

<Communication>

Study on the Interaction between Curcumin and Ethylamines by Absorption and Fluorescence Spectroscopic Techniques

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Abstract: The interaction between curcumin(1,7-bis[4-hydroxy-3-methoxyphenyl]-1,6-heptadiene-3,5-dione) and ethylamines was studied in DMSO:H₂O(5:1, v/v) using absorption and fluorescence measurements. The association constant, K_{ass} , and the Stern-Volmer constants were calculated by the Benesi-Hildebrand and Stern-Volmer equation, respectively. Curcumin displayed marked UV-vis absorption changes and highly responsive fluorescence quenching in the presence of ethylamine and the quenching ability was enhanced almost linearly with the concentration of ethylamines. The apparent Stern-Volmer constant measured for the ethylamine-curcumin system was about 1000-fold greater than that of the triethylamine-curcumin system, indicating considerably greater quenching efficiency of ethylamines.

Keywords: curcumin, ethylamines, Benesi-Hildebrand, Stern-Volmer, fluorescence, absorption

1. Introduction

Curcumin is a yellow compound isolated from the root of *Curcuma longa* rhizomes and has been widely used as food additive in India and China for hundreds of years. Recently, curcumin has attracted much interest because several studies have demonstrated that this natural polyphenol has anti-inflammatory^{1,2}, antioxidant^{1,3,4}, antiviral⁵, antitumor⁶ and free radical scavenger properties⁷.

Single crystal X-ray diffraction studies⁸ showed that in curcumin, the planar keto-enol form is stabilized by strong intramolecular-bonding between the hydroxyl and keto moieties. In a structural analysis of curcumin using Density Functional Theory(DFT), Kolev et al.⁹ showed that, according to the B3LYP/6-311G* calculation, the planar enol form was more stable than the nonpolar diketo form.

A wide range of amines are pollutants in industrial and manufacturing areas because they are extensively used in the preparation of fertilizer, herbicides, pharmaceuticals, surfactants, rubber latex, biological buffer substances and colorants.

Turner et al. investigated the ability of a hemithioacetal-based polymer to react with primary amines and to form a fluorescent isoindole complex¹⁰.

Among various types of amines, ethylamine is a colorless, flammable liquid and an ammonia-like odor. It has an air odor threshold concentration of 0.95ppm of air. Inhalation exposure to ethylamine may cause eye irritation, tearing, conjunctivitis, and corneal edema.

Qiu et al. worked with a supramolecular metal-organic frame work(MOF) constructed by two-dimensional infinite coordination polymers, [Zn(1,4-benzenedicarboxyate)-(H₂O)]_m, and they evaluated the fluorescence response of the MOF nanosheets in the presence of ethylamine solution¹¹.

We have previously reported the colorimetric signaling of mono-, di-, and triethylamine based on intermolecular CT interaction¹² and have also described the naked eye sensing of ethylamine gas based on n- π intermolecular CT interaction using 2-chloro-3,5-dinitrobenzotrifluoride as an acceptor¹³. In addition, the effect of acid/base on the absorption and emission of curcumin was investigated¹⁴.

In this paper, we attempted to investigate the interaction between curcumin and ethylamines by spectro-

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spectroscopy. The association constant and the Stern-Volmer constants were calculated by the Benesi-Hildebrand and Stern-Volmer equation.

2. Results and Discussions

2.1 The absorption spectrum

Figure 1 shows the changes in the absorption spectrum of curcumin upon addition of the ethylamines.

Upon addition of ethylamines, the band at 410nm progressively decreased, whilst a new band with a peak at 550nm formed, resulting in a red colored solution.

The maximum absorption band displayed a bathochromic shift of 140nm. The presence of an isobestic point at 455nm indicates that only two species coexist at the equilibrium. Upon addition of HCl, the red colored solution of curcumin became gradually yellow and recovered the initial state.

2.2 The association constant K_{ass} by the Benesi-Hildebrand

The stoichiometry and association constant of the curcumin-ethylamine complex are established by use of the Benesi-Hildebrand method¹⁵⁻¹⁸.

When assuming a 1:1 association between curcumin and ethylamines, the Benesi-Hildebrand expression(1) is given as follows:

$$\frac{1}{A-A_0} = \frac{1}{K_{ass}(A_{max}-A_0)[ethylamines]} + \frac{1}{A_{max}-A_0} \dots (1)$$

where,

A : the absorbance obtained with anion

A_0 : the absorbance of curcumin

A_{max} : the absorbance obtained with excess amount of ethylamines

[ethylamine] : the concentration of the ethylamines

According to the linear Benesi-Hildebrand expression, the measured absorbance $[1/(A-A_0)]$ at 550nm varied as the function of $1/[ethylamines]$ in a linear relationship.

