOH-water. Diffuse reflectance UV-Vis spectrophotometry was used to characterize the solid complex. Diffuse reflectance a measurement from 9,090 to 20,000 cm^{-1} was recorded as polycrystalline sample using a Perkin–Elmer Lambda 2S spectrophotometer equipped with an integrating sphere attachment. Sample preparation for IR study was done by using KBr disk technique. The Bio-Rad FTS 175C FTIR spectrophotometry was used to observe the stretching frequency of the carbonyl group of the β-diketone moiety in curcumin and the Cu(II)-curcumin complex.

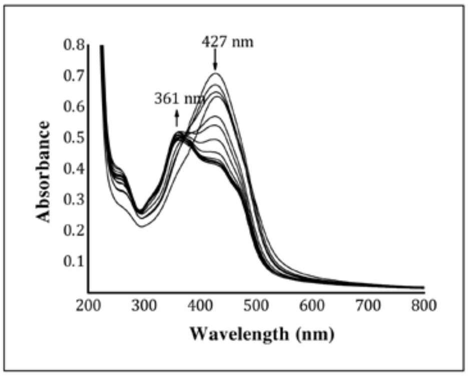


Figure 2. Electronic absorption spectra of curcumins (2.5×10^{-5} M) in aqueous solution in the absence and presence of copper(II) from 0 to 2.5×10^{-5} M at pH 5.5

Results and Discussion

UV-Visible Spectra of Curcumin in Aqueous Solution and at pH 5.5

It was found that increasing the Cu(II) concentration decreases the absorption band at 427 nm of curcumin and also results in the appearance of a new band at 361 nm of new compound. The effect of the Cu(II) concentration on the visible spectra (λ_{max}) of Cu(II) curcumins with pH control at 5.5 is shown in Figure 2 and indicates a large hypsochromic shift of 66 nm in band 427 nm correspond with the study of Barik (Barik *et al.*, 2007) and Zhao (Zhao *et al.*, 2005).

Barik reported that the UV-Vis region showed 2 absorption bands of curcumin ligands: an $n \rightarrow \pi^*$ transition at ~360-430 nm and $\pi \rightarrow \pi^*$ transition at ~240-290 nm (Barik *et al.*, 2007). The absorption band showed decay of the parent Cu(II)-curcumins band at 427 nm after being mixed with copper(II) ions. The UV-Vis spectrum of curcumin in aqueous solution at pH 5.5 exhibits a maximum adsorption band at 427 nm with an extinction coefficient of 31528 M^{-1}cm^{-1}. A new band which increases with the amount of added copper(II) appeared at 361 nm with an extinction coefficient of 18772 M^{-1}cm^{-1}.

The 427 nm peak due to curcumin in

aqueous solution is attributed to the $n \rightarrow \pi^*$ transition of curcumin. A past study of the stoichiometry of various metals with curcumin showed different ratio of 1:1, 1:2, and most 1:2 complexes were arranged in nearly planar form (Shen *et al.*, 2005). A 361 nm band (Figure 2) is attributed to the curcumin →Cu(II) charge transfer band (Tønnesen and Karlsen, 1992). This study corresponds to Barik *et al.* (2007) in which the β–diketone of curcumin chelated with copper in DMSO and Zhao *et al.* (2005) showing a large blue shift of the β–diketone of trans-ASTX with copper from 480 nm to 373 nm in ethanol.

Complex Stoichiometry of Curcumin and Copper(II) in Aqueous Solution at pH 5.5

In this study, the stoichiometry of the complex was determined by using the molar ratio method. Increasing the copper(II) ion resulted in a decrease of absorbance at 427 nm (Figure 3), which showed inflection at [Cu]/[curcumin] = 0.45, and indicates stoichiometric of Cu(II) to curcumin of 1:2 for the complex.

The diffuse reflectance UV-Vis spectrum of the solid crystal of Cu(II)-curcumin (Figure 4) showed 3 major absorption bands with wavelength maxima at 316 nm (band I), 472 nm (band II), and 701 nm (band III), respectively. An intense band I which occurred in the UV region is considered to be associated with the absorption due to the $\pi \rightarrow \pi^*$ transition of curcumin, and band II at 400-550 nm was due to the $n \rightarrow \pi^*$ transition of curcumin ligand (Annaraj *et al.* 2004; Barik *et al.*, 2007). A broad band III centered on 701 nm is usually assigned to a *d-d* transition band (Welch and Chapman, 1993), indicating that the solid was a compound of copper(II) with curcumin. Cu(II) was present in the complex and coordinated to the curcumin ligand (Figure 4).

The IR spectra of the curcumin copper(II) complex showed the υ (C=O) a large intense band at 1509 cm^{-1} which is different from band at 1513 cm^{-1} and 1588 cm^{-1} of free curcumin (Figures 5-6). The copper(II) curcumin complex showed a symmetrically large broad band at 3448 cm^{-1} of O-H stretching indicating a symmetrical structure of complex compound (Shen *et al.*, 2005). The υ (C-O-Cu) band of the complex at 478 cm^{-1} suggested that curcumin forms a complex with copper(II) and using β-diketone part as the binding site (Barik *et al.*, 2007). Figure 7 showed the proposed structure of the $Cu(Cur)_2$ complex in aqueous solution and in solid state.

