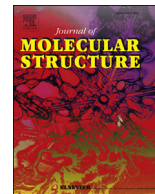




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Solvatochromic study on chlortetracycline in binary and ternary solutions

G. Oanca^a, C. Nadejde^a, N. Fifere^b, A. Gritco Todirascu^a, D. Creanga^{a,*}, D. Dorohoi^a, Jernej Stare^c^a University "Alexandru Ioan Cuza", Faculty of Physics, Iasi, Romania^b "P. Poni" Institute of Macromolecular Chemistry, Iasi, Romania^c National Institute of Chemistry, Ljubljana, Slovenia

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ABSTRACT

Molecular modeling of chlortetracycline was performed based on DFT approach implemented in Gaussian software. The differences between simulated electronic spectra and those recorded experimentally were analyzed. Experimental investigations were carried out using electronic absorption spectra as well as fluorescence ones. Spectral shift to the changing of solvent polarity was measured in various solvents (binary solutions) and graphical correlations were evidenced between the electronic band wavenumbers and some theoretical functions on solvent electro-optical macroscopic parameters (refractive index and dielectric constant); interpretation was done based on the solvatochromic theory dedicated to universal interaction forces. Fluorescence spectra, studied in mixture of solvents (ternary solutions), evidenced also specific interactions in water-alcohols not considered in the classical solvatochromic approach.

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1. Introduction

Previous literature sources let us know that UV–Vis spectroscopy methods were reported as useful in the detection of food loading with tetracycline derivatives; HPLC/UV–Vis method was applied for the identification of oxytetracycline, tetracycline and chlortetracycline in honey [1].

Simple UV–Vis investigation of honey in methanol solutions allowed chlortetracycline and oxytetracycline content assay based on the absorption at 319 and respectively 364 nm [2]. Fluorescence spectroscopy was found suitable for the study of the interaction of trypsin (proteolytic enzyme, excreted by the pancreas) with chlortetracycline that occurs naturally because of pharmaceutically polluted environment that seems to become a real threatening for the health of human and animals [3].

UVVisible absorption spectrometry was found adequate for the determination of dissociation constants of tetracyclines in acetonitrile–water ternary solutions which are very important for liquid chromatography and capillary electrophoresis that use such

solvent mixtures [4]. Other studies were focused on spectral assay of tetracycline compounds related to their stability and bioactivity [5,6].

2. Theoretical background

Solute–solvent interactions in various solvents were investigated according to mathematical approaches proposed for describing universal intermolecular forces developed in diluted solutions.

Widely used solvatochromic theories [7–10] were applied in previous studies on various molecules used as spectral probes for the investigation of intermolecular forces diluted solutions. Brief presentation of such mathematical approach [11] can be done as follows.

According to [11] the total spectral shift $\Delta\tilde{\nu}$ of a solute molecule's electronic absorption band (EAB) when passing from isolate state (gas) to solution, can be written as the sum of the contributions of main type of universal solute–solvent interactions (Eq. (1)) – the indexes “pol”, “disp”, “ind” and “or” being assigned to the main types of universal intermolecular interactions: polarization, dispersion, induction and orientation.

* Corresponding author.

E-mail address: dorina.creanga@gmail.com (D. Creanga).

$$\Delta\tilde{\nu} = \Delta\tilde{\nu}_{\text{pol}} + \Delta\tilde{\nu}_{\text{disp}} + \Delta\tilde{\nu}_{\text{ind}} + \Delta\tilde{\nu}_{\text{or}} \quad (1)$$

The four contributions of the universal solute-solvent interactions to the spectral shift depend on the solvent macroscopic parameters n (refractive index) and ϵ (dielectric constant) and thus can be grouped as follows:

$$hc\Delta\tilde{\nu} = A(n) \frac{n^2 - 1}{n^2 + 2} + B(n) \frac{\epsilon - 1}{\epsilon + 2} \quad (2)$$

$$A(n) = (\alpha_g - \alpha_e) \frac{3}{2a^3} \frac{II'}{I + I'} - \frac{he^2 f}{8\pi m_e \tilde{\nu}_0 a^3} + \frac{2n^2 + 1}{n^2 + 2} \frac{\mu_g^2 - \mu_e^2}{a^3} \quad (3)$$

$$B(n) = \frac{2n^2 + 1}{n^2 + 2} \frac{2\mu_g(\mu_g - \mu_e \cos \varphi)}{a^3} \quad (4)$$

where the term $A(n)$ (Eq. (2) and (3)) corresponds to the sum of the first two terms from the Eq. (1), describing dispersive-polarization forces while $B(n)$ (Eq. (2) and (4)) describes the orientation-induction interactions. The microscopic parameters of the solute molecule in the ground and respectively the excited state are noted as μ_g and μ_e (electric dipole moments), α_g and α_e (electric polarizabilities), while a stands for the average radius of the solute; e and m_e are the electron charge and mass, f is the oscillator strength, φ is the angle between the two dipole moment vectors and, I and I' are the ionizing potentials of the solute and the solvent molecules (Eqs. (3) and (4)). The solvent refractive index, is n , while the dielectric constant is ϵ . The quantities $A(n)$ or $B(n)$ could be estimated by statistical method (regression line), based on measured wavenumbers and known solvent macroscopic parameters.

