Theoretical and Experimental Estimation of some Electro – Optical Parameters of B12 Vitamin in Polar Solvents

CRISTINA MARCELA RUSU*
"Al. I. Cuza" University, Faculty of Physics, 11 Bulevardul Carol I, 700506, Iasi, Romania

The aim of this paper is the study of the influence of some solvents on the electronic absorbtion spectra of B12 vitamin by using the cell model of pure liquid proposed by Takehiro Abe. The radius of the first and second solvatation sphere, the number of particles from the first two solvatation sphere were calculated and then it was estimated the potential interaction by dispersion forces between the spectrally active molecule (vitamin B12) and the solvent molecules which surrounded it. The linear dependence between a and b Abe coefficients permits to estimate the polarizability and the dipole moment of the spectrally active molecule (B12 vitamin) in the first excited state. Some electrical parameters were calculated after Langevin dynamics applied to investigate system.

Keywords: Vitamin B12, electronic absorbtion spectra, polarizability in the electronic state, Langevin dynamics, total energy

B12 vitamin called cyanocobalamin, is a water soluble vitamin which plays an important role in the normal functioning of the nervous system, brain and it is involved in the manufacturing of every cell of the human body.

Vitamin B12 consists of class of vitamer and contains the biochemically rare element cobalt.

The molecular formula is $C_{63}H_{88}CoN_{14}O_{14}P$.

The molecular structure of B12 vitamin is:

