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THE INFLUENCE OF SOLVENT NATURE ON THE ELECTRONIC ABSORPTION SPECTRA OF SOME ORGANIC COMPOUNDS

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The study of solvent influence on the molecular electronic spectra of biologically active compounds is crucial for the explanation of chemical and physical properties of studied compounds, in establishing of solute-solvent interaction nature, in obtaining information on the nature of energetic transitions underlying the generation of electronic spectral bands as well as for the understanding of reaction mechanisms. The main purpose of this study was the application of spectral method for revealing the rifampicinei interaction ability with various organic solvents. From the accomplished study it was found that to the increase of the solvent refractive index the red shift also increased, as proof of the dominancy of dispersive interactions in the rifampicin diluted solutions.

Keywords: solvent influence, rifampicin, nonpolar solvent.

Studiul influenței solventului asupra spectrelor electronice moleculare ale compuşilor biologic activi este important pentru explicarea proprietăților chimice şi fizice ale compuşilor studiaţi, în stabilirea naturii de interacțiune dintre substanţă dizolvată şi solventul, în obținerea informațiilor cu privire la natura tranziției energetice care stau la baza în generarea benzilor spectrale electronice, precum şi pentru înțelegerea mecanismelor de reacție. Scopul principal al acestui studiu a fost aplicarea metodei spectrale pentru dezvăluirea capacității de interacțiune a rifampicinei cu diverşi solvenţi organici. Din studiul realizat s-a constatat că la creşterea indicelui de refracție al solventului de asemenea a crescut şi deplasarea spre roşu, ca rezultat al predominării interacțiuniilor dispersive în soluțiile diluate de rifampicină.

Cuvinte-cheie: influenţa solventului, rifampicină, solventul nepolar.

INTRODUCTION

The solid powder solvation in adequate solvents induces changes on the absorption spectra. The study of solvent influence on the molecular electronic spectra of biologically active compounds is crucial for the explanation of chemical and physical properties of studied compounds, in establishing of solute-solvent interaction nature, in obtaining information on the nature of energetic transitions underlying the generation of electronic spectral bands as well as for the understanding of reaction mechanisms. In the theory of liquid state the spectral changes have been correlated with solvent electro-optical parameters so at the present time it is possible both describing of local order in liquid solutions and estimating of electro-optical parameters of spectrally active molecules.

Since the begining of spectroscopy, the comparison of spectra recorded in isolated, gaseous state and in liquid solution has evidenced that solvent causes changes in position, intensity and shape of electronic absorption bands. This phenomenon was named "solvatochromism" by Hantzsch [1] than while Scheibe [2] showed that solvent influence on reaction rate, chemical equilibirum or absorption bands is due to the solvent capacity of solvation.

ELECTROMAGNETIC RADIATION – OPTICAL SPECTRUM

The mechanism of absorption energy is different in the ultraviolet, visible or infrared regions of electromagnetic spectrum (fig. 1) – optical radiations although the fundamental process is the absorption of certain amount of energy (quantum).

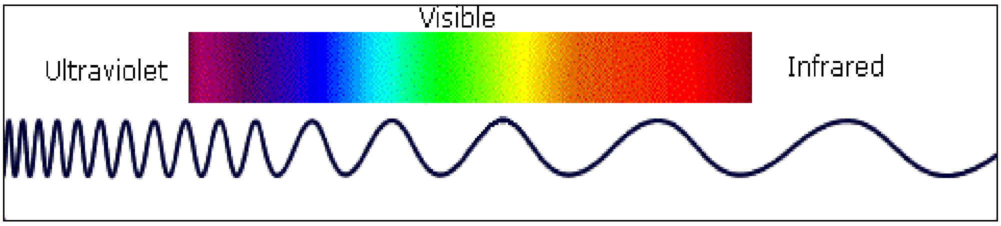

Fig. 1. Optical radiation spectrum

The energy required for the transition from a lower energy state to a higher energy one is directly related to the frequency of electromagnetic radiation that causes the transition and to the molecular structure of absorbing molecule. While energy absorption in IR domain results in nuclei vibrations and rotations (energy absorption in far IR) the absorption of UV-VIS range energy results in atoms or molecules excitation (and sometimes molecular dissociation in free radicals= photolysis); this occurs when the absorbed energy is sufficiently high to exceed the energy of formation of certain bonds among molecular atoms.

