



Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

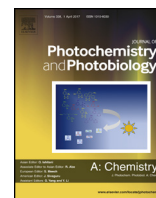
journal homepage: www.elsevier.com/locate/jphotochem

Photo-physical behaviors of various active forms of curcumin in polar and low polar environments

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ARTICLE INFO

Article history:

Received 4 June 2017

Received in revised form 27 July 2017

Accepted 18 August 2017

Available online 24 August 2017

Keywords:

Curcumin

Enol

Diketone

Deprotonated form

Solvent polarity

Time-dependent density functional theory

ABSTRACT

The naturally occurring yellow-orange curcumin with wide applications in medical, biological and chemical phenomena have drawn considerable attention during the last years. The properties of molecular surrounding media can modify its various characteristics. In this paper, tautomerism of curcumin was investigated in the wide variety groups of solvents. In this case, photo-physical properties of curcumin in enol, diketone and deprotonated forms were investigated separately in polar and low polar solvents at room temperature by spectroscopic and theoretical techniques. Moreover, the most probable excitations of possible forms of curcumin in different solvent media were investigated by time-dependent density functional theory. Our results indicated that photo-physical behaviors of these forms depend strongly on the solvent polarity. In order to investigate the interactional behaviors of various forms of curcumin, we used the concept of linear solvation energy relationship proposed by Kamlet and Taft. Furthermore, according to the obtained results, the excited state dipole moments of various forms of curcumin with different resonance structures are higher than those in the ground state that increase the probability of charge transfer mechanism.

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1. Introduction

Curcumin or 1, 7-bis-(4-hydroxy-3-methoxy phenyl)-1, 6-heptadiene-2, 5-dione is extracted from the rhizomes of *Curcuma longa* and known as turmeric [1–3]. This compound belongs to β -diketonic group which its conformation highly depends on the solvent polarity and can show tautomerism process in solvent media. Despite different theoretical and experimental investigations on the spectral properties of enol form of curcumin, the studies on the photo-physical characteristics of its other forms are limited [4–7].

At recent years, curcumin has been considered due to its unique properties as anti-inflammatory [8,9], antioxidant [10], anticancer [11] and antibacterial [12] species. Indeed, interactions between curcumin molecules and their surrounding environment play an important role in the biological systems. Therefore, understanding about different types of interactions between this molecule and its surrounding media is clearly important in describing many of its

chemical and physical behaviors. These interactions can be divided into non-specific (dielectric enrichment) and specific (hydrogen bonding and intermolecular charge transfer) interactions [13,14].

Curcumin is insoluble in water but dissolves in polar solvents such as methanol. The studies have shown that photo-chemical and photo-physical properties of curcumin depend on the polarity of environment. Solvent effects can be investigated by means of solvent polarity scales and solvatochromic parameters [15]. There are many different chemical and physical processes that individual solvent polarity parameters cannot describe completely the nature and degree of solute-solvent interactions. Therefore, multi-parameter solvent polarity scales are used commonly. This method is based on linear free-energy relationship concept and formulated as Kamlet-Abboud-Taft equation [15,16].

$$\nu = \nu_0 + a\alpha + b\beta + s\pi^* \quad (1)$$

π^* , β and α indicate dipolarity/polarizability [17], hydrogen bond acceptor (HBA) basicity [18], and hydrogen bond donor (HBD) acidity [19], respectively. ν_0 is also a regression value for the solute polarity in the reference solvent. The remaining parameters (a , b and s coefficients) are acquired from employing multi-linear regression analysis. These coefficients measure the relative

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contribution of each solvent polarity parameters in photo-physical characteristics of the samples.

Recently, density functional theory (DFT) with appropriate results and reasonable accuracy has provided valuable opportunity for quantum chemical study of molecules and crystals. Along with various applications of DFT for synthetic and natural materials, several DFT studies have been done for description of photo-physical properties of organic molecules [20–25]. Specially, some of DFT studies have been focused on curcumin molecule [26–30]. These studies emphasized on the existence of enol-keto tautomerism and more thermodynamic stability of enol form. In this case, the obtaining results about molecular vertical electronic excitations and their orbitals can give useful information about charge transfer mechanism throughout these excitations. For this purpose, time-dependent DFT (TDDFT) method is an appropriate option [31]. Unfortunately, it has not been reported a comprehensive TDDFT study on the possible various forms of curcumin in polar and low-polar solvents.

