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**CONTRIBUTIONS TO ESTIMATING SOME ELECTRO-
OPTICAL PARAMETERS USING SOLVATOCHROMIC
EFFECT**

THESIS SUMMARY

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We inform you that on 19 December 2014, 12:00 in L1 Hall, Mrs. Școban (Rusu) Marcela Cristina will support in public session the thesis:

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PARAMETERS USING SOLVATOCHROMIC EFFECT"**

to obtain a PhD title in Fundamental Sciences, Physics field.

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We invite you in this way, to attend the public hearing to support the thesis.

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Introduction

Vitamins are organic compounds that are required in small amounts (milligrams or micrograms) in various cellular metabolic processes and are important for maintaining health and normal growth of the organism. Vitamins are classified into two broad categories: fat-soluble (vitamins A, D, E, K) and water-soluble (Group B vitamins and vitamin C).

The B vitamins improve resistance to stress, help digestion and are useful for good muscle tone and healthy skin. In addition, they reduce muscle spasms, cramps, tingling sensations in the limbs and help regulate blood pressure. The study of the solvent is important both theoretically and practically, being particularly important that the solvation of substances in various solvents involves the knowledge of intermolecular interactions in the obtained solutions.

The results of spectrophotometric measurements can be interpreted based on theories of solvent interactions that occur in condensed environments. The knowledge of dissolution mechanisms as well as the nature of intermolecular interactions in solutions is of extreme interest for the chemical and pharmaceutical industries.

The research on molecular solvation has shown that some molecular features and electro-optical parameters or structure parameters can be obtained by combining the experimental methods with molecular modeling. In this paper we have analyzed three vitamins (B_3 , B_6 and B_{12}) which are important for the pharmaceutical industry. We have considered the study of the interaction of these vitamins with some protic polar solvents. This paper contains five chapters.

The first chapter refers to the present research on the properties of spectrally active molecules. This chapter presents the main current theories on the phenomenon of solvation.

In the second chapter there have been emphasized the orientation - induction and dispersion interactions that occur in the binary solutions of these vitamins in polar protic solvents.

Applying the Abe cell model and using the HyperChem 8.0 and Spartan 08 molecular modeling programs to estimate the electro-optical parameters from the ground state, there have been estimated the dipole moments and the polarizabilities of these vitamins in the excited state. There have been also estimated the contributions of different interactions to the total spectral shifts of these vitamins.

In the third chapter there have been highlighted the interactions which occur in ternary solutions of these vitamins in the mixture of two solvents ethanol-water.

In the fourth chapter there has been estimated the influence of hydrogen bonding on the properties of molecular complexes made from vitamins and polar protic solvents and there have been calculated some global descriptors, the total energy, the HOMO-LUMO frontier level energy, dipole moments and polarizabilities in the ground and excited states were calculated by using the Spartan molecular program.

Also, there have been performed simulations which highlight the formation of the molecular complexes of these vitamins, as well as the map of the electrostatic potential density and the map of LUMO density in binary and ternary solutions.

In the fifth chapter, there have been presented some aspects related to the complex fluid dynamics (blood considered complex fluid), as well as its laminar and turbulent flow regimes and the Reynolds number was calculated for different diameters of blood vessels.

The paper includes a final part which contains the general conclusions on the experimental results.

Some of the results were presented at national and international scientific meetings and published in journals from home and abroad.

The results obtained in this paper are part of the current orientation which combines the experimental results with theoretical aspects to estimate the electro-optical parameters of the molecules in excited state.

Part I – Theoretical aspects

CHAPTER I

General current status of research on the influence of the solvent on the electronic absorption spectra of binary and ternary solutions

I.1. THEORETICAL CONSIDERATIONS

The studies on the electronic absorption spectra of the solution of biologically active molecules have led to the production of an explanation of some physico-chemical properties of the molecules being investigated, to the determination of the nature of solute-solvent interactions between the molecules but also to the information about the type of transition responsible for the appearance of the electronic absorption bands.

The aims of this study is to analyze the influence of protic polar solvents on UV-Vis electronic absorption spectra of some vitamins to obtain information on the nature of solute-solvent intermolecular interactions.

Any solution involves the interaction between solute and solvent molecules. Using spectroscopy means we can analyze a solution using as a probe a spectrally active molecule for very low concentration in a pure solvent. The solvation of organic molecules in various solvents affect the absorption electronic spectra as the interactions between the solute molecules and the solvent ones determines the shift of the spectral bands and the alteration of their shape and strength.

In the thesis I have tried to study the spectral behavior of spectrally active molecules (vitamin B3, vitamin B6, vitamin B12) with biomedical implications in

binary and ternary solutions to estimate the electro-optical parameters of these vitamins such as dipole moment, polarizability, HOMO – LUMO energy levels, their interaction energies with various polar solvents, bond lengths, etc. as well as the solvatochromic effects occurring in electronic absorption spectra of these molecules when they are solvated in polar solvents.

1.2 Estimating electro-optical parameters using existing molecular solvent theories

1.2.1 Abe cellular model for a pure liquid

Abe [54,55] proposes a statistical model for investigating spectra for some spectrally active substances introduced in solutions.

To express the spectral shift of spectrally active molecule there is used the dipole moment of a molecule of type "u" located in the ground state. Abe establishes a relationship of the form (I.1) between the electric dipole moment values of spectrally molecule active in the states participating in the transition:

$$\left[\mu_e^2 - \mu_g^2 \right] + a \cdot \alpha_e = b \quad (\text{I.1})$$

By measuring the spectral shift of the absorption electronic spectra and electrical polarizability of the spectrally active molecule "u" in the ground state by using molecular methods, we can determine the polarizability of the molecule "u" in the excited state.

To determine the electric moment of the spectrally active molecule in the excited state we follow the correlation between the parameters a and b estimated by Abe and if we get a linear dependence of the form (I.1) then the cut at the ordinate equals the difference of the squares of electric dipole moments of the solvite molecule corresponding to the two states involved in the transition.

1.2.2. The classical theory of Bakhshiev

Bakhshiev [15,16] takes into account the dipolar interactions between the solvated molecule and the solvent molecules and considers the changes in the

electrical characteristics of molecules when they pass from the state of vapor in solution during the processes of absorption or emission of energy.

He considers that the spectral shift can be written as a sum of three terms corresponding to each type of universal interaction:

$$hc\Delta\tilde{\nu} = hc(\Delta\tilde{\nu}_{\text{disp}} + \Delta\tilde{\nu}_{\text{or}} + \Delta\tilde{\nu}_{\text{ind}}) \quad (\text{I.2})$$

Using the model proposed by Bakhshiev there have been estimated the contributions of the various types of interactions that occur in binary and ternary solutions of spectrally active molecules [89-92].

The solvatochromic effect can be explained as the influence of the solvent on the position, intensity and shape of the absorption bands.

The solvatochromic effect can be positive if the action of the solvent absorption bands move to higher wavelengths (the bathochrom effect) or negative when the absorption bands move to lower wavelengths (the hypsochrom effect), the solvatochromic effect being limited by the physical interactions between the molecules of the solvent and solute [112,113].

I.2.3. The solvatochromic Kamlet-Taft model

This model [66] allows the separation of the specific and the nonspecific interactions. The solute-solvent specific interactions (hydrogen bonding) are expressed by the parameters a and b and nonspecific interactions are expressed by Kamlet-Taft parameter π in equation (I.3), [93-95]:

$$\tilde{\nu}_{\text{max}} = \tilde{\nu}_0 + s \cdot \pi^* + a \cdot \alpha + b \cdot \beta \quad (\text{I.3})$$

where $\tilde{\nu}_0$ is the number of the wave electronic absorption band maximum in the absence of solvent.

I.3. Global descriptors

The quantitative description of the chemical reactivity can be done using global and local descriptors. For this study we have considered the energetical and global descriptors:

1. The energy of the highest occupied molecular orbital E_{HOMO} ;
2. The energy of the lowest free molecular orbital E_{LUMO} ;
3. The electronegativity;
4. The chemical hardness;
5. The chemical potential;
6. The electrophilicity index;
7. The dipole moment;
8. The polarizability.