Conclusions

The interaction of curcumin and Cu(II) was studied by UV-Vis spectroscopy and the significant large hypsochromic shift was

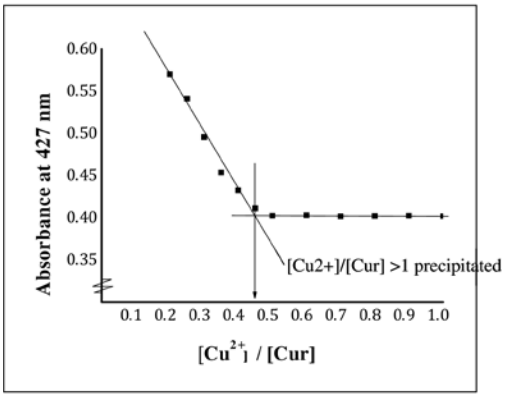


Figure 3. Absorbance versus [Cu]/[curcumin] molar ratio plots at 427 nm at pH 5.5

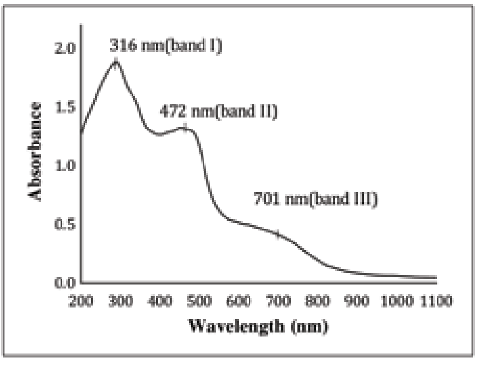


Figure 4. The diffuse reflectance UV-Vis spectrum of solid crystal of Cu-curcumin complex

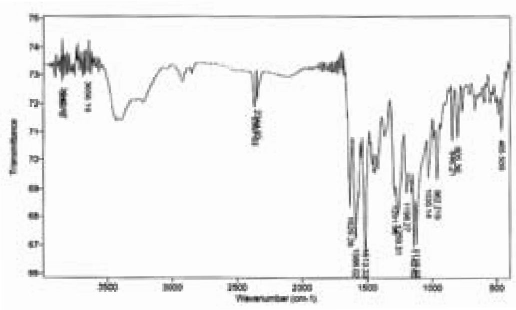


Figure 5. FT-IR spectrum of curcumin alone

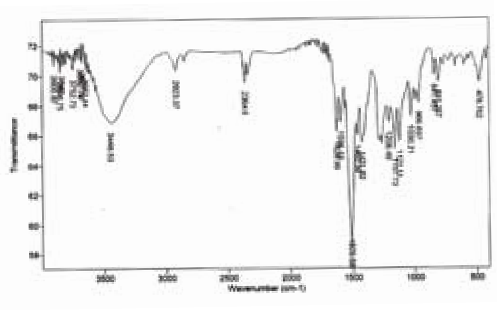
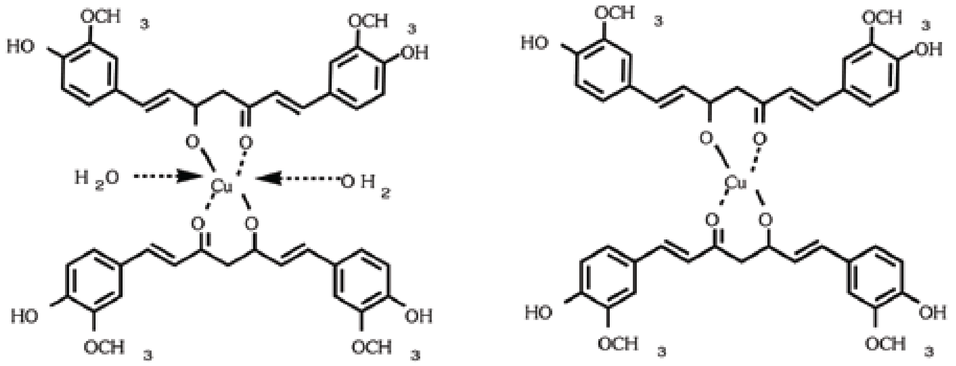


Figure 6. FT-IR spectrum of of the Cu (curcumin)$_2$ complex



aqueous solution

aqueous solution

Figure 7. The proposed structure of the Cu(curcumin)$_2$ complexes

observed for the absorption band of the Cu(II)-curcumin complex. Using the molar ratio method, it was found that the stoichiometric composition of the complex in aqueous solution was Cu(curcumin)$_2$. The diffuse reflectance UV-Vis spectra and IR spectra indicated that the complex was reasonably stable both in aqueous solution and in solid state.

Acknowledgements

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