As depicted in Figure 2, plot of $1/(A-A_0)$ versus $1/[ethylamines]$ presents a linear relationship, which indicates that the interaction of curcumin with ethylamine, diethylamine and triethylamine is in a 1:1 stoichiometry having the binding constant of $K_{ass} = 1.96 \times 10^4$, 2.86×10^2 and $3.22 M^{-1}$ for ethylamine, diethylamine and triethylamine, respectively, which indicates that the reaction occurs more readily in fo-

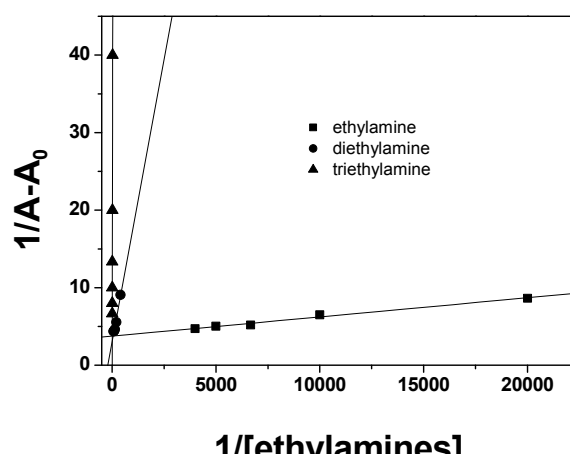


Figure 2. Benesi-Hildebrand plot(absorbance at 550nm) of curcumin assuming 1:1 binding stoichiometry with (■) ethylamine, (●) diethylamine, (▲) triethylamine.

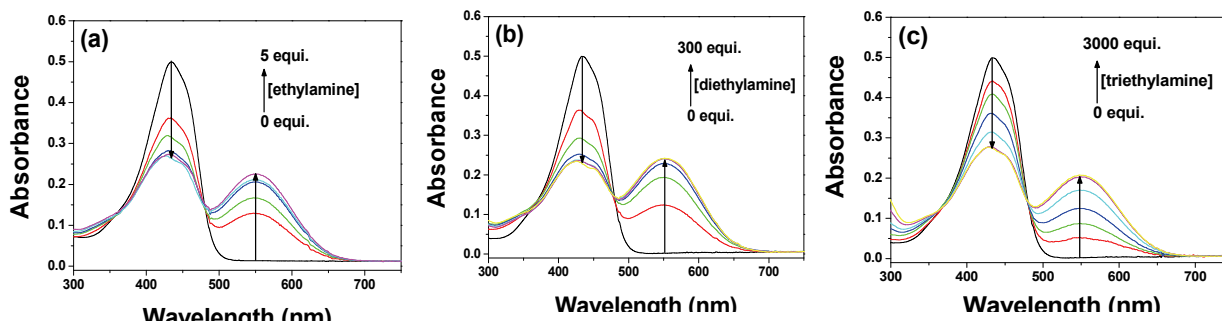


Figure 1. UV-vis spectra changes of curcumin($1 \times 10^{-5} M$) upon addition of (a) ethylamine, (b) diethylamine, (c) triethylamine in DMSO:H₂O(5:1, v/v).

llowing order: ethylamine > diethylamine > triethylamine.

2.3 Chemical structure of curcumin

Chemically, curcumin is diferuloylmethane molecule, containing two ferulic acid residues linked by a methylene bridge, as shown in Figure 3.

While the beta-diketone moiety undergoes keto-enol tautomerization, curcumin exists in solutions predominantly in the enol form¹⁹.

The curcumin molecules are deprotonated by added ethylamines thus giving rise to red solutions.

A theoretical study in agreement with the formula

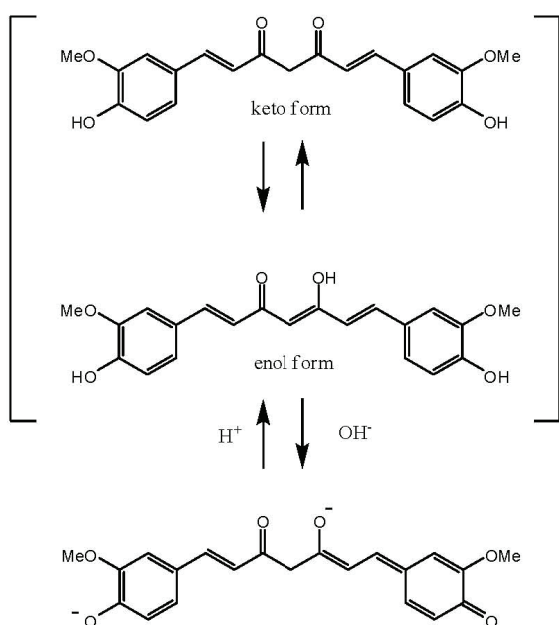


Figure 3. Chemical structure of keto, enol and dianion forms of curcumin.

shown in the Figure 3 has suggested the formation of a dianion in basic media²⁰.