I.4. Vitamins

Vitamins are organic substances which are found in small amounts in food and are essential for the normal growth and development of the organism. Each vitamin of the B complex vitamin is involved in maintaining the metabolic balance properly, also complementing in their various functions.

I.5 Complex fluid dynamics

The complex fluid dynamics can be analyzed using the scale relativity theory (SRT) which implies that fluid particles move along the continuous and non-differentiable curves (fractal curves). Considering that the convective and dispersive effects are dominant, fluid dynamics have been analyzed; in this approximation of the motion, there have been identified two flow regimens of the complex fluid by measuring the cnoidal vibration modes of the complex speed field.

The real part of the complex velocity V_D is the classical speed which do not depend on the resolution while the imaginary part is a value which comes from a fractal-dependent resolution.

The presence of two flow regimes when the blood is considered a complex fluid involves both the structural separation of its components depending on the velocity field values (for non-cvasiautonom regime) and the generation of patterns for cvasiautonom regime.

Part II Personal contributions

CHAPTER II

Experimental investigation on the electronic absorption spectra of vitamins B₃, B₆ and B₁₂ in binary solutions

The theoretical and experimental results presented in this chapter have been published in journals [141 142 143].

II.1. The importance of studying B₃, B₆ and B₁₂ vitamins

The present study have analyzed the influence of protic solvents on electronic absorption spectra of binary solutions containing vitamin B₃, B₆, B₁₂ and some polar protic solvents.

➤ Vitamin B₃

Vitamin B₃ (C₆H₅NO₂), also known as nicotinic acid, niacin or vitamin PP, participates in the metabolism of protein, lipid, carbohydrate and mineral, normalizing the adrenal function.

➤ Vitamin B₆

Vitamin B₆ or pyridoxine (C₈H₁₁NO₃) is a water-soluble vitamin which is very sensitive to light but resistant to heat and oxidation process.

➤ Vitamin B₁₂

Vitamin B₁₂ (cobalamin, C₆₃H₈₈CoN₁₄O₁₄P) is the most powerful anti-anemic factor known up to present.

II.2 Materials and working methods

The binary solutions were obtained by dissolving the active spectral molecule (B_3 / B_6 / B_{12}) in five polar protic solvents (water, methanol, ethanol, 1-butanol, 1-pentanol) in a 50:50 volume ratios.

The electronic absorption spectra have been recorded in the UV-Vis with the Shimadzu UV-1700 spectrophotometer and there have been identified frequencies in maximum UV-Vis absorption bands for each binary solution.

II.3 Experimental results on the effect of solvent on the electronic absorption spectra of vitamins B_3 , B_6 and B_{12} in binary solutions

The influence of polar solvents on the electronic absorption spectrum of vitamin B_3 , B_6 and B_{12} was analyzed and the electronic absorption spectra were obtained - Figure II.1 (a) - (c).

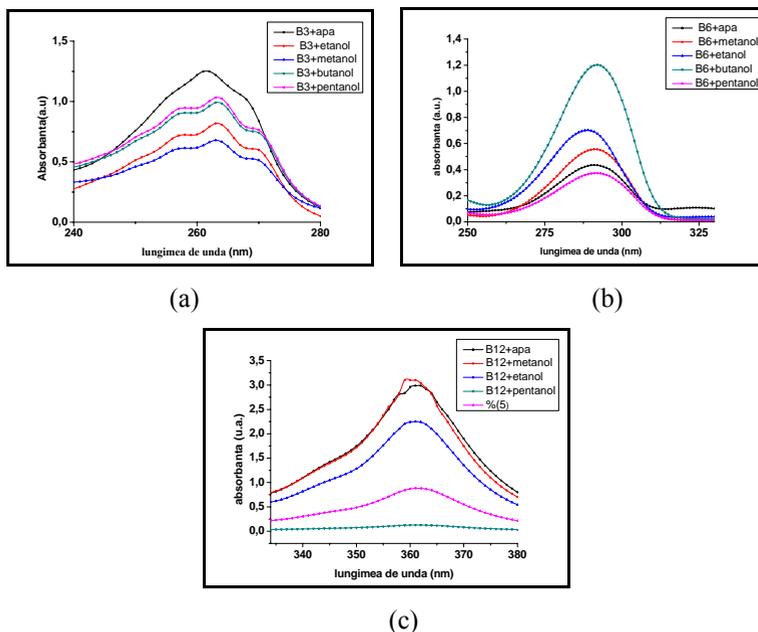


Fig. II.1 electronic absorption spectrum (UV) in polar protic solvents for B_3 (a), B_6 (b), B_{12} (c)

II.4 Estimating the contributions of different types of interactions to the total spectral shift of electronic absorption spectra of B₃, B₆ and B₁₂ vitamins

The total spectral shift from liquids may be influenced by the orientation-induction, the polarization dispersion interactions and specific interactions.

In order to separate the interactions that produce the spectral shift the empirical relationship was used (II.1) whose terms are correlated with various types of interactions which determine the total spectral shift:

$$\Delta\tilde{\nu} = \Delta\tilde{\nu}_{\text{orient.-ind.}} + \Delta\tilde{\nu}_{\text{polariz.}} + \Delta\tilde{\nu}_{\text{disp.}} + \Delta\tilde{\nu}_{\text{inter.sp.}} \quad (\text{II.1})$$

An empirical equation of the form (II.2) can be used to express the contribution of all interactions to the total spectral shift:

$$\tilde{\nu}_{\text{calc.}} = \tilde{\nu}_v + C_1 \cdot f(\epsilon) + C_2 \cdot f(n) + \Delta\nu_{\text{inter.sp.}} \quad (\text{II.2})$$

where functions $C_1 \cdot f(\epsilon)$ express the contribution of orientation interactions and $C_2 \cdot f(n)$ represent the induction, polarization and dispersion interactions to the total spectral shift. These functions can be expressed in terms of macroscopic parameters of the solvent by expressions of the form (II.3 - II.5):

$$f(\epsilon) = \frac{\epsilon - 1}{\epsilon + 2} \quad (\text{II.3})$$

$$f(n) = \frac{n^2 - 1}{n^2 + 2} \quad (\text{II.4})$$

$$f(\epsilon, n) = \frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \quad (\text{II.5})$$

The contribution of specific interactions in protic solvents can be estimated empirically by a term of the form $\Delta\nu_{\text{inter.sp.}} = C_3 \cdot \delta(\text{ppm})$ where $\delta(\text{ppm})$ is the chemical shift.

The coefficients C_i , $i = 1, 2, 3$ involved in equation (II.2) may be statistically determined if known the wavenumbers of electronic absorption band highs recorded in several solvents.

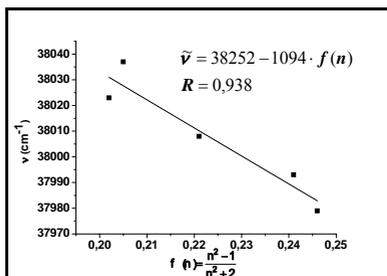
To analyze the vitamin B_3 , B_6 and B_{12} were used five protic polar solvents: water, methanol, ethanol, 1-butanol, 1-pentanol.

Using relations (II.3 - II.5) there were obtained the following values for the functions of solvent shown in Table II.2.