3. Materials and methods

3.1. Quantum chemical approach

Molecular optimized structure, HOMO – LUMO eigenvalues, and dipole moment by quantum chemical simulations were done using Gaussian 09 package [12] with DFT B3LYP level of theory with 6-31G++(d,p) basis set.

UV–Vis spectra simulation was accomplished also in Gaussian 09, starting from previously found (optimized) geometry with time dependent DFT (TD-B3LYP) with 6-31++G(d,p) basis set.

For visual representation of the molecules we used VMD and Avogadro softwares.

The calculations were done on the computer cluster at National Institute of Chemistry, Ljubljana, Slovenia.

3.2. Experimental

Experimental recording was accomplished using Shimadzu UV–Vis double beam device, and spectrofluorimeter device Model LS 55 PerkinElmer; excitation light wavelength was of 340 nm.

Chlortetracycline crystallized powder (CTC) and pure solvents from Merck were used without further purification. The solvents used for recording experimental spectra and their macroscopic electro-optical parameters are given in Table 1.

4. Results and discussion

The mathematically simulated optimized geometry of chlortetracycline and electrostatic potential map are presented in Fig. 1.

The four atom rings were labeled from I to IV (Fig. 1 a) considering the further discussion of simulated orbitals. The map of

Table 1

The solvents used for recording experimental spectra.

	Solvent	n, refractive index	ϵ , dielectric constant
1	acetic acid	1.3719	6.20
2	n-pentanol	1.4100	13.90
3	isopentanol	1.4072	15.19
4	n-buthanol	1.3993	17.51
5	isobuthanol	1.3959	17.93
6	isopropanol	1.3772	18.92
7	n-propanol	1.3856	20.45
8	ethanol	1.3614	24.55
9	methanol	1.3284	32.66
12	N, N' dimethylformamide	1.4305	36.71
10	ethylene glycol	1.4318	37.70
11	water	1.3330	78.36

electrostatic potential distribution corresponding to the optimized molecular structure (Fig. 1 b) highlights higher electron cloud density toward the IV ring – the molecule edge containing chloride.

According to Fig. 2, during the chlortetracycline passing from ground state to excited one the electron density is redistributed from the atom rings I and II toward the rings III and IV. When dissolved in water the energy of HOMO and LUMO states remain negative –indicating stable structure [13], and do not change significantly while dipole moment increased with about 25% (Table 2).

In literature we found dipole moment estimation only for basic tetracycline in buffer surrounding medium (H3Tetracycline), of about 14D as resulted from lower accuracy computational approach with PM3 [14].

The maxima of visible range electronic absorption bands of chlortetracycline provided by mathematical simulation with DFT are shifted toward lower wavenumbers (from 30,600 cm^{-1} to 29,000 cm^{-1} and from 37,850 cm^{-1} to 37,500 cm^{-1}) when interactions with water surrounding molecules are considered (Fig. 3 a, b); this could be correlated also with increased dipole moment of CTC-HOH.

Experimentally recorded spectrum of chlortetracycline in water (10^{-4} M) in Fig. 4 is presented being in concordance with literature data [5].

The spectrum shape is similar to the modeled one in the visible and near UV range; but the band in the visible range shifted from 29,000 cm^{-1} at 27,170 cm^{-1} , while in the UV domain, the first band (only a shoulder at 31,800 cm^{-1} in modeled spectrum of CTC-HOH (Fig. 3 b)) shifted to 36,360 cm^{-1} and the next one, from 37,500 cm^{-1} in the modeled spectrum to 44,050 cm^{-1} in the real one. Protonation with sulfuric acid aliquot didn't change the spectrum, which usually is characteristic to $\pi-\pi^*$ bands. Band assignment is based mostly on relatively low intensity, hypsochromic shift to the solvent polarity increase, and also, as mentioned, no sensitivity to solution protonation. In Fig. 5 the comparative behavior to the change of solvent characteristics can be seen for the absorption band at the highest wavelength (lowest wavenumber).

Universal solute-solvent interactions were analyzed in diluted solutions according to solvatochromic theories for the electronic band at lowest wavenumbers, where solvent transparency criterion was fulfilled for alcohols, water and water-alcohol mixtures (binary solvents) – as presented further below.

Since the wavenumber appears to depend linearly on the solvent parameter through the function $f(\epsilon)$ it seems that orientation-induction intermolecular interactions dominate (Fig. 6 a) in the chlortetracycline solutions.

The contribution of dispersive-polarization forces were evidenced through the relatively slighter correlation of wavenumber

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