2.4 Fluorescence intensity

The effect of the ethylamines on curcumin fluorescence intensity is shown in Figure 4.

The fluorescence intensity of curcumin also decreases upon addition of ethylamines without obvious changes in emission wavelength.

2.5 The Stern-Volmer constants by the Stern-Volmer equation

The fluorescence quenching was described by the Stern-Volmer equation(2):

$$\frac{I_0}{I} = 1 + K_{ass}[\text{ethylamines}] \dots \dots \dots (2)$$

where,

I, I_0 : the fluorescence intensities of the curcumin in the absence and presence of ethylamines

$[\text{ethylamine}]$: the concentration of the ethylamines

Figure 5 shows the Stern-Volmer plots describing the I_0/I as a function of ethylamine concentration. The coefficient of the linear fits are 0.999, 0.979 and 0.989 for ethylamine, diethylamine and triethylamine, respectively.

It indicated that the quenching ability of ethylamines to curcumin is enhanced almost linearly with

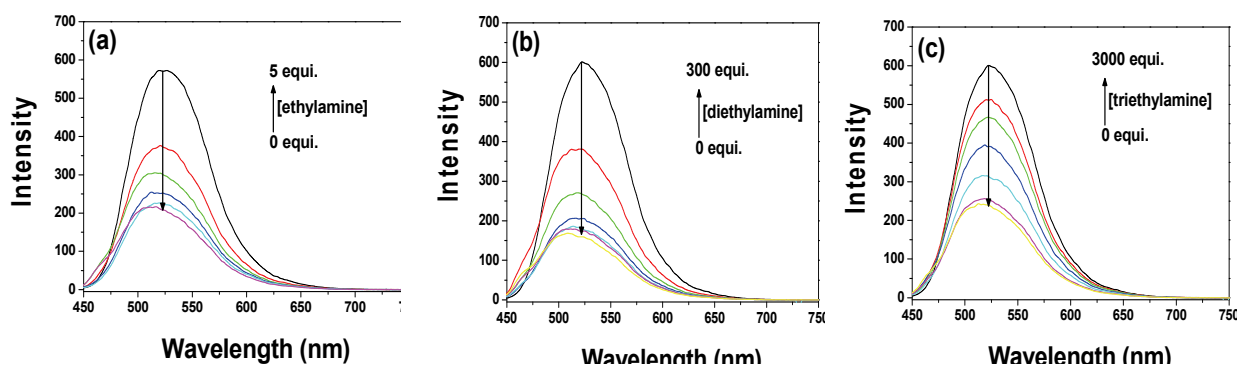


Figure 4. Fluorescence spectra of curcumin(1x10⁻⁵M) upon addition of (a) ethylamine, (b) diethylamine, (c) triethylamine in DMSO:H₂O(5:1, v/v).

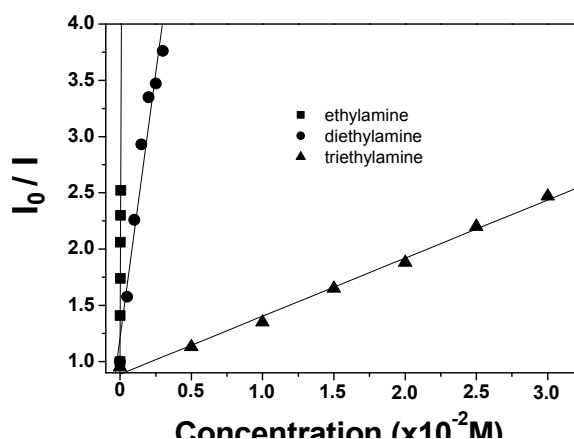


Figure 5. Stern-Volmer plots for the fluorescence quenching of curcumin (1×10^{-5} M) by (■) ethylamine, (●) diethylamine, (▲) triethylamine at 20°C . $\lambda_{\text{ex}} = 430\text{nm}$.

the concentration of ethylamines.

The apparent Stern-Volmer constant measured for the ethylamine-curcumin system was $K_{\text{sv}} = 3.08 \times 10^4$ which is about 1000 fold greater than for the triethylamine-curcumin system ($K_{\text{sv}} = 5.16$), indicating considerably greater quenching efficiency of ethylamine.

Acknowledgements

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