



Spectral behavior and computational studies of fuchsin in various solvents



J.P. Graham^{a,*}, M.A. Rauf^b, S. Hisaindee^b, A. Alzamy^b

^a Department of Environmental Science, Sligo Institute of Technology, Sligo, Ireland

^b Department of Chemistry, PO Box 15551, UAE University, Al-Ain, UAE

ARTICLE INFO

Article history:

Received 27 February 2017

Received in revised form 26 April 2017

Accepted 30 April 2017

Available online 04 May 2017

Keywords:

Fuchsin

Spectroscopy

UV/Vis

Multivariate analysis

DFT

ABSTRACT

Absorption spectra of fuchsin were measured in various solvents. Two solvent-dependent absorption maxima were observed between 511 and 538 nm and 552–567 nm. Time-dependent density functional theoretical calculations assigned the transitions between the 510–540 nm and 540–557 nm to π - π^* transitions between the HOMO-1 to LUMO and HOMO to LUMO respectively. The absorption data were analyzed using the Kamlet-Aboud-Taft, Catalan and Katritzky models of solvatochromic behavior. The Catalan model was found to provide the best correlation with the experimental absorption maxima, followed by the Katritzky model. Both the Catalan and Katritzky models suggest that polarizability of the solvent is the primary factor affecting the transition energy.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The presence of solute in a given solvent environment can give rise to various interactions which may be intra or intermolecular in nature. These interactions play an important role in many fields of chemistry such as organic and biochemical reactions, supramolecular chemistry, solution chemistry and drug interactions. These interactions are the basis of understanding the various aspects of physical, chemical and biological processes including formation of aggregates and micelles. The physico-chemical nature and the degree of intermolecular interactions are highly dependent on the type of the solvent which interacts with the solute. This results in various types of solute-solute and solute-solvent interactions such as donor-acceptor, dipole-dipole, H-bonding and other cohesive forces. These interactions induce changes in the electronic transitions of a solute in a given solution (commonly known as solvatochromism).

Spectroscopic studies of compounds in various solvents can provide important information towards understanding solvation interactions and photophysical behavior. A shift in absorption wavelength of a probe molecule in various solvents reveals information about the solute-solvent interactions [1–6]. The spectral shifts in various solvents originate from either nonspecific (dielectric enrichment) or specific (e.g. hydrogen-bonding) solute-solvent interactions, and are known as solvatochromism. The electronic structure of the probe and solvent

molecules contributes to the intermolecular solute-solvent interactions in the ground and the first excited states. Positive or negative shifts in λ_{\max} may be observed, which depends on the relative stabilization of the ground and excited states. Spectroscopic methods based on absorption spectra give valuable information on the contribution of different types of solute-solvent interactions using multi-parameter solvent polarity scales [7–10]. These changes have been used to understand various physical-organic reactions of probe molecules, which are important in different fields of pure and applied chemistry [11–15].

Fuchsin, also known as Magenta II, is a triaminotriphenylmethane dye. The structure of fuchsin is shown in Fig. 1. The molecule is biologically active and a suspected carcinogen [16]. Fuchsin is used as a dye in the textiles industry and also has applications in chemical analysis [17] and as a microbiological stain [18]. Fuchsin's derivative acid fuchsin, which is synthesized by the addition of sulfonic groups, is used in histology as a stain for distinguishing different tissue types [19]. Recently, the degradation and removal of fuchsin from aqueous solutions has been a topic of considerable interest [20–23]. In this work, spectral features of fuchsin in different solvents were studied in order to understand the effect of specific and non-specific interactions on solvation of this molecule. Spectral data were analyzed using three different models and the suitability of each model to describing the behavior of fuchsin in various solvents is assessed.

Recently, computational methods such as Density Functional Theory (DFT) calculations [11,24,25] have been used as tools to support experimental studies of structure, intermolecular interactions and spectra. In this work, DFT calculations are used to optimize the structure of fuchsin. Time-Dependent DFT calculations on the optimized structure are then

* Corresponding author.

E-mail address: Graham.JohnP@itsligo.ie (J.P. Graham).

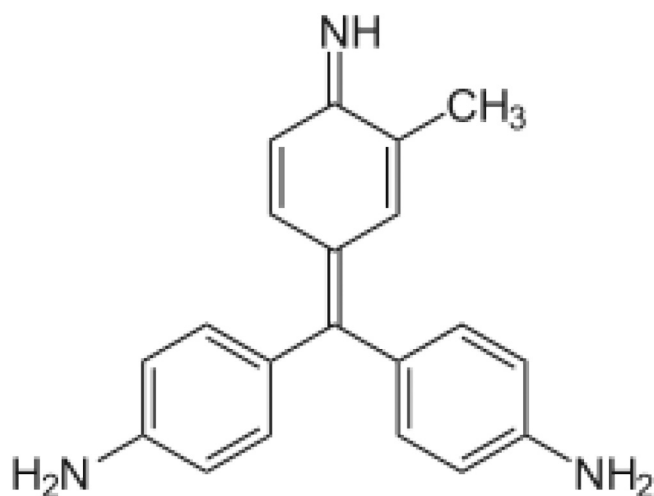


Fig. 1. Molecular structure of fuchsin.