When the white light, (which contains a whole spectrum of wavelengths in visible region), interacts with an object, only some of the component radiations/wavelengths will be absorbed, while the unabsorbed radiations/wavelengths are transmitted or re-emitted (reflected); those visible radiations give the object color.

Ultraviolet and visible radiations have sufficient energy to cause transitions of the outermost or valence electrons.

THE MAIN DOMAINS OF OPTICAL ELECTROMAGNETIC SPECTRUM AND OPTICAL SPECTROSCOPY

The **ultraviolet** region (UV) extends from about 10 to 380 nm (fig. 2).

The most useful region for analytical applications is ranging from 200 to 380 nm - named the near- ultraviolet region or quartz UV region.

The **visible** (VIS) region extends from about 380 to 780 nm.

The infrared (IR) region extends from about 0.78 µm to 300 µm.

The near-infrared (IR) region extends from about 0.80µm to 2.5 µm.

The far-infrared (IR) region extends from about 2.5µm to 16 µm.

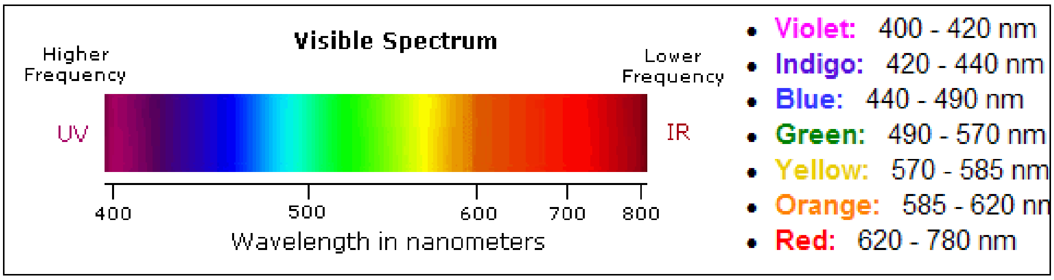

Fig. 2. Visible spectrum of electromagnetic radiation

In the electromagnetic radiation spectrum the ultraviolet domain is placed between the X-ray region and visible radiation domain, ranging between 10 and 400 nm wavelength.

There are also three sub-domain of UV spectral domain: UV-A (400-320 nm), UV-B (320-280 nm) and UV-C (280-10 nm), established in concordance with differentiated biological effects in living bodies.

Electromagnetic optical radiation used to investigate biological compounds by spectral techniques is the so called ***near UV radiation*** (with characteristic wavelenghts between ***200-400 nm***) or ***visible radiation*** (from the spectral domain between ***400-800 nm***).

Absorption spectrum of certain material is a plot/graph of the absorbed light by a studied material sample as a function of wavelength or energy or wavenumber.

Molecule total energy. The total energy of a molecule is given by:

$$\mathbf{E_{total}=E_{electronic}+E_{vibrational}+E_{rotational}}$$

At room temperature most substances are in their lowest energy or **ground state** ($\mathbf{E^{g}_{electronic}}$). When an atom, molecule (or molecular chromophore) or ion absorbs electromagnetic radiation, it is promoted to higher energy states or **excited states** ($\mathbf{E^{ex}_{electronic}}$) (where “ex” and “g” are for excited and ground state nomination).

$\mathbf{E^{ex}_{electronic}-E^{g}_{electronic}}= h\nu$ -the energy of the absorbed photon [3]; ν is the frequency of the absorbed radiation. When a molecule interacts with photons of UV or VIS radiation then electron excitation takes place to higher electronic energy level *at any of its vibrational level*. Pure rotational transitions can be caused by microwave radiation absorption.

Wave properties. The wave is described either in terms of its **wavelength (λ)**, the distance between successive maxima or minima of a wave (nm), or in terms of the **frequency (ν)**, the number of oscillation of the field per second (fig. 3).

The velocity of light, c, is given by the equation: **c= ν λ , ν** $= \frac{\nu}{c} = \frac{1}{\lambda}$.

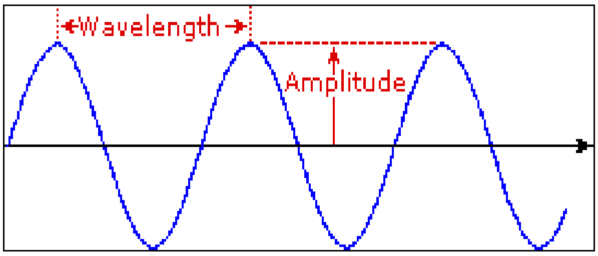

Fig. 3. Light wave physical parameters

TYPES OF ELECTRON ORBITALS: BONDING, NONBONDING, ANTIBONDING AND CORRESPONDING ELECTRON TRANSITIONS

In the ultraviolet range the highest energy transitions occur at generating spectral electronic bands: σ→σ* and π→π* types. Excited (short life time) orbitals are denoted with "*". In the visible range some lower energy transitions of π→π* type could be also found; nonbonding electronic states can be found only in some molecular structures so that n→π* transitions are rather rare (as well as n→σ* type); they can be recorded in the visible range of electromagnetic spectrum. Electronic transitions in the UV-Vis spectral range are given by an electron excitation from a valence bonding molecular orbital (MO) of σ or π type, to a non-bonding orbital of type *n* or to an antibonding molecular orbital (MO) of σ* or π* type (fig. 4).

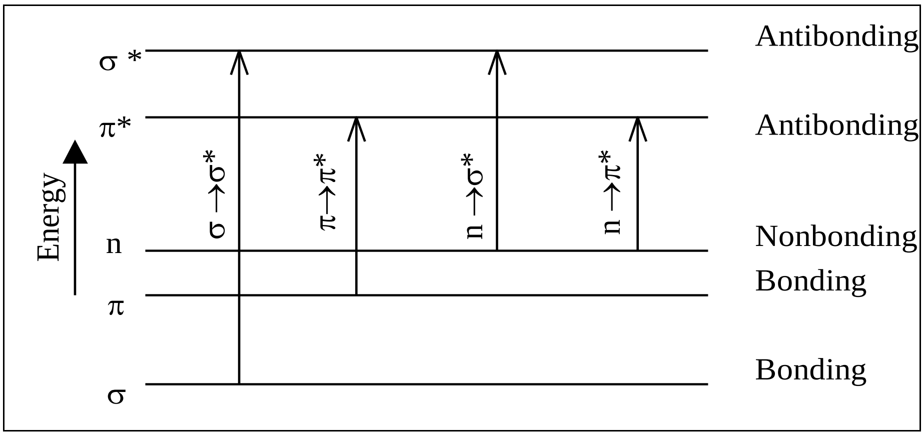

Fig. 4. Usual notations for the molecular orbitals

In the case of UV-Vis spectra of organic compounds with complex structure, the most probable is the π→π* transition which determines the promotion of an electron from *Highest Occupied Molecular Orbital* (HOMO) to the vacant *Lowest Unoccupied Molecular Orbital* (LUMO).

However other transitions can be also observed from other occupied MO to some unoccupied MO if the selection criteria for electronic transitions are fulfilled. Most general classification of electronic transitions allowed between organic compounds MOs is given bellow [4]:

– **σ→σ* transitions** for electron promotion from a σ type bonding MO to antibonding σ* MO. Since there are relatively high energy difference between σ and σ* MO (≈185kcal/mol) the occurence of such bands involves UV radiations with short wavelengths (λ≈150 nm), being situated outside of spectral recording domain. They are characteristic to alkan molecules that, due to this fact, can be used as ”transparent” solvents to record UV-Vis specta of absorbing compounds.

– **n→σ* transitions** of an *n* type electron from an electron pair non-participant to heteroatom system bonds that can be promoted from an atomic orbital to an antibonding MO type σ*. Selection rules allow such molecular transitions so that corresponding intense bands appear in the UV spectrum at short wavelenght (λ≈150-250 nm). Molecular substances characterized by *n*→σ*spectral bands are saturated organic compounds containing functional groups formed by atoms having electrons not involved in molecular bonds (halogen derivatives like ethers, alcohols, amines and thiols). These compounds are often used as solvents to record spectral bands in UV range for other molecules with intense absorption at longer wavelengths.

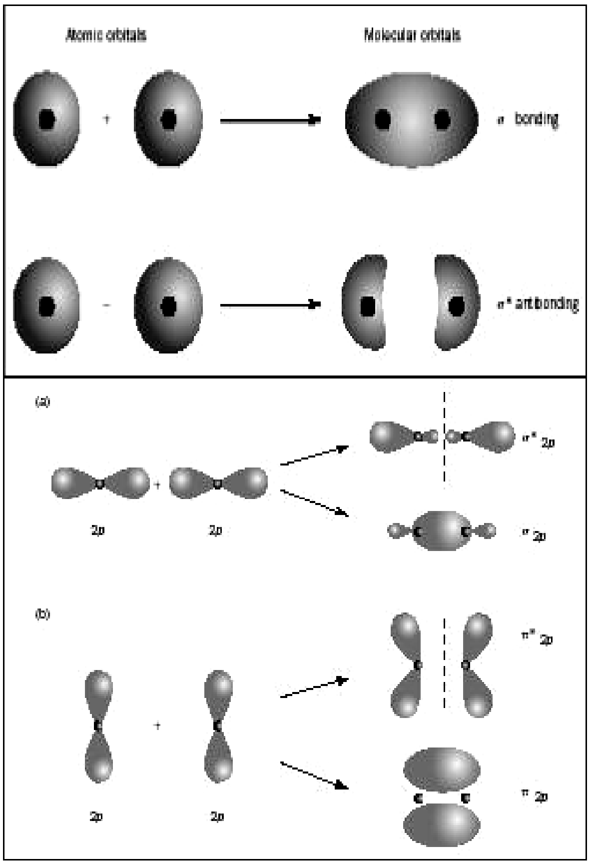

Fig. 5. Formation of molecular orbitals from atomic orbitals (according to [5])

– ***π→π**** **transitions** with promotion of bonding π MO to an non-bonding *π** MO. These transitions occure at wavelengths situated at usual measure domain (near UV and visible); they are the most studied from experimental view point. The *π→π** bands are the most intense from UV domian, characterizing organic compounds containing nonsaturated groups like alkines, alkenes aldehydes, cetones etc).

– **n→*π** transitions** involving an *n* electron from non-participating electrons to molecular bands that can be promoted from atomic orbital to antibonding *π** type MO. These transitions are forbiden by selection rules based on symmetry properties, so that the probability of their occurence is rather small (low), while the intensity of corresponding bands from UV-Vis spectra is also rather small (law). The main categories of electron orbitals are presented in (fig. 5).

QUANTITATIVE ASPECTS IN MOLECULAR ELECTRONIC SPECTROSCOPY

The nature of molecular electronic transitions related to the main types of energetic states provides the general, qualitative features of molecule electronic spectra (absorption and emission ones, fig. 6). ***Absorption*** (a) represents a transition from a lower level to a higher level with transfer of energy from the radiation field to an absorber molecule; and ***emission*** (b); it is a transition from a higher level to a lower level with transfer of energy from the emitter to the radiation field. If no radiation is emitted, the transition from higher to lower energy levels is called non radiative decay.