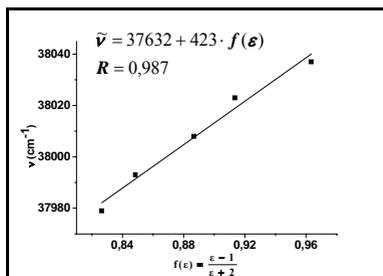
Table II.2 Functions $f(n)$, $f(\epsilon)$ and $f(\epsilon, n)$ and wavenumbers in maximum electronic absorption band (UV) of molecules B_3 , B_6 and B_{12}

No.	solvent	$f(n) = \frac{n^2 - 1}{n^2 + 2}$	$f(\epsilon) = \frac{\epsilon - 1}{\epsilon + 2}$	$f(\epsilon, n) = \frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2}$	$\tilde{\nu}$ (cm^{-1}) B_3	$\tilde{\nu}$ (cm^{-1}) B_6	$\tilde{\nu}$ (cm^{-1}) B_{12}
1	water	0.205	0.9634	0.7584	38037	34488	27747
2	methanol	0.202	0.9134	0.7114	38023	34412	27732
3	ethanol	0.221	0.8867	0.6657	38008	34435	27716
4	1-butanol	0.241	0.8484	0.6074	37993	34341	27670
5	1-pentanol	0.246	0.8265	0.5805	37979	34294	27699

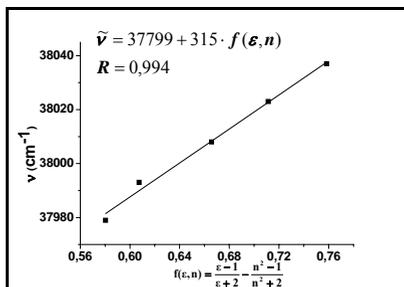
Plotting the dependence of the wavenumber of the maximum electronic absorption band (UV-Vis) and functions $f(n)$, $f(\epsilon)$ and $f(\epsilon, n)$ for each binary solution analyzed there were obtained the graphics II 2 (a) - (c).



(a)



(b)



(c)

Fig. II.7 The linear correlation between the wavenumber of the maximum electronic absorption band in the UV and functions $f(n)$, $f(\epsilon)$ and $f(\epsilon, n)$ for the vitamin B_3

Similar correlations were obtained for the vitamins B_6 and B_{12} both in the UV and visible domain.

Knowing the values of the functions $f(\epsilon)$ and $f(n)$ of protic solvents an equation of the type (II.6) for the vitamin B_3 is obtained. Similar equations were obtained for the other vitamins.

$$B_3 \begin{cases} \tilde{\nu}_{\text{calc.}} = 37795 + 318 \cdot f(\epsilon) - 307 \cdot f(n) + 233 \cdot \delta(\text{ppm}) \\ R = 0.992 \end{cases} \quad (\text{II.6})$$

Knowing the values of $f(\epsilon)$ and $f(n)$ functions we determined the percentage contribution of orientation - induction or dispersion interactions for the binary solutions of vitamins B_3 , B_6 and B_{12} , values shown in Table II.3 for Vitamin B_3

Table II.3 Percentage contribution of interactions to total spectral shift for binary solutions of vitamin B_3 (UV)

solvent	$C_1 \cdot f(\epsilon)$	$C_2 \cdot f(n)$	$C_3 \cdot \delta(\text{ppm})$
water	50,88%	10,45%	38,66%
methanol	49,63%	10,59%	39,77%
ethanol	48,40%	11,64%	39,95%

1-butanol	46,79%	12,83%	40,37%
1-pentanol	46,02%	13,22%	40,75%

The results from Table II.3 show that the orientation interactions have a dominant role in the total spectral shift followed by those made by hydrogen bonds. Similar analyzes were performed for vitamins B₆ and B₁₂.

It was found that in all binary solutions made by dissolving vitamins B₃, B₆ and B₁₂ in protic polar solvents the orientation interactions are dominant and cause a hipsochrom effect and the dispersive interactions, of a weaker intensity, determine a bathochrom effect.

Then the applicability of the Abe model was checked for binary solutions of the vitamins investigated.

By measuring the spectral shift of the absorption electronic spectra and calculating the polarizability of the spectrally active molecule "u" in the ground state by using molecular methods, we can determine the electric polarizability and dipole moment of the molecule "u" in the excited state.

The cut to origin signifies the wavenumber in the maximum electronic absorption band of the molecules investigated in the gas phase.

The estimated values of the dipole moment and the polarizability of the spectrally active molecules in the excited state are shown in Table II.4.

For the dipole moment in the excited state there were not taken into account the angles between the directions of the dipole moments of the states participating in the transition, which may influence the value of the dipole moment in the excited state. Table II.4 Polarizability and dipole moments in the ground and excited states obtained with Abe model for vitamins B₃, B₆ and B₁₂ vitamin (using the relationship I.20)

Vitamin	μ_g (D)	$\mu_e^2 - \mu_g^2$ (D ²)	R	μ_e (D)	$\alpha_e \cdot 10^{-24}$ (cm ³)
B ₃	3,003	-1,583	0,975	2,732	2,076

B ₆	3,188	-4,936	0,93	2,286	4,788
B ₁₂	8,334	-4,863	0,957	8,036	71,79

It is noted that the values of the dipole moment in the excited state of the spectrally active molecules decrease, which shows that the excited states are less polar. Simultaneously, the values of polarizability decrease in the excited state.

A similar analysis for the investigated vitamins was done in the visible range of the electromagnetic radiation spectrum emphasizing an hipsochrom effect. For the visible range of binary solutions of vitamin B₁₂ there have also been found a decrease in the value of the dipole moment and polarizability in the excited state.

Solvatochromic equation Equation Kamlet -Taft for binary solutions of vitamin B₃ is of the form (II.7).

$$(B_3) : \tilde{\nu} = (38,363 \pm 0,23) \cdot 10^3 + (0,035 \pm 0,009) \cdot 10^3 \cdot \pi^* + (0,304 \pm 0,138) \cdot 10^3 \cdot \beta + (0,123 \pm 0,166) \cdot 10^3 \cdot \alpha, R = 0,924 \quad (II.7)$$

From the dependence $\tilde{\nu} = f(\pi^*, \alpha, \beta)$ we can find out the values of the coefficients a and b which can be found in Table II.5.

Table II.5 Values of a and b parameters for binary solutions of investigated molecules

No.	Molecular complex	s (10 ³)cm ⁻¹	b(10 ³ cm ⁻¹)	a(10 ³ cm ⁻¹)
1.	B ₃ +protic solv.	0,035	0,304	0,123
2.	B ₆ +protic solv.	0,152	1,294	1,273
3.	B ₁₂ +protic solv.	0,134	0,391	0,02

Analyzing Kamlet-Taft equation (see Table II.5) there were found positive values of the coefficients (s), (b) and (a) indicating a hipsochrom effect along with the increasing of the polarity/ polarizability of the solvent and the donor, respectively

acceptor ability of the solvent to achieve the hydrogen bonds with the solvents used. This suggests a stabilization of the ground state to the excited state.

II.5 Conclusions

1. In the binary mixtures of B₃ vitamin there is a positive value of the coefficient C₁ which shows that orientation forces cause a shift of the maximum absorption band to lower wavelengths.
2. The C₂ coefficient is negative and therefore universal interaction increases the maximum $\pi \rightarrow \pi^*$ wavelength band.
3. The contribution of the specific interactions between the polar protic solvent and the solvent molecules was approximated by the distance between the first bisector and the line which contains the points corresponding to the protic solvents in the plane $(v_{\text{calc}}, v_{\text{exp}})$.

CHAPTER III

Experimental investigation on electronic absorption spectra of vitamins B₃, B₆ and B₁₂ in ternary solutions

The theoretical and experimental results presented in this chapter have been published in journals [144, 145].

III.1 Experimental methods

For different volume ratios 100: 0, 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, 10:90, 0: 100 there were plotted graphs of the functions $f(\epsilon)$, $f(n)$ and $f(\epsilon, n)$ versus the wavenumber of maximum absorption band in the visible range. The electronic absorption spectra of vitamins B₃, B₆ and B₁₂ recorded in the mixture ethanol - water are shown in Figure III.1 (a) - (c).

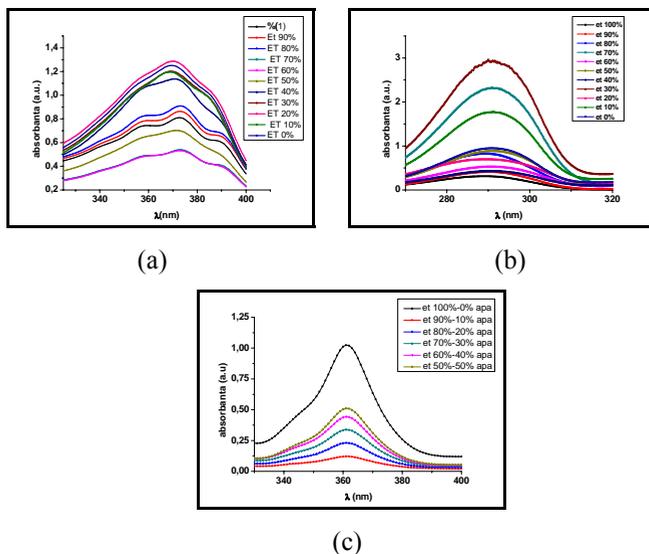


Fig. III.1 Electronic absorption spectrum (UV) of the ternary solution formed between water-ethanol-vitamin: B₃ (a); B₆ (b) B₁₂ (c) in different volume ratios

Table III.2 Concentrations and wavenumbers in electronic absorption band in the UV ternary mixtures composed of (ethanol - water) and molecule B₃ / B₆ / B₁₂.

No.	Etanol (%)	$\tilde{\nu}$ (cm ⁻¹) (B ₃)	$\tilde{\nu}$ (cm ⁻¹) (B ₆)	$\tilde{\nu}$ (cm ⁻¹) (B ₁₂)
1	100	37908	34530	27701
2	90	37918	34507	27709
3	80	37936	34507	27716
4	70	37951	34483	27732
5	60	37965	34412	27739
6	50	37994	34406	27740
7	40	38052	34388	27747
8	30	38081	34364	27754
9	20	38139	34356	27762

10	10	38226	34341	27762
11	0	38256	34317	27770

To highlight and interpret the various interactions that occur between the spectrally active molecules $B_3/B_6/B_{12}$ and solvent molecules linear regressions between have been drawn between the wavenumber of maximum absorption band in the UV and VIS, and functions $f(n), f(\epsilon), f(\epsilon, n)$.

In the case of the ternary solutions B_3 - ethanol -water and B_{12} - ethanol -water we find that, as the concentration of ethanol increases there is an electronic absorption spectrum shift in the UV-Vis towards larger wavelengths (bathochrom effect), as shown in the graph III.2 (a), (c). For the solution formed between B_6 -ethanol-water there is the hipschrom effect as the concentration of ethanol increases, as shown in the graph III.2 (b).

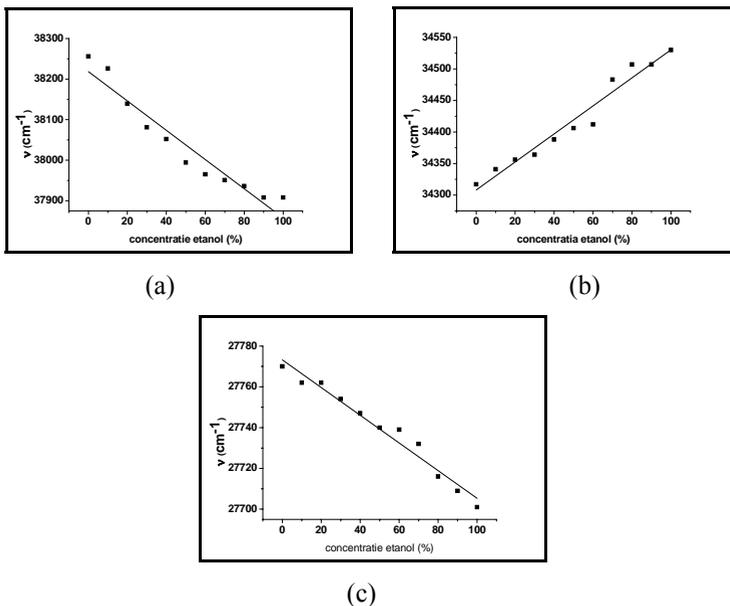


Fig. III.2 The variation of the wavenumber in the maximum electronic absorption band in the UV with the concentration of ethanol in the ternary mixture

ethanol-water-B₃ ($R^2 = 0.9206$) (a), B₆-ethanol-water ($R^2 = 0.9555$) (b); B₁₂-ethanol-water ($R^2 = 0.957$) (c)

Linear correlations were achieved between the wavenumber in the maximum electronic absorption band and the functions $f(\epsilon)$, $f(n)$ and $f(\epsilon, n)$. The linear correlations which are obtained from graphs III.3 (a) - (c) for the case of vitamin B₃ confirm the coexistence of these interactions. Similar analyzes were done for B₆, B₁₂ vitamins.

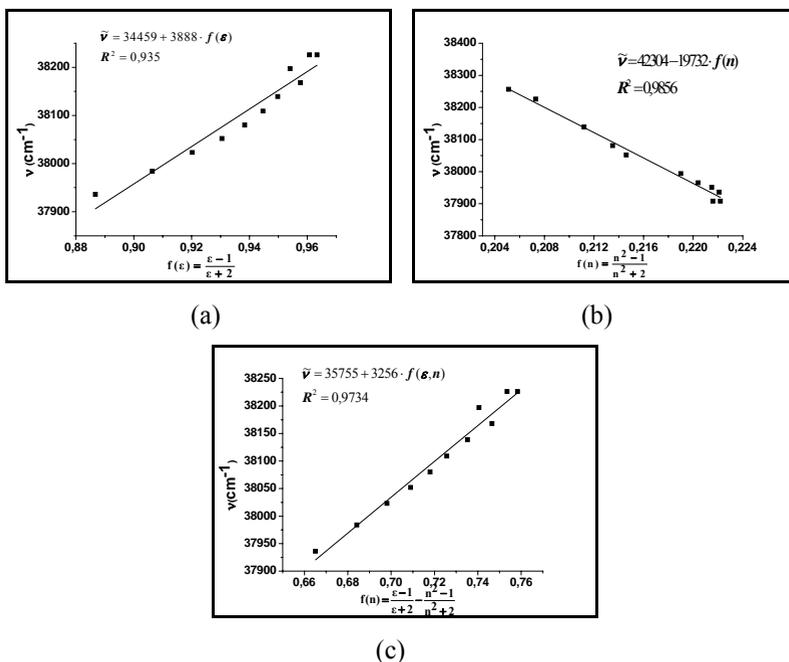


Fig. III.3 Linear correlation between the wavenumber in the maximum electronic absorption band (UV) and the functions $f(\epsilon)$ (a), $f(n)$ (b) and $f(\epsilon, n)$ (c) for the ternary mixture formed between B₃ ethanol-water

In the case of ternary solutions of the vitamin B₃ the contribution of different interactions to the total spectral shift is given by the values of the coefficients C_1 , C_2 , C_3 from the empirical equations (III.2):

$$\begin{aligned} \text{UV : } \tilde{\nu} &= 41377 + 572 \cdot f(\epsilon) - 17922 \cdot f(n) + 2519 \cdot \delta(\text{ppm}), R^2 = 0,98045 \\ \text{VIZ : } \tilde{\nu} &= 24671 + 3775 \cdot f(\epsilon) - 4679 \cdot f(n) + 841 \cdot \delta(\text{ppm}), R^2 = 0,96847 \end{aligned} \quad (\text{III.2})$$

Similar equations were established for ternary molecular systems of B₆ and B₁₂ vitamins.

Using the relation III.2 there was estimated the percentage of different types of interactions that determine the spectrum shift, the percentage values being found in Table III.4.

Table III.4 Percentage contributions of interactions to the total spectral shift for ternary mixtures of vitamins B₃, B₆, B₁₂ (UV)

Conc. ethanol	C ₁ · f(ε)			C ₂ · f(n)			C ₃ · δ(ppm)		
	B ₃	B ₆	B ₁₂	B ₃	B ₆	B ₁₂	B ₃	B ₆	B ₁₂
100	57,65	46,54	51,38	9,40	4,58	19,04	32,93	48,88	29,58
90	58,17	46,49	51,08	9,31	4,50	19,12	32,51	49,01	29,80
80	58,00	46,45	50,80	9,14	4,44	18,9	31,93	49,11	30,60
70	58,29	46,38	50,76	9,06	4,37	18,48	31,73	49,25	30,76
60	58,52	46,09	50,69	8,97	4,28	18,09	31,59	49,63	31,02
50	58,72	46,09	50,64	8,88	4,23	18,06	31,48	49,77	31,30
40	58,95	45,98	50,58	8,69	4,11	17,62	31,44	49,91	31,80
30	59,09	45,94	50,48	8,63	4,07	17,41	31,37	49,99	32,11
20	59,23	45,92	50,36	8,53	4,01	17,12	31,33	50,07	32,52
10	59,41	45,86	50,30	8,37	3,91	16,73	31,32	50,23	32,97
0	59,52	45,77	50,26	8,27	3,85	16,56	31,30	50,38	32,98

III.2 Conclusions

From Table III.4 we find that in the UV range for vitamin B₃ orientation interactions mainly occur, followed by specific interactions.

For the ternary systems of vitamin B₆ we find a very important and approximately equal contribution of orientation and specific interactions to the total spectral shift. Also, it is found that as the ethanol concentration decreases, the

orientation interactions decreases but increases the specific interactions by hydrogen bonds.

For the ternary system of vitamin B₁₂, the calculations suggest that the orientation interaction plays a dominant role as interaction-inducing-polarization dispersion has a small contribution to the total spectral shift; the specific interactions also contribute significantly to the total spectral shift since both ethanol and water can form hydrogen bonds with the B₁₂ molecule.

The value of coefficient C₁ (relationship III.2) is positive indicating that the orientation interactions determine a spectral shift to lower wavelengths. The value of C₂ coefficient is negative suggesting that the universal interactions determine a spectral shift toward higher wavelengths. Due to the higher value of the coefficient C₂ compared to C₁ we can say that in the UV there is an increase in the maximum wavelength band, so there is a bathochrom effect.

CHAPTER IV

Estimation of electro-optical molecular parameters using molecular modeling methods

For the structures of the three vitamins there was chosen the operator PM3, RHF and accelerated convergence process. The SCF convergence limit was 10^{-4} , the maximum number of iterations to achieve convergence was elected to the 500, the gradient Ribierre Polak was chosen to optimize the geometry with a RMS gradient of 10^{-2} (kcal / mol Å •) and there was selected a maximum of 1000 cycles for geometry optimization.

The analysis of the investigated systems aimed at estimating the electro-optical parameters, such as the dipole moment, the polarizability, the energy values of frontier levels, the total energy, the energy of formation, the length of the hydrogen bond, etc. The optimized geometries of vitamin B₃, B₆ are shown in Figures IV.1- IV.2.

The values of HOMO and LUMO orbital energy and the electrical parameters for vitamin B₃ are given in Table IV.1. We mention that similar results were obtained for vitamin B₆.

Table IV.1 The calculated values of total energies, energies of HOMO and LUMO frontier orbitals, dipole moment and polarizability of binary solutions formed between B₃ vitamin with protic solvents

No.	Molecular complex	E (kJ/mol)	E _{HOMO} (eV)	E _{LUMO} (eV)	$\Delta E = E_{LUMO} - E_{HOMO}$	μ (Debye)	α (a.u)
1.	B ₃ +water	-461,540	-10,481	-0,624	9,857	2,75	50,317
2.	B ₃ +methanol	-471,644	-10,479	-0,626	9,813	2,81	52,046
3.	B ₃ +ethanol	-494,04	-10,440	-0,629	9,811	2,86	53,550
4.	B ₃ +1-butanol	-548,081	-10,429	-0,630	9,799	3,34	56,472
5.	B ₃ +1-pentanol	-570,431	-10,423	-0,637	9,786	5,18	57,962

There are obtained the correlations between the various parameters and the polarity of the solvent as we mentioned the variation in total energy, the electric dipole moment, etc. of binary systems considered as shown in Figure IV.3.

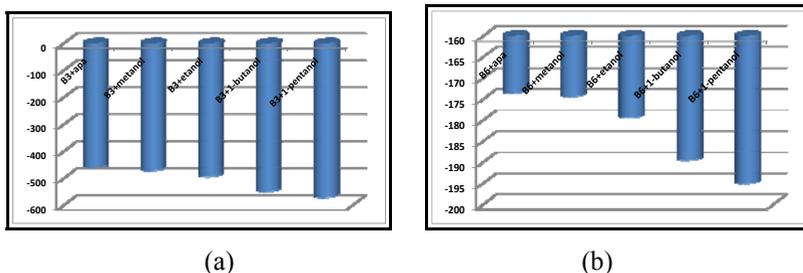


Fig. IV.3 Variation of the total energy (kJ / mol) of molecular complexes formed between B₃ and polar protic solvents

From Table IV.1 and Figure IV.3 it is observed an increase in the total energy value B₃ molecule along with the decreasing of the dielectric constant of the solvation

environment. Thus, there is a destabilization of the molecules of B_3 to the introduction of 1-pentanol, so the system is the more stable than with the solvent water.

The HOMO energy level, which is considered a measure of the ionization potential of a molecule I, allows an assessment of the donor properties of a molecule. We can say that the more polar the solvent, the higher the ionization potential of the new molecular complex. If the absolute value of the HOMO energy level is high, the structure is more stable and will hardly give electrons on this level.

From the graph IV.4 there is a close correlation between the value of the electric dipole moment and the solvent polarity ϵ along with the increasing of the solvent polarity, the dipole moment of the complex decreases, therefore becomes less polar.

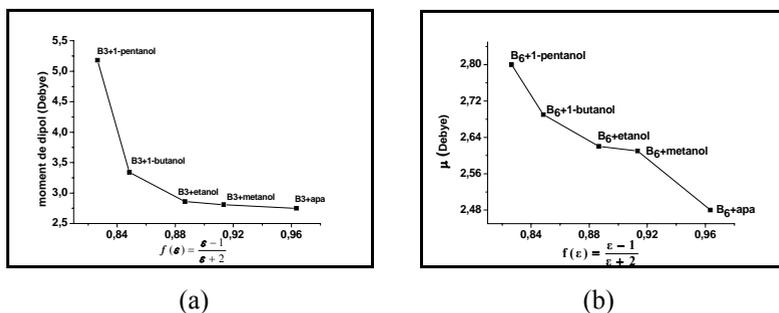


Fig. IV.4 The variation of the electric dipole moment of the molecular complexes of B_3 (a) and B_6 (b) vs. the polarity of the solvent

From Figure IV.4 (a) it is observed a decrease in the electric dipole moment of the molecule B_3 along with the increase of the solvent polarity. The highest value of the dipole moment ($\mu = 2,80$ Debye) is obtained for the system formed between (1-pentanol) and B_3 , where the solvent is water ($\mu = 2,48$ Debye) characterized by the dielectric constant $\epsilon = 80,1$. Also, for the binary solutions of vitamin B_6 there is a decrease in the value of the moment dipole along with the increase of the solvent polarity (Fig.IV.4 (b)).

There were calculated the global descriptors of the investigated molecular systems and the results are shown in Table IV.2.

Table IV.2 The global descriptors values: the electronegativity, the chemical hardness, the chemical potential and the electrophilicity index for the binary solutions of B₃ and B₆ vitamins

No.	χ (eV)		η (eV)		μ (eV)		ω (eV)	
	B ₃	B ₆	B ₃	B ₆	B ₃	B ₆	B ₃	B ₆
1.	5,5725	5,195	4,91	4,471	-5,5725	-5,195	3,161	3,018
2.	5,552	5,077	4,9265	4,458	-5,552	-5,077	3,128	2,89
3.	5,5345	5,062	4,9055	4,456	-5,5345	-5,062	3,1218	2,875
4.	5,5295	4,948	4,8995	4,468	-5,5295	-4,948	3,1202	2,741
5.	5,525	4,907	4,898	4,445	-5,535	-4,907	3,12	2,708

From the data in Table IV.2 it is found that the electron affinity has molecular complexes formed between B₃ and water or water and B₆; the lower hardness have the molecular systems consisting of vitamin B₃, respectively, B₆ with 1-butanol, being the most reactive. The same downward trend is found in other global descriptors such as chemical hardness and electrophilicity index.

There were estimated the hydrogen bond energies for the binary mixtures of B₃ and B₆ vitamins obtaining the values contained in Table IV.3.

Table IV.3 Length and energy of hydrogen bond for molecular systems vitamins of B₃ and B₆ vitamins

No.	Solvent	Length of hydrogen bond (Å)		Energy of hydrogen bond (kcal/mol)	
		B ₃	B ₆	B ₃	B ₆
1.	water	1,808	1,841	2,301	3,055
2.	methanol	1,813	1,844	3,875	4,20

3.	ethanol	1,814	1,845	4,251	4,464
4.	1-butanol	1,818	1,858	6,025	5,441
5.	1-pentanol	1,827	1,859	6,98	5,558

There was obtained a satisfactory correlation between the length of the hydrogen bond and the polarity of the solvent, as shown in the graph IV.5 (a-b) and the energy of the hydrogen bonding as seen in the graph IV.6.

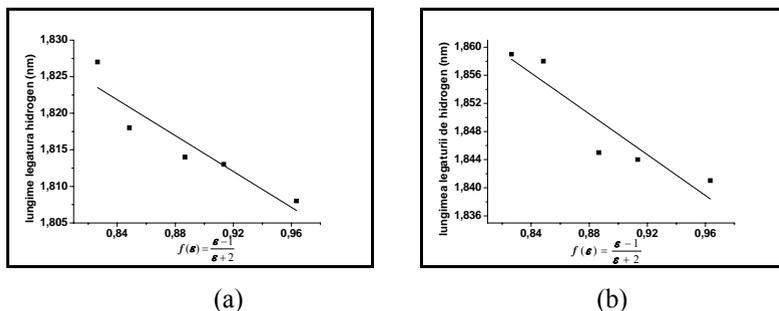


Fig. IV.5 Hydrogen bond length vs. $f(\epsilon) = \frac{\epsilon - 1}{\epsilon + 2}$ for molecular complexes of the B₃

(R = 0.908) (a); B₆ (R = 0.904) (b)

From the graph IV.5 (a -b) it is found for all molecular complexes of the two vitamins, a decrease in hydrogen bond length along with the increase of the solvent polarity demonstrating that the less polar solvent, the greater the hydrogen bond length.

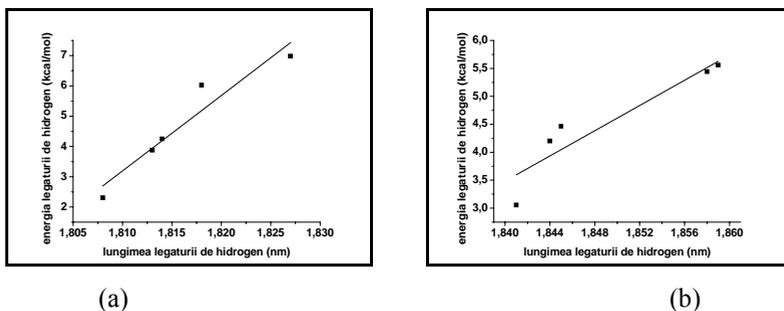


Fig. IV.6 Variation of the hydrogen energy vs. hydrogen bond length for binary mixtures of B3 (R = 0.946) (a) and B6 (R = 0.908) (b)

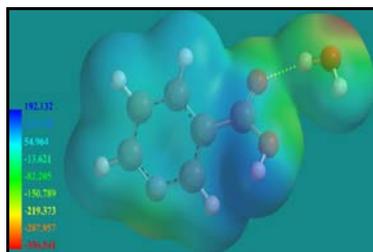
In the case of binary solutions of both vitamins, from Graph IV.6 (a) - (b) it is noted that if the length of the hydrogen bond increases, its energy increases.

To describe the chemical reactivity of molecules the molecular orbitals HOMO and LUMO are used. The electrophilic attack occurs most likely in the atomic site with a high density of atomic orbital HOMO while nucleophilic attack is correlated with the atomic site with high-density LUMO orbital.

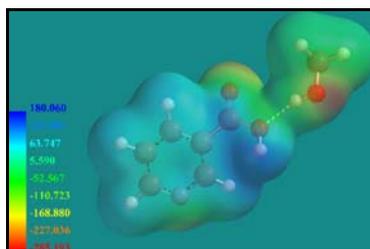
The map of distribution of the potential density for the molecular complexes investigated are shown in Figures IV.7 (a-e) for the vitamin B₃. The map of the distribution density of molecular orbital LUMO of vitamin B₃ complexes are illustrated in Figures IV.8 (a-e).

For the potential density, by convention color towards red means a negative potential while the colors towards blue means a positive potential. Thus, in Figure IV.7 (a-e) it can be seen the negative potential region, *ie* the region of the oxygen atoms and the positive potential region located in the vicinity of the hydrogen atoms.

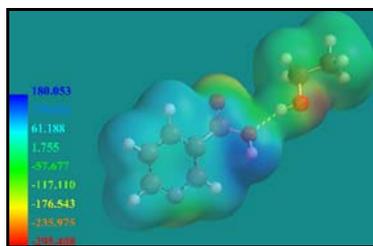
For the map of orbital LUMO (Figure IV.8 (a-e)), by convention blue colors indicate a high concentration of orbitals while the colors towards red indicate a low concentration. The LUMO orbital map is important because it shows the possible areas where nucleophilic attack will occur. In the case of carbon atoms it is observed their characteristic electrophilicity. The intense red region shows where it is the most likely be held the nucleophilic attack.



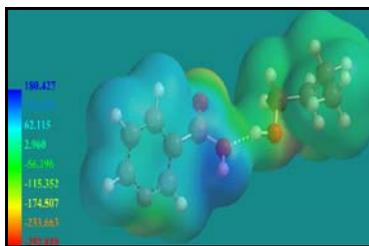
(a)



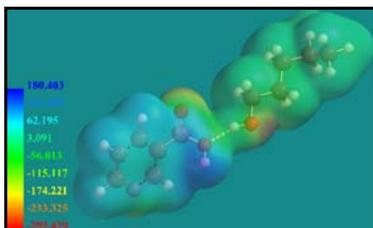
(b)



(c)

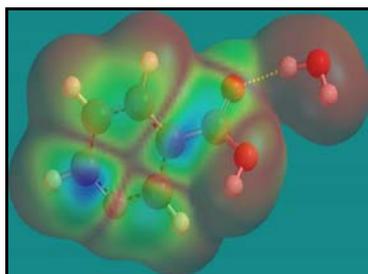


(d)

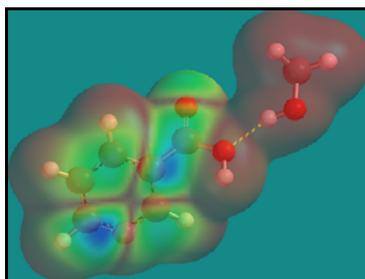


(e)

Fig. IV.7 Distribution map of electrostatic potential density for molecular complexes formed between vitamin B₃ with water (a), methanol (b) ethanol (c), 1-butanol (d), 1-pentanol (e)



(a)



(b)

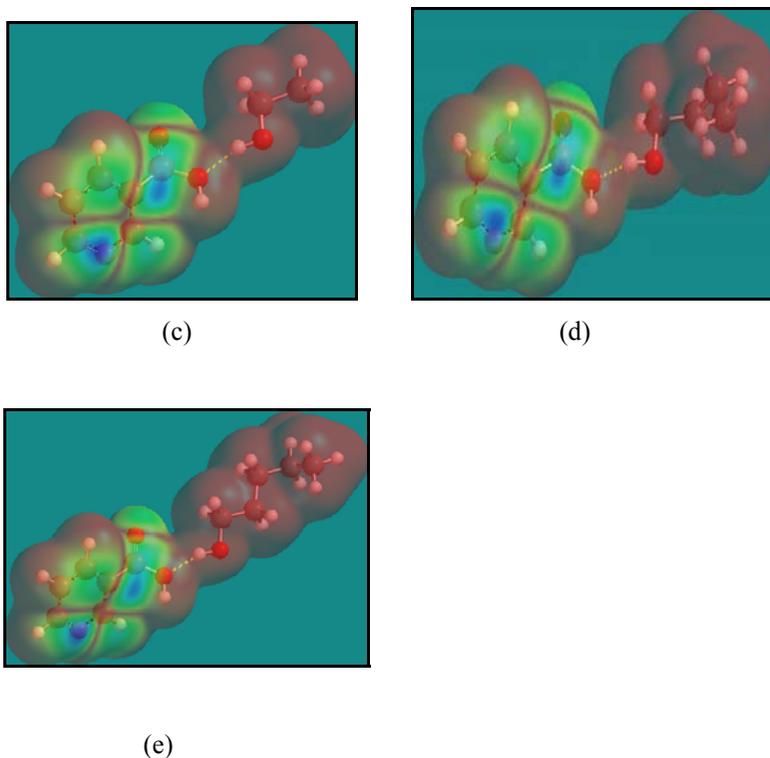


Fig. IV.8 Distribution map of density LUMO orbital for molecular complexes formed of B₃ and water (a), methanol (b) ethanol (c), 1-butanol (d), 1-pentanol (e)

Conclusions

1. Calculations show that the molecular complexes formed by B₆ vitamin with protic solvents have lower values of LUMO compared with the molecular complexes formed between B₃ vitamin with the same solvent. These descriptors indicate a greater tendency of vitamin B₆ to accept electron density and have a higher reactivity than vitamin B₃.
2. The higher reactivity of the molecular complexes of vitamin B₃ is demonstrated by the hardness descriptor, η , as seen from the results contained

in Table IV.2. In accordance with the principle of maximum hardness, it is noted that the values of this parameter are lower for molecular complexes of vitamin B₆ which suggests that it is more reactive than B₃. The chemical hardness of the molecular complexes of vitamin B₆ shows that these complexes are more stable.

3. The higher values of the HOMO electronic descriptor for the molecular complexes of B₃ vitamin indicates a lower tendency to donate electron density in a nucleophilic attack.

For the ternary structures of the investigated vitamins there were obtained the molecular geometry from Figure IV.9 (a) - (b).

For the investigated ternary systems there were obtained the following values of energy and global descriptors listed in Table IV.4.

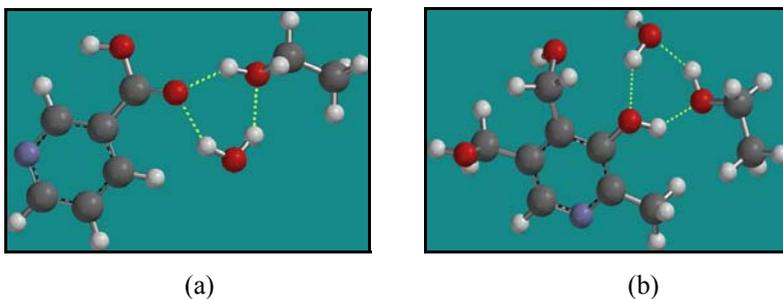


Fig. IV.9 Optimized geometries of ternary mixtures of water-ethanol-B₃ (a) and B₆-water-ethanol (b) (Spartan)

Table IV.4 Energy and global descriptors of the investigated ternary systems

Descriptor	B ₃ -water-ethanol	B ₆ -water-ethanol
Formation energy (kcal/mol)	-174,23	-233,34
Energy length bond (kcal/mol)	5,10	5,98
Dipole moment (Debye)	4,16	2,77
Polarizability (a.u.)	54,967	58,935
E _{HOMO} (eV)	-10,588	-9,333
E _{LUMO} (eV)	-1,326	-0,270
Electronegativity (eV)	-5,957	-4,801

Hardness (eV)	4,631	4,531
Chemical potential (eV)	5,957	4,801
Electrophilicity index (eV)	3,831	2,543

Conclusions

1. Based on the principle of maximum hardness, we can say based on the values contained in Table IV.4 that the ternary mixture consisting of B₆-water-ethanol ($\eta = 4,531\text{eV}$) is more reactive than the ternary mixture consisting of B₃-water-ethanol ($\eta = 4,631\text{eV}$).
2. When comparing the electric dipole moment values estimated for binary mixtures of these vitamins (Table IV.1) with those obtained for ternary mixtures of vitamins (Table IV.4), we can say that ternary mixtures are more polar than the binary.
3. Chemical hardness values obtained for binary mixtures are higher than those obtained for ternary systems which allows us to say that ternary systems are more reactive to the binary of the same vitamins.

The maps of the potential distribution density and LUMO molecular orbital distribution density for the ternary mixture composed of water-ethanol-B₃ are shown in Figure IV.10 (a) - (b).

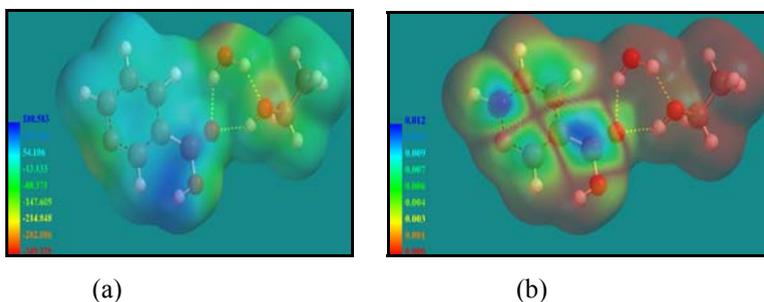


Fig.IV.10 Maps of density electrostatic potential (a) and LUMO molecular orbital density for the ternary system, water-ethanol B₃ (b)

As it can be seen from Figure IV.10 the areas most likely to be held a nucleophilic attack are marked with red in the vicinity of the hydroxyl group OH from the vitamin structure and solvents water and ethanol.

CHAPTER V

The dynamics of the complex fluid

The theoretical and experimental results presented in this chapter have been published in journals [137, 138].

V.1 Blood - as complex fluid

The cardiovascular system is made up of the heart, the pump aspire-repellent part and a continuous network of closed containers with different cross-sections (arteries, veins and capillaries) through which blood flows, the network fractal structure. Blood circulation, outside the parameters characterizing the flow of any fluid (viscosity, pressure gradient, blood vessel diameter) has specific features due to its blood and blood vessel walls:

- blood is a non-newtonian fluid;
- Walls of blood vessels are elastic;
- Blood flow is not continuous but pulsatory.

Blood is a liquid non-newtonian, pseudoplastic, heterogeneous, representing a complex dispersive system. It is a suspension of cellular components (50% of its volume) in an aqueous solution (plasma) electrolyte, macromolecular substances.

Non-Newtonian fluids do not meet the real relationship of proportionality between force and velocity gradient viscosity because their viscosity depends on the flow rate or pressure. Relatively high viscosity of the blood, its inhomogeneity, the cyclical expulsion at the high pressure and different shape and variable blood vessels determine the flow that is not strictly laminar, the velocity profile is not parabolic. The turbulent flow itself is observed, usually, only in the initial part of the aorta and the pulmonary artery. In other large vessels there occurs an intermediate regime between

laminar and turbulent flow. This type of flow facilitates the exchange between blood and vessel walls, and the homogenization of solutes (including vitamins).

V.2 Blood flow velocity

Blood flow in small vessels can be considered laminar blood flow, in most large vessels is intermediate between laminar and turbulent regime. The laminar flow of blood is layered in the form of thin concentric cylinders that slide one over the other with the maximum speed in the axis and the minimum at the vessel wall. Turbulent flow occurs when the speed of movement exceeds a certain critical speed, and therefore laminar regime is replaced by a turbulent, messy, in which the movement along the axis of the blood vessel overlap on the transverse movement of the fluid layers, thereby forming the vortices.

The Reynolds number (Re) measures the tendency of occurrence of turbulent flow which varies in direct proportion to the speed of the blood vessel, diameter and the blood density, and inversely proportional to the viscosity:

$$R_e = \frac{\rho v l}{\eta} \quad (V.1)$$

where ρ is the density of the fluid, v - rate of flow of the fluid, l - length of the capillary tube, η - viscosity coefficient. For large arteries blood there is a critical value of the Reynolds number. There are several blood flow regimes depending on the value of Reynolds number:

1. $R_e < R_e^{cr}$ the flow is laminar;
2. $1000 < Re < 2000$ flow is unstable;
3. $Re > 3000$ flow is turbulent.

V.3 Dispersive blood flow

Given the complexity of the flow geometries of the aorta and capillaries in this chapter we have presented a model of complex fluid flow considered applicable blood and subjected to constraints using fractal theory [134-136].

Considering that convective and dispersive effects are dominant, the nature "non-differentiable" of space by moving "particles" of complex fluid on continuous curve and non-differentiable (fractal curves) implies a spontaneous breaking of scale invariance in infinitesimal time. Knowing that fractal operator has the form [134]:

$$\frac{\hat{d}}{dt} = \frac{1}{2} \left(\frac{d_+ + d_-}{dt} \right) - \frac{i}{2} \left(\frac{d_+ - d_-}{dt} \right) \quad (\text{V.2})$$

the velocity becomes a complex quantity:

$$\begin{aligned} \hat{v} &= \frac{d\mathbf{X}}{dt} = \frac{1}{2} \left(\frac{d_+ \mathbf{X} + d_- \mathbf{X}}{dt} \right) - \frac{i}{2} \left(\frac{d_+ \mathbf{X} - d_- \mathbf{X}}{dt} \right) = \\ &= \frac{\mathbf{V}_+ + \mathbf{V}_-}{2} - i \frac{\mathbf{V}_+ - \mathbf{V}_-}{2} = \mathbf{V}_D - i\mathbf{V}_F \end{aligned} \quad (\text{V.3})$$

where \mathbf{X} is the position vector.

The real part V_D of complex velocity $\hat{\mathbf{V}}$ is the classical velocity that is independent of classical resolution, while the imaginary part, V_F is a new size that comes from fractality and is dependent on the resolution.

V.4 Dispersive behavior of complex fluid

If we separate the real part from the imaginary part of velocity field, we obtained two equations, one to the resolution scale differentiable and another to fractal scale resolution [137, 138].

The dimensional spatio-temporal dynamics of complex fluid are given by the cnoidal oscillation modes of the normalized field of the velocity.

Cnoidal oscillation modes have the following characteristics:

- i) wavenumber;
- ii) the phase velocity;
- iii) quasi-period.

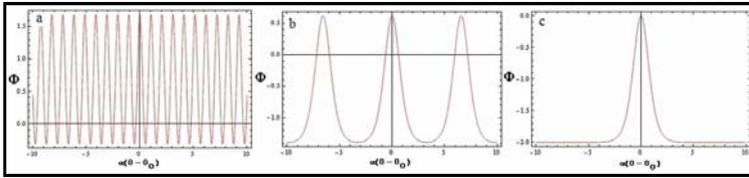


Fig. V.11 Sequences obtained by degeneration of cnoidal oscillation modes of the field velocity: harmonic sequences packet type (a) package type sequences solitons (b) soliton-type sequence (c)

V.5. Conclusions

1. Assuming that the motion of complex fluid particle occurs on a continuous curve but non-differentiable, geodesic equations were obtained in fractal space. These equations are identified with the current lines of complex fluid flow, in which every point on such a line we have a balance between acceleration own self-convection, self-dissipation and self-dispersion of the complex velocity field;

2. If auto-dissipative effects are negligible in comparison with the self-convective and self-dispersive flow, the spatio-temporal of flow dynamics are given by the cnoidal oscillation modes of the complex velocity field;

3. The spatial-temporal degeneration of cnoidal oscillation modes, resulting sequence harmonics, harmonic packages, solitons, packages solitons;

4. The degree of nonlinearity 0.7 requires two flow regimes: non-cvasiautonom, characterized by harmonic sequence type, package cvasiautonomous regime characterized by harmonic sequences packages solitons and soliton type;

The presence of two flow regimes with blood considered as complex fluid involves both structural separation of its components depending on the velocity field values (for non-cvasiautonomous regime) and generate patterns for cvasiautonomous regime.

The separation of blood components has the purpose of atherosclerotic disease while patterns generating results in blockage of blood vessels.

Table V.1 Values of the velocity, diameter and Reynolds number for different blood vessels ($\rho = 1055\text{kg/m}^3$)

No.	Blood vessel	Velocity (cm/s)	Diameter (cm)	Reynolds number
1.	Aorta	48	2,5	3617
2.	Arteries	40	0,4	482
3.	Arterioles	5	0,005	0,753
4.	Capillaries	0,05	0,0008	0,0012
5.	Venules	0,2	0,002	0,012
6.	Veins	10	0,5	151
7.	Pulmonary artery	38	3	3436

Reynolds number values from Table V.1 shows that in the large blood vessels (aorta, pulmonary artery) the flow is turbulent and in the small vessels (capillaries) it is laminar blood flow and the arteries have a transitional regime and can easily pass from one regime to another.

GENERAL CONCLUSIONS

In the present study, they were used some methods based on UV-Vis spectroscopy with which there were highlighted the different types of intermolecular interactions from the binary and ternary solutions made from these vitamins and some polar protic solvents.

When the vitamins are solvated in different polarity solvents it is found that, the position, intensity and shape of the absorption band are changed. We established correlations between these spectral shifts and the macroscopic parameters of the solvent - refractive index and dielectric constant of the solvent.

Using the Bakhshiev theory, the linear correlations of the wavenumber from the maximum electronic absorption band on the $f(\epsilon)$, $f(n)$ and $f(\epsilon, n)$ functions were obtained.

Also, using the Abe cell model, the dipole moments and the polarizabilities of these vitamins in the excited states were calculated.

For all the vitamins it was found that the value of the dipole moment in the excited state is lower than the ground state which shows that the ground state is more stabilized than the excited state. With the increase of the solvent polarity there has been a shift towards smaller wavelengths, *ie* the hypsochrom effect.

The effect of the solvent on the electronic absorption spectrum is described by the solvatochromic Kamlet-Taft equation and the sign of the regression coefficients indicating the type of solvatochromic effect that appears in the analyzed molecular complex.

For the binary and ternary solutions of these vitamins with pure protic solvents there were done simulations to highlight the hydrogen bond and there were estimated some electro-optical molecular parameters of the molecular complexes formed, such as the total energy, the formation heat, HOMO - LUMO of the molecular orbital energy,

dipole moment, polarizability; also, it was obtained the distribution of electrostatic potential density in binary and ternary solutions.

For the molecular complexes, the global descriptors such as electronegativity, hardness, chemical potential and electrophilicity index as a measure of their stability were calculated.

From the point of view of the absorption of these vitamins in the blood it was analyzed a blood flow – Non-Newtonian fluid – using the scale relativity theory. Because the plasma is a Newtonian fluid, the figurate elements of the blood are those that confer non-Newtonian character.

The blood flow in the small vessels can be considered a laminar flow and in the most large vessels is intermediate between laminar and turbulent regime. The turbulent flow of blood in large vessels (greater in the initial part of the aorta and pulmonary artery) is very important because it facilitates the changes between the fluid and the blood vessels and homogenizes the solutes (eg. the vitamins)

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