

# THEORETICAL AND SPECTRAL STUDY OF VITAMIN B<sub>3</sub> IN POLAR SOLVENTS<sup>#</sup>

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*Abstract.* The aim of this paper was the study of polar solvents influence on the electronic absorption spectra of vitamin B<sub>3</sub> based on Abe's theory. The values of some electro-optical parameters such as the dipole moment and polarizability of the vitamin B<sub>3</sub> in the ground state were calculated by molecular modeling technique. The interpretation of spectral data according to Abe's model allowed the estimation of the compound polarizability and dipole moment in the first excited state.

*Key words:* vitamin B<sub>3</sub>, dipole moment, polarizability, ionization potential, electronic absorption spectra, polar solvents.

## INTRODUCTION

Niacin (also known as vitamin B<sub>3</sub>) is an organic compound with molecular formula C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>, being a derivative of pyridine with a substituted carboxyl group (–COOH) and soluble in water. The molecular structure of vitamin B<sub>3</sub> is shown in Figure 1.

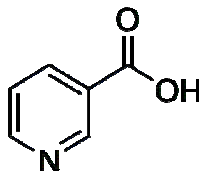


Fig. 1. The molecular structure of vitamin B<sub>3</sub>.

The general features of UV spectra of some pharmaceutical products have been previously investigated [8]. The studies of solvent influence on the electronic absorption spectra (EAS) are important since they allow to estimate some physical-chemical properties of the investigated molecules, establishing the nature of

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intermolecular interaction between solute–solvent molecules and enabling assignment of the electronic transitions which determine the experimentally observed electronic absorption bands. The solvent influence on the EAS of some organic molecules in solutions has been already investigated by our research team in several reports [1, 3, 6, 9].

In the molecular electronic spectra of organic compound solutions, the solute–solvent interactions often cause the shift of UV-VIS bands. The solvent influence on EAS band positions was approached in terms of intermolecular interactions, which change the energy from ground and excited states of the absorbing molecule. By using UV–VIS molecular spectroscopy one can evidence the different type of solute-solvent intermolecular interactions in binary solutions. Based on the correlations between the spectral shifts, induced by the polar or non-polar solvents and some solvent macroscopic physical-chemical parameters, one can compute the microscopic parameters of solute molecule such as the dipole moment and polarizability in the ground and excited states. To estimate the type of universal interaction among the spectral molecule and the solvent ones, some theoretical models focused on the relationship between the absorption band shift and certain functions of the macroscopic parameters of the solvent (dielectric constant –  $\epsilon$ , and refractive index –  $n$ ) were proposed. The diluted binary solutions can be approximated as a system formed by one spectrally active molecule denoted by “u” and the surrounding solvent molecules, denoted by “v” disposed into a molecular attraction sphere. The basic hypotheses of the cell model are [2, 5]:

- the molecules of the solvent and the solute are spherical and isotropic;
- the ground state of the system corresponds to the case when all the molecules of the system are in the ground state, while the excited state corresponds to the case when the spectrally active molecule is in the excited state, but the solvent molecules are in the ground state;
- the distance between the center of spectrally active molecule and the center of solvent molecule of the  $p$  solvation sphere is :

$$R_{uv(p)} = r_u + (2p - 1) \cdot r_v \quad (1)$$

When the spectrally active molecule is passing from the gaseous state into diluted solution, the frequency shift of the EAS maxima (corresponding to the transition between ground and excited electronic levels) is given by:

$$hc(\tilde{\nu}_1 - \tilde{\nu}_v) = W_e(u) - W_g(u) \quad (2)$$

where  $\tilde{\nu}_1$  and  $\tilde{\nu}_v$  are the wavenumbers of the studied absorption band in isolated state and respectively, in the presence of solvent molecules,  $h$  is Planck’s constant,  $c$  is the vacuum velocity of the light,  $W_e(u)$  and  $W_g(u)$  represent the studied

molecule energies in the two electronic states involved in the transition. When one takes into account the zero approximation for the ideal gaseous state of the system, then the energies of the solvent and solute molecules (denoted by the superscript 0) are given by summation as follows:

$$W_g^0 = W_g^0(u) + W_g^0(v) \quad (3)$$

$$W_g^0 = W_g^0(u) + W_g^0(v) \quad (3')$$

where  $W_g^0(u)$  is the energy of the isolated molecule of type “u” and  $W_g^0(v)$  is the total energy of the  $N$  surrounding molecules of type “v” which do not interact with each other. In the liquid state, the corresponding energy values of the molecules that are interacting between them [4] are given by:

$$W_g = W_g^0 + W_g(u) + W_g(v) \quad (4)$$

$$W_e = W_e^0 + W_e(u) + W_e(v) \quad (4')$$

The radius of the spectrally active molecule “u” and of the solvent molecules “v” can be calculated by using relations below:

$$r_u = 3 \sqrt[3]{\frac{3}{4\pi N_A} \cdot \frac{M_u}{\rho_u}} \quad (5)$$

$$r_v = 3 \sqrt[3]{\frac{3}{4\pi N_A} \cdot \frac{M_v}{\rho_v}} \quad (5')$$

where  $M_u$  and  $M_v$  are the molecular masses,  $\rho_u$  and  $\rho_v$  are the densities and  $N_A$  is Avogadro’s number.

The interactions from liquid state may be classified in two categories [4]:

- the local interactions, which are known also as specific interactions, that generally occur between two or three molecules – such as the hydrogen bonds;
- the universal interactions, known also as volume interactions, involve considerably a larger number of molecules and may be: orientation, induction and dispersion interactions. The universal forces act within the sphere of molecular attraction. The interaction potential corresponding to dispersion forces can be expressed by the relation [5]:

$$U_{\text{disp}} = -\frac{3}{2} \cdot \frac{I_u \cdot I_v}{I_u + I_v} \cdot \frac{\alpha_u}{r_u^3} \cdot \frac{n^2 - 1}{n^2 + 2} \quad (6)$$

In Eq.(6)  $\alpha_u$ , and  $r_u$  are the polarizability and the radius of the “u” molecule (vitamin B<sub>3</sub>);  $I_u$  is the ionization potential in the excited state of type “u” molecule and  $I_v$  is the ionization potential of the type “v” (solvent) molecule in the ground state,  $n$  is the refractive index of the solvent.

### MATERIALS AND METHODS

Vitamin B<sub>3</sub> pure crystalline powder (purchased from Sigma-Aldrich Company) was used in our experiment, dissolved in an array of polar solvents. Solvent refractive indices were measured with Abbe type refractometer.

The absorption electronic spectra were recorded with UV-VIS Shimadzu UV-1700 spectrophotometer provided with quartz cells of 1 cm width.

HyperChem 8.0 molecular program (PM3 semi-empirical method and QSAR application) [7] was used to compute some electro-optical parameters of vitamin B<sub>3</sub>.

### RESULTS AND DISCUSSION

According to the theoretical background presented above, the calculated radii of solvent molecules are given in Table 1.

Table 1

The calculated values of solvent molecules radii

Solvent	$r_v (\times 10^{-8} \text{ cm})$
Water	1.925
Methanol	2.523
Ethanol	2.850
Acetic acid	2.831
n-Butanol	3.324
n.n <sup>2</sup> -Dimethylformamide	3.127
n-Pentanol	3.507

The radius of the spectrally active molecules (vitamin B<sub>3</sub>) was also calculated:  $r_u = 3.212 (\times 10^{-8} \text{ cm})$ .

The values of the radius of the first and the second solvation spheres,  $R_{uv(1)}$  and  $R_{uv(2)}$ , calculated by using Eq. (1), are given in Table 2.

Table 2

The calculated radii of the first and second solvation spheres

Solvent	$R_{uv(1)} (\times 10^{-8} \text{ cm})$	$R_{uv(2)} (\times 10^{-8} \text{ cm})$
Water	5.137	8.987
Methanol	5.735	10.781
Ethanol	6.062	11.762
Acetic acid	6.043	11.705
n-Butanol	6.536	13.184
n.n'-Dimethylformamide	6.339	12.593
n-Pentanol	6.719	13.733

By using Eq. (7), the number of molecules (Table 3) from the first solvation sphere  $N(1)$  was obtained:

Table 3

Calculated molecule number from the first and second solvation sphere

Solvent	$N(1)$	$N(2)$	$N = N(1) + N(2)$
Water	22	68	90
Methanol	16	57	73
Ethanol	15	53	68
Acetic acid	15	54	69
n-Butanol	12	49	61
n.n'-Dimethylformamide	13	51	64
n-Pentanol	11	48	59

Table 4

Solvent parameters:  $n$  (refractive index) and  $I_v$  (ionizing potential)

Solvent	$n$	$\frac{n^2 - 1}{n^2 + 2}$	$I_v$ (eV)
Water	1.333	0.205	12.316
Methanol	1.328	0.202	11.138
Ethanol	1.361	0.221	10.898
Acetic acid	1.371	0.226	11.440
n-Butanol	1.399	0.241	10.887
n.n'-Dimethylformamide	1.431	0.258	9.296
n-Pentanol	1.407	0.246	10.782