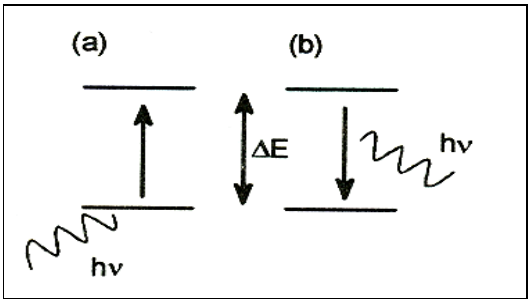

Fig. 6. Absorption (a) and emission (b) diagrams

The qualitative description of molecular spectra contains the positions (in the frequency scale) of the recorded spectral bands with no precise values of band intensity.

When band intensity is measured then we have to do with quantitative approach based on some parameter definitions.

BEER-LAMBERT LAW

Radiation parameters (fig. 7):

- Light transmittance: $T = I_1/I_0$;
- I_1 – and I_0 - light intensity at the issue from the absorbent sample and respectively at the entrance in the molecular sample;
- Absorbance: $A = -\log_{10} T = \log_{10} I_0/I_1$.

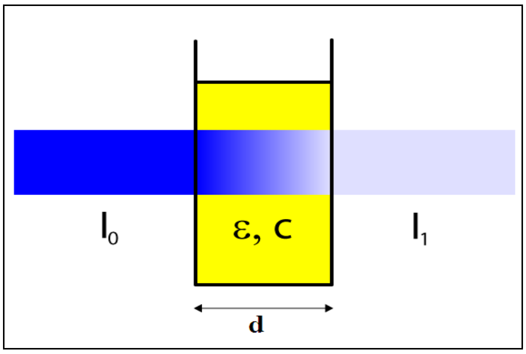

Fig. 7. Illustration of Beer-Lambert spectral law [5]

Molecular sample parameters:

– The sample layer width (transverse to the radiation light beam direction) – **d**;

– Sample concentration – the concentration of absorbing chemical species in the diluting non-absorbent solvent – ***c*** (expressed in mol L^{-1} (or M, molarity).

The spectral extinction coefficient (or molar absorptivity with units of L mol^{-1} cm^{-1}), that characterizes the absorbent molecule capacity of absorb differently light radiations with different wavelengths -ε_λ.

Beer-Lambert Law can be given through the mathematical relations:

$$I_1 = I_0 \exp(-\varepsilon_\lambda dc)$$

$$A = \varepsilon_\lambda dc$$

where the absorbance A has no units, since $A = \log10\ I_0/I_1$.

Linear absorbance dependence on concentration - directly proportionality -makes UV spectroscopy useful for quantitative analysis and in HPLC detectors.

NOTE: Above a certain concentration the linearity curves is no more observed, because of molecular associations of dissolved molecular substance at higher concentrations. It must be demonstrated the linearity in validating response in an analytical procedure.

Interactions solute-solvent. The main types of interactions that may occur between solute and solvent molecules are:

- electrical interaction between permanent dipoles (if both species are characterised by nenule molecular dipole moments) which are named **the orientation interactions**;

- interactions between permanent dipole moments of solvent molecules and the dipole moments induced by them in solute molecules: **the polarization - induction interactions**;

- interactions that may occur even when both molecular species brought into contact are non-polar but because of Brownian motion, temporary deformation of electronic molecular clouds are induced in form of small electric dipolare moments-the dispersion **interactions**;