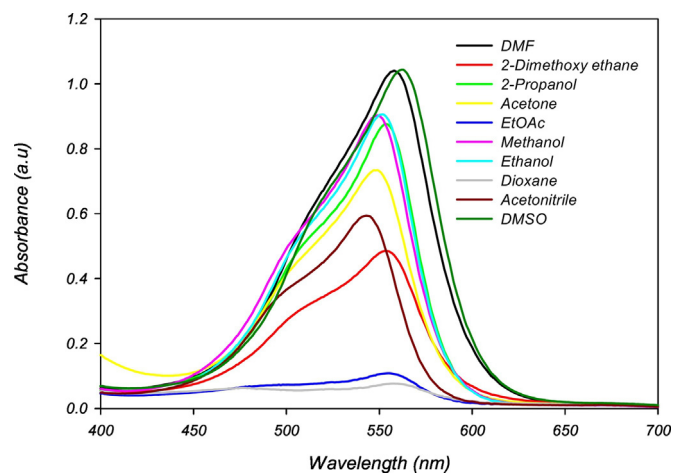


Fig. 2. Absorption spectra of fuchsin in various solvents.

employed to investigate the nature of the visible-region electronic transitions of fuchsin.

2. Experimental

All the solvents used in this work, namely, dimethyl formamide, dimethyl sulfoxide, 1,2-dimethoxy ethane, acetone, acetonitrile, ethanol, methanol, 2-propanol, dioxane and ethyl acetate were purchased from Aldrich and were of analytical grade. Prior to use, they were dried over 4 Å molecular sieves for a week. The working solutions in a given solvent were prepared by dilution from the stock solutions of fuchsin. The final concentration of the solutions was maintained at 70 μM in all cases. CARY 50 UV/Vis spectrophotometer was used to obtain the absorption spectrum of each solution using a 1 cm quartz cell. The absorption values were ascertained to fall in the linear range of Lambert-Beer's law. Absorption maxima for the two low energy transitions were resolved by fitting Gaussian functions to the experimental spectra using the Origin 9.0 program (Table 1). Multivariate regression using MS-Excel was performed to fit observed absorption spectra to the Kamlet-Aboud-Taft, Catalan and Katritzky models of solvatochromic behavior.

3. Computational details

All calculations were performed using the Gaussian 09 program [26]. The structure of fuchsin was optimized without symmetry constraints using the B3LYP functional and 6–311 + G(d,p) basis set [27]. The optimized structure was confirmed to be energy minimum through vibrational frequency calculations. The electronic spectrum of fuchsin was calculated by TDDFT using the CAM-B3LYP functional and 6–311 + G(d,p) basis set [28]. Solvent effects were modeled using the PCM model with the default solvent parameters of Gaussian 09 [29].

4. Results and discussion

Absorption spectra of fuchsin were recorded in various solvents of different polarity at room temperature (25 ± 2 °C) and are shown in Fig. 2. The difference in spectral behavior indicates an interaction between the probe molecule and the solvent environment. These changes were correlated with various solvent parameters and analyzed by the Kamlet-Aboud-Taft, Catalan and Katritzky models.

4.1. DFT calculations

Time Dependent DFT calculations using the CAM-B3LYP functional performed in the gas phase and using the PCM model of solvation overestimate the transition energy for fuchsin. The experimentally observed absorption in the region 543–562 nm is assigned to the HOMO \rightarrow LUMO transition which is calculated to occur between 405 and 410 nm using the PCM model for the solvents studied. The transition is $\pi \rightarrow \pi^*$ in nature as illustrated by the isosurfaces for the HOMO and LUMO given in Fig. 3. No significant correlation for solvent effects between experimental absorption maxima and those calculated using the PCM model for various solvents was observed. The calculated dipole moment for fuchsin in the ground state is 7.05 D and that for the first excited state is 8.71 D. The higher energy transition observed between 511 and 538 nm is assigned to the HOMO-1 \rightarrow LUMO transition, which is calculated to occur between 314 and 326 nm. The calculations indicate this transition should have an oscillator strength of approximately 0.43, compared to 1.06 for the HOMO \rightarrow LUMO transition, consistent with the experimental spectra. The dipole moment of this second excited state is calculated to be 14.3 D. This large increase in dipole moment indicates significant charge transfer character and is consistent with the difference in spatial distribution of the LUMO and HOMO-1 orbital isosurfaces (Fig. 4).

Table 1
Experimental absorption data of fuchsin along with solvent parameters of the Katritzky model.

Solvent	$\lambda_{\text{abs}}(1)$ (nm)	$\nu_{\text{abs}}(1)$ (cm^{-1})	$\lambda_{\text{abs}}(2)$ (nm)	$\nu_{\text{abs}}(2)$ (cm^{-1})	ϵ	n	$E_T(30)$
Dimethyl formamide	562.4	17,780.9	534.7	18,702.1	36.7	1.431	43.2
1,2-Dimethoxy ethane	557.5	17,937.2	525.6	19,025.9	7.2	1.354	51.7
2-Propanol	556.5	17,969.5	522.2	19,149.8	17.9	1.377	48.4
Acetone	551.5	18,132.4	516.4	19,364.8	20.7	1.359	42.2
Ethyl acetate	556.0	17,985.6	517.0	19,342.4	6.02	1.372	38.1
Methanol	552.8	18,089.7	519.6	19,245.6	32.7	1.326	55.4
Ethanol	554.9	18,021.3	522.2	19,149.8	24.5	1.359	51.9
Dioxane	558.7	17,898.7	524.4	19,069.4	2.25	1.422	36
Acetonitrile	546.2	18,308.3	511.0	19,569.5	37.5	1.344	45.6
Dimethyl sulfoxide	566.6	17,649.1	538.5	18,570.1	46.7	1.476	45.1

Download English Version:

<https://daneshyari.com/en/article/5408945>

Download Persian Version:

<https://daneshyari.com/article/5408945>

[Daneshyari.com](https://daneshyari.com)