In this experimental work, the solvent polarity effects on the photo-physical characteristics of enol, diketone and deprotonated forms of curcumin are investigated. Then, spectral characteristics of this sample are investigated in polar and low polar solvents, separately. UV–vis absorption and emission spectra in solvents with different polarities and obtained spectral shifts are also used for measuring dipole moments of ground and excited states. Beside these experimental studies, TDDFT calculations are performed for possible forms of curcumin in polar and low polar solvents, in order to understand more about vertical excitations and related charge transfer during these phenomena. The Obtained quantitatively results via Kamlet-Abboud-Taft equation and molecular charge distribution characteristics in polar and low polar solvents will give important information about solute-solvent specific and non-specific interactions that can be useful in biological systems.

2. Experimental

2.1. Materials

Curcumin (Table 1) in the form of powder was purchased from Merck and used without further purification. All of the solvents used in this work were selected with highest available purity from Merck as well and the spectroscopic solvent polarity parameters of them were listed in Table 2 [15,32].

2.2. Absorption and emission spectroscopy

First, the solution of sample with a low concentration was prepared in various solvents. Then Double beam Shimadzu UV-2450 Scan Spectrophotometer and JASCO FP-6200 Spectrofluorometer were used for recording the absorption and fluorescence spectra, respectively. Spectroscopic measurements were also done with quartz cuvettes with 1 cm optical length.

Table 2

Spectroscopic polarity parameters, physical properties and polarity functions of employed solvents.

solvent	ϵ_r	n	α	β	π^*	$f(\epsilon, n) + 2g(n)$	$f(\epsilon, n)$
DMSO	46.68	1.479	0	0.76	1	1.488	0.84
DMF	38	1.43	0	0.69	0.88	1.422	0.838
Ethylene glycol	37	1.43	0.9	0.52	0.92	1.419	0.836
Methanol	32.7	1.329	0.98	0.66	0.6	1.302	0.854
Ethanol	24.5	1.361	0.86	0.75	0.54	1.304	0.812
Acetone	21.01	1.359	0.08	0.48	0.62	1.281	0.792
2-propanol	19.92	1.377	0.76	0.84	0.48	1.291	0.778
1-Butanol	17.5	1.399	0.84	0.84	0.47	1.292	0.75
1-Hexanol	13	1.418	0.67	0.94	0.4	1.253	0.686
Dichloromethane	8.93	1.424	0.13	0.1	0.73	1.165	0.59
1-Decanol	8	1.437	0.7	0.85	0.45	1.145	0.552
THF	7.58	1.407	0	0.55	0.58	1.102	0.549
Chloroform	4.81	1.445	0.2	0.1	0.69	0.974	0.371
Diethyl ether	4.34	1.349	0	0.47	0.24	0.854	0.379
Toluene	2.38	1.496	0	0.11	0.49	0.699	0.029
Benzene	2.28	1.501	0	0.1	0.59	0.681	0.005
CCl ₄	2.24	1.46	0	0.1	0.21	0.646	0.023
1,4-Dioxane	2.22	1.42	0	0.37	0.49	0.615	0.045
Cyclohexane	2.02	1.426	0	0	0	0.574	-0.003
Isooctane	1.94	1.391	0	0	0.01	0.532	0.001
n-Heptane	1.92	1.388	0	0	-0.08	0.526	-0.001

2.3. Estimation of dipole moments

UV–vis absorption and emission spectra in solvents with different polarities and obtained spectral shifts of samples provide a simple technique for measuring dipole moments of ground and excited states. The study of this parameter of a molecule is an important property that provides information on the electronic and geometrical structure of the molecule in ground and excited states.

Kawaski and co-workers [33,34] used quantum mechanical second order perturbation theory in order to obtain a simple expression for relation between absorption (ν_a) and fluorescence (ν_f) band shifts in solvents with different polarities. Such solvent dependent variations for the difference and sum of absorption, ν_a , and fluorescence, ν_f , maxima (in cm^{-1}) have been defined by following independent equations:

$$\nu_a - \nu_f = m_1 f(\epsilon, n) + \text{const.} \quad (2)$$

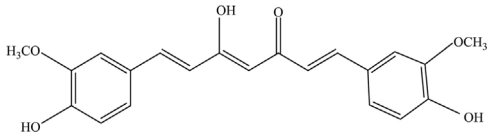
$$\nu_a + \nu_f = -m_2 [f(\epsilon, n) + 2g(n)] + \text{const.} \quad (3)$$

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \quad (4)$$

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \quad (5)$$

Table 1

The structure of used sample and its molecular weight and density.

Molecular structure	Molecular weight (g/mol)	$\rho(\text{g/cm}^3)$	Molecular name
	368.38	1.374	Curcumin

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