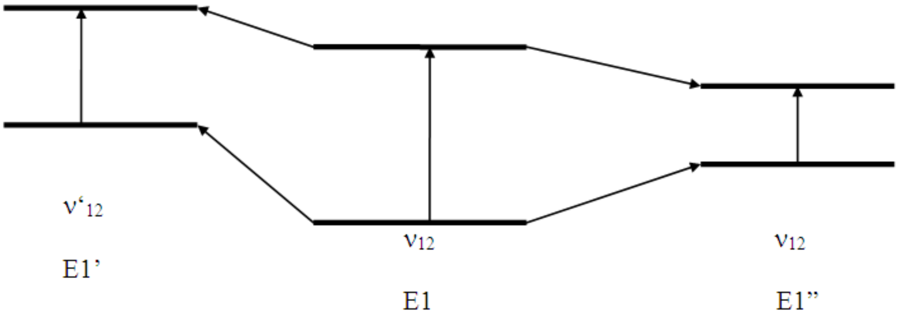

Fig. 7. Electronic transition frequency shift toward lower values

- when the molecular structures allowed, interactions of the hydrogen bond type may appear, but no longer have universal character;

- since do not involve all molecules in a considered volume - but are so-called specific or local interactions. The main effect of dispersion environment consists in shifing of electronic bands in the electronic spectrum of solute molecule, so moving energy levels between which are placed these transitions.If the level of the original absorption transition is even the fundamental/ground level then it can only be moved toward lower energy values while final level can be moved in both directions.

PROPOSED QUANTITATIVE RELATIONSHIPS

In the case of dispersive interactions, theory shows that the wavenumbers $\bar{\nu}_{disp.}$ in the maximum of electronic absorption band of molecule disolved in - a non-polar solvent characterized by the refractive index *n* and the ionizing potential *I* - in comparison with the same molecule in isolated state can be written as a function of the refractive index:

$$hc\Delta\bar{\nu}_{disp.} = hc\left(\bar{\nu}_{disp} - \bar{\nu}_0\right) = \left(\alpha_g - \alpha_e\right)\frac{3}{2a^3}\frac{II'}{I+I'}\frac{n^2-1}{n^2+2}$$

where wavenumber of isolated molecule is ν_0, molecule volume is a^3 and molecule polarizability in ground and excited states is α_g and α_e .

This proposed relationship is based on some simplifying hypotheses or some approximations: both molecules are non-polar while solute is a polar molecule.

In the case of polarization interactions the next relationship has been deduced:

$$hc\Delta\bar{\nu}_{pol.} = hc(\bar{\nu}_{pol.} - \bar{\nu}_0) = -\frac{hc^2 f}{8\pi m\nu_0 a^3}\frac{n^2-1}{n^2+2}$$

where *m* is the molecule solute mass and *f* is the strength of the oscillator associated to the studied absorption transition - linked to the full surface of the absorption band in spectral recording.

Interactions of orientation-induction type lead to the relationship:

$$hc\Delta\bar{\nu}_{or.ind.} = hc(\bar{\nu}_{or.ind.} - \bar{\nu}_0) = -\frac{2n^2+1}{n^2+2}\left\{\frac{2\mu_g\left(\mu_g - \mu_e\cos\varphi\right)}{a^3}\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right] + \frac{\left(\mu_g-\mu_e\right)^2}{a^3}\frac{n^2-1}{n^2+2}\right\}$$

where ε is solvent electric permittivity and μ_g and μ_e are electric dipolar moments in ground state (before absorption) and excited (after absorption) of the solute molecule.

In more general case when all of these types of interactions coexist one could write simply:

$$hc\Delta\bar{\nu} = hc\left(\Delta\bar{\nu}_{disp.} + \Delta\bar{\nu}_{pol.} + \Delta\bar{\nu}_{or.ind.}\right)$$

that is:

$$hc\Delta\bar{\nu} = \left\{\left(\alpha_g - \alpha_e\right)\frac{3}{2a^3}\frac{II'}{I+I'} - \frac{hc^2 f}{8\pi m\bar{\nu}_0 a^3} + \frac{2n^2+1}{n^2+2}\left[\frac{2\mu_g\left(\mu_g - \mu_e\cos\varphi\right)}{a^3} - \frac{\left(\mu_g-\mu_e\right)^2}{a^3}\right]\right\}\frac{n^2-1}{n^2+2} -$$

$$-\frac{2n^2+1}{n^2+2}\frac{2\mu_g\left(\mu_g - \mu_e\cos\varphi\right)}{a^3}\frac{\varepsilon-1}{\varepsilon+2}$$

It can be written also:

$$\boxed{hc\Delta\bar{\nu} = A\frac{n^2-1}{n^2+2} + B(n)\frac{\varepsilon-1}{\varepsilon+2}}$$

where:

$$A = \left(\alpha_g - \alpha_e\right)\frac{3}{2a^3}\frac{II'}{I+I'} - \frac{hc^2 f}{8\pi m\bar{\nu}_0 a^3} + \frac{2n^2+1}{n^2+2}\left[\frac{\left(\mu_g^2 - \mu_e^2\right)}{a^3}\right],$$

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

Practically the researcher should proceed to the recording of electronic absorption of the solute substance in different solvents and verify dependencies which exist between wavelengths numbers and functions of n or ε - or of n and ε - referred to the solvatochromic theory. Interpretation of these dependences makes it possible to assess major types of interactions that exist between solute and solvent.

EXPERIMENTAL PART

Rifampicin is is a semi-synthetic compound derived from the rifamycin B family, produced by strains of *Nocardia (Streptomyces) mediterranei* which focused not only the microbiologist attention, but also the interest of several multidisciplinary research groups (fig. 8).

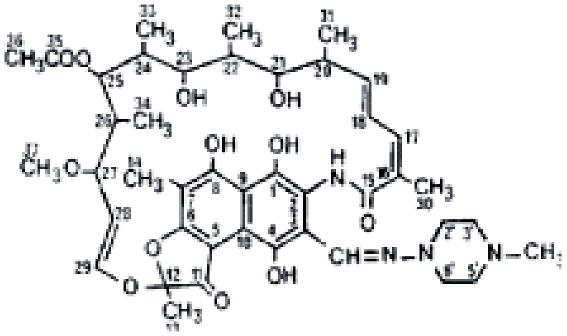

Fig. 8. Rifampicin chemical structure

The main purpose of this study was the application of spectral method for revealing the rifampicin interaction ability with various organic solvents. Pure crystalline powders of rifampicin (from SIGMA) was solved in an array of non-polar solvents (Table 1) resulting in highly diluted (about 10^{-5} M) solutions.

Table 1. Solvent macroscopic parameters

No.	Solvent	*n*	ε
1	*n*-Hexane	1.3749	1.89
2	Petroleum ether	1.3650	2.20
3	Carbon tetrachloride	1.4602	2.24
4	Toluene	1.4969	2.38
5	Diethyl ether	1.3524	4.33
6	Chloroform	1.4459	4.81

The electronic absorption spectra (EAS) of the rifampicin diluted solutions were recorded by a Shimadzu UV-1700 double beam UV/Visible spectrophotometer (quartz cells of 1 cm width versus the reference corresponding solvent) with data acquisition software.

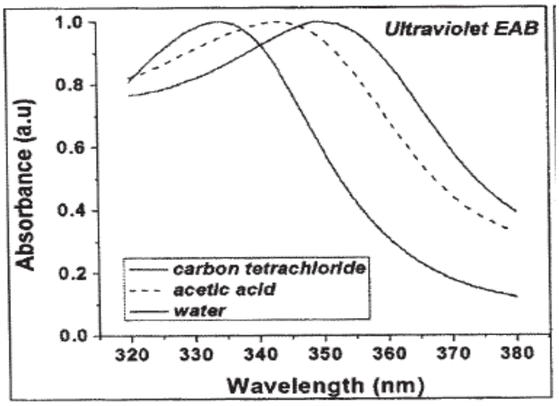

Fig. 9. The rifampicin ultraviolet EAB recorded in various solvents emphasizing the solvatochromic shift

THE RESULTS

In order to evidence the solute interactions with nonpolar solvents based on the theory of solvent influence on the electronic transitions energy two bands of rifampicin EAS, from ultraviolet and respectively visible domains, were analyzed. The nature of the studied electronic transitions was discussed according to the literature data [7-8], so that the band at about 340 nm was assigned to the π-π^* transition of the naphthohydroquinone chromophore, while the band at about 474 nm was assigned to a n-π^* transition.

In the next figures (Fig. 9), the EAB taken into the study is presented, aiming to evidence the solvatochromic shift of the spectral maxima in some non-polar solvents.

We can assume that the coefficient corresponding to the theoretical term that depends on the solvent dielectric constant becomes non-significant (as in the case on non-polar solvents, fig. 10 a-b), where linear regression line was fitting the dependence of experimental wavenumbers on the function $f(n)$. The statistical significance of the correlation coefficient was found to be $p < 0.0005$ [9].

This red shift is in concordance with aromatic chromophores behavior due to the dispersive solute-(nonpolar) solvent interactions, the shift being usually larger, for larger refractive index of the solvent. The interpretation of the bathochromic shift may be understood based on the stabilization of the excited state more than that of the ground state.

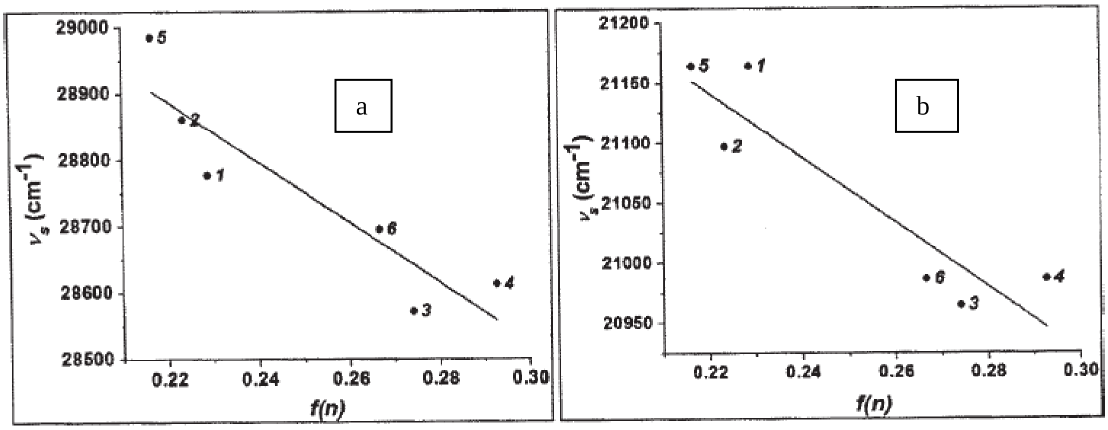

Fig. 10. The linear dependence on the function f(n) of the wavenumbers from a) UV and b) VIS range, in the case of non-polar solvents

CONCLUSIONS

Linear dependences between the frequencies in the absorption band maxima and distinct functions on the solvent macroscopic parameters (*n* - the refractive index of non-polar solvents, and both *n* and ε - the dielectric constant - in the case of polar solvents) were studied.

From the accomplished study it was found that to the increase of the solvent refractive index the red shift also increased, as proof of the dominancy of dispersive interactions in the rifampicin diluted solutions.

One may conclude that the dispersive interaction dominancy in nonpolar solvents stabilized the excited state electronic level relatively to the ground state one for both analyzed bands, while the role of orientation-induction interactions is lower as well as that of possible specific interactions.

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