In the  $p$  solvation sphere,  $N(p)$  molecules are supposed to be found as given by Eq. (7) [4] (Table 3):

$$N(p) = \frac{4\pi \cdot R_{uv(p)}^2}{(2r_v)^2} \quad (7)$$

In the liquid state, the molecules interact with each other by forces which cannot be neglected. The ionization potential,  $I_v$  (Table 4), of the solvent molecules in the ground state can be approximated by using the Koopman theorem:  $I_v \approx -E_{\text{HOMO}}$  (eV), where  $E_{\text{HOMO}}$  was provided by applying molecular modeling software HyperChem [7]. The ionization potential in the excited state of the solute molecule can be calculated from the measured wave number in the maximum of the recorded EAS by using relation (8):

$$I_g(u) - I_e(u) = hc\tilde{\nu}_1 \quad (8)$$

The ionization potential of vitamin B<sub>3</sub> can be approximated as  $I_u \approx -E_{\text{HOMO}} = 10.50$  eV. Table 5 lists the dispersion potential, calculated by using Eq. (6).

Table 5

Solvent dispersion potential

Solvent	$U_{\text{disp}}$ (eV)
Water	-0.644
Methanol	-0.635
Ethanol	-0.655
Acetic acid	-0.686
n-Butanol	-0.715
n.n'-Dimethylformamide	-0.706
n-Pentanol	-0.726

In Figure 2, the linear correlation between the dispersion interaction potential and the calculated number of molecules from the first solvation sphere is presented. It can be observed that, as the number of the molecules is higher, the dispersion potential increases.

In Figure 3, the studied near UV band from the recorded EAS in polar solvents is presented.

In Figure 4 the processing of spectrally measured data is represented in correlation with the function of solvent refractive index from Abe's theory [1–2]:  $f(n) = (n^2 - 1)(n^2 + 2)$ . Because the polar solvents are grouped around the regression line ( $R = 0.903$ ), we can say, according to the theoretical background, that dispersion interactions are present in this molecular system.

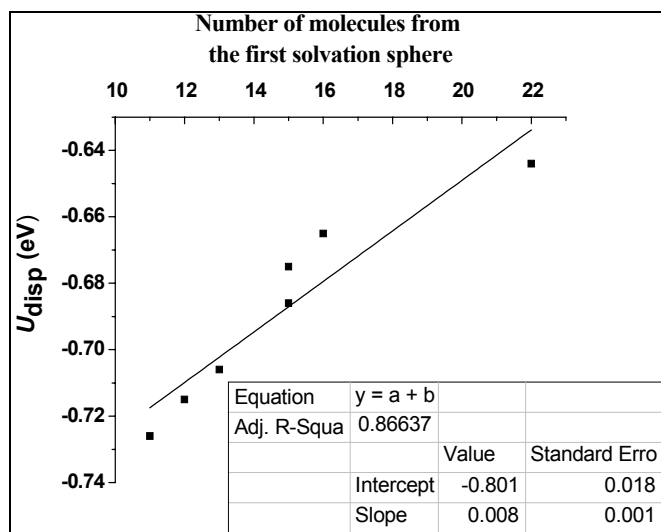


Fig. 2. The dispersion interaction potential vs. number of molecules from the first solvation sphere.

Other correlations between the wave number in maximum of the studied UV electronic absorption band and the functions of solvent dielectric constant  $f(\epsilon) = (\epsilon - 1)(\epsilon + 2)$  or  $f(\epsilon, n) = [(\epsilon - 1)(\epsilon + 2) - (n^2 - 1)(n^2 + 2)]$  were not found ( $R < 0.80$ ), so one can assume that the orientation or induction forces are not dominant in the binary solutions studied. Thus, our analysis suggests that, in the first approximation, only dispersion forces are acting in the solutions of vitamin B<sub>3</sub> with polar solvents.

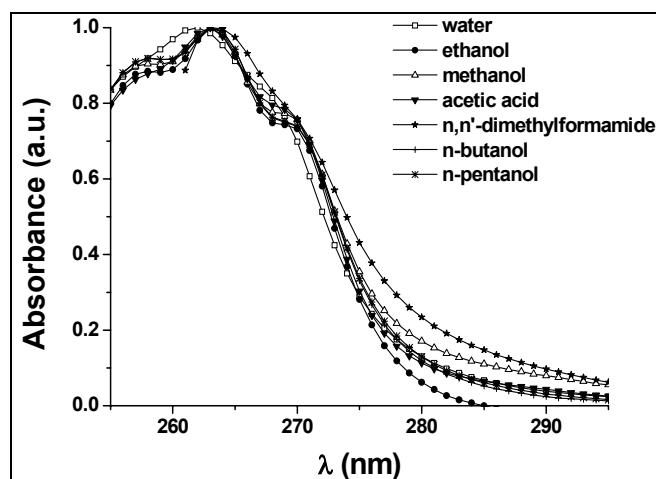


Fig. 3. The electronic absorption spectra of vitamin B<sub>3</sub> in various polar solvents.

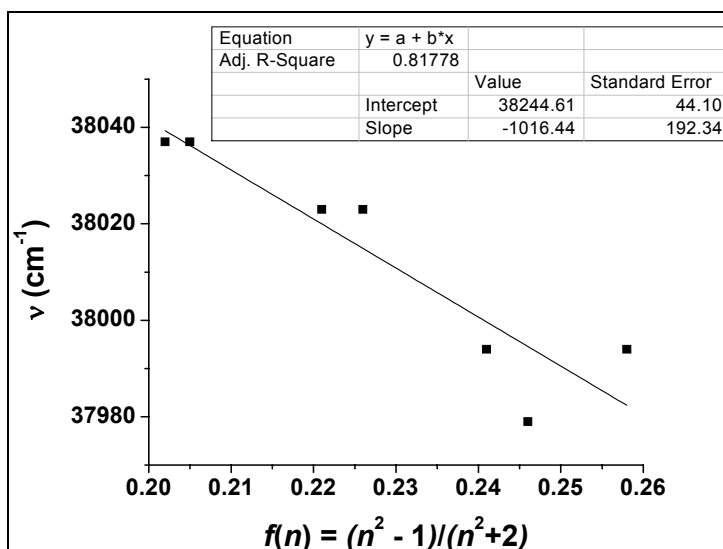


Fig. 4. The linear correlation between the wavenumber in the maximum of near UV absorption band for vitamin B<sub>3</sub> in polar solvents and the function  $f(n)$  from Abe's theory.

By using the notations from [10], we have further defined the  $X$  parameter:

$$X = \frac{3}{2} \cdot \frac{I_g(u) \cdot I_g(v)}{I_g(u) + I_g(v)} \cdot \frac{8066}{r^3(u)} \cdot \frac{n^2 - 1}{n^2 + 2} \quad (9)$$

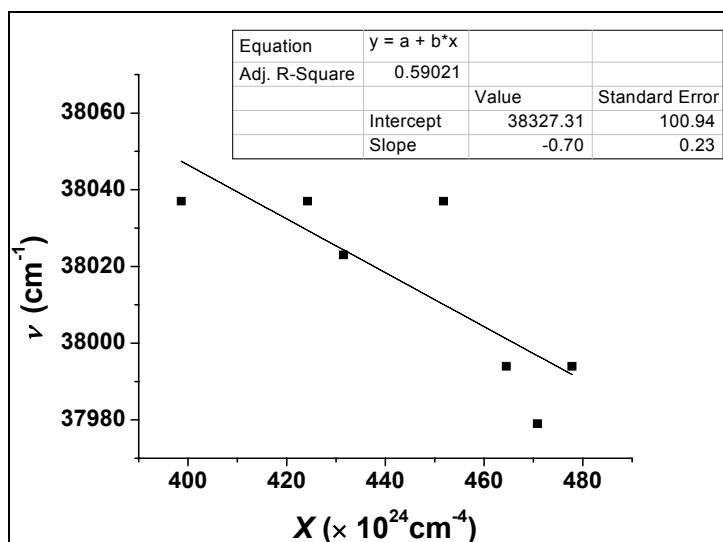


Fig. 5. The spectral shift vs. dispersion function for vitamin B<sub>3</sub>.



In figure 5, the linear correlation between the wave number in the maximum of the electronic band and the dispersion function, given by the parameter  $X$ , is presented. The slope of this linear dependence gives the polarizability of spectrally active molecule in the excited state by using Eq. (10) and the polarizability in the ground state (estimated by molecular modeling):

$$\tilde{\nu} = \tilde{\nu}_1 + [\alpha_g(u) - \alpha_e(u)] \cdot X \quad (10)$$

Indeed the slope of the straight line represents the difference of the polarizabilities in the two states involved in the transition, while the intercept approximates the wave number of the solute molecule in isolated (vapor) state.

By using HyperChem 8.0 molecular modeling program (QSAR method) [7], the polarizability of the spectrally active (type “u”) molecule in its ground state was calculated, i.e.  $\alpha_g(u) = 12.28 \times 10^{-24} \text{ cm}^3$ .

So, by using Eq. (10) and the slope of the linear dependence from Figure 6, the polarizability of spectrally active molecules in the excited state was estimated as  $\alpha_e(u) = 12.98 \times 10^{-24} \text{ cm}^3$ , which is slightly increased compared to the ground state. The intercept of the linear dependence from Eq. (11) gives the difference between the square of the dipole moments of the two states involved in transition [6]. Knowing the values of the polarizability in the excited state of the spectrally active molecule, the dipole moment of the molecule in the excited state can be further calculated by using equation (11):

$$[\mu_e^2(u) - \mu_g^2(u)] + a \cdot \alpha_e(u) = b \quad (11)$$

where “a” and “b” parameters are given by expressions (14):

$$a = \frac{\frac{3}{2} I_g(v) \cdot \alpha_g(v) \cdot \frac{I_g(u) - hc\tilde{\nu}_1}{I_g(v) + I_g(u) - hc\tilde{\nu}_1}}{\frac{3}{4\pi \cdot N_A} \cdot \frac{M_v}{\rho_v} \cdot \left[ \frac{(\epsilon_v - n_v^2) \cdot (2\epsilon_v + n_v^2)}{\epsilon_v(n_v^2 + 2)} + \frac{n_v^2 - 1}{n_v^2 + 2} \right]} \quad (12)$$

$$b = \frac{-\frac{\tilde{\nu}_1 - \tilde{\nu}_v}{C} + \frac{3}{2} \alpha_g(v) \cdot \alpha_g(u) \cdot \frac{I_g(u) \cdot I_g(v)}{I_g(v) + I_g(u)}}{\frac{3}{4\pi \cdot N_A} \cdot \frac{M_v}{\rho_v} \cdot \left[ \frac{(\epsilon_v - n_v^2) \cdot (2\epsilon_v + n_v^2)}{\epsilon_v(n_v^2 + 2)} + \frac{n_v^2 - 1}{n_v^2 + 2} \right]} \quad (13)$$

The estimated value of the difference of the square dipole moments is given by:

$$\left[ \mu_e^2(u) - \mu_g^2(u) \right] = 4.413D^2; \mu_g(u) = 3.003D \quad (14)$$

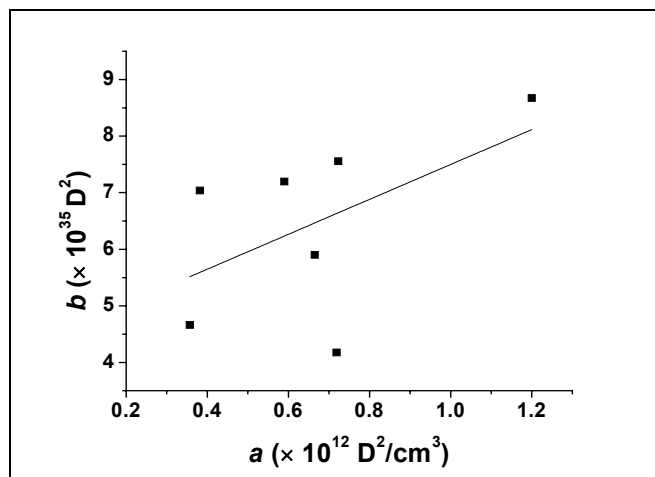


Fig. 6. The linear correlation between “b” and “a” parameters.

The dipole moment of the solute molecule in the ground state was computed by molecular modeling (Eq.14). Finally,  $\mu_e(u) = 3.673$  D was calculated, the value denoting a significant increase for the excited state compared to the ground state.

## CONCLUSIONS

Summarizing the above results, Abe’s theory was applied in order to discuss the influence of the polar solvents on the near UV electronic absorption band of vitamin B<sub>3</sub>. In the linear dependence plotted between “a” and “b” coefficients, the slope represents the polarizability of the spectrally active molecules in the excited state  $\alpha_e(u)$ , while the intercept corresponds to the difference between the square of the dipole moments of a solute (type “u”) molecule in the excited and ground state. Since the dipole moment of the vitamin B<sub>3</sub> molecule in the ground state was provided by using quantum-chemistry calculations, its dipole moment in the excited state could be estimated. Comparing the results between the values of the polarizability and the dipole moment of the spectrally active molecule in the excited state and the ground state, an increase in both the polarizability and dipole moment by excitation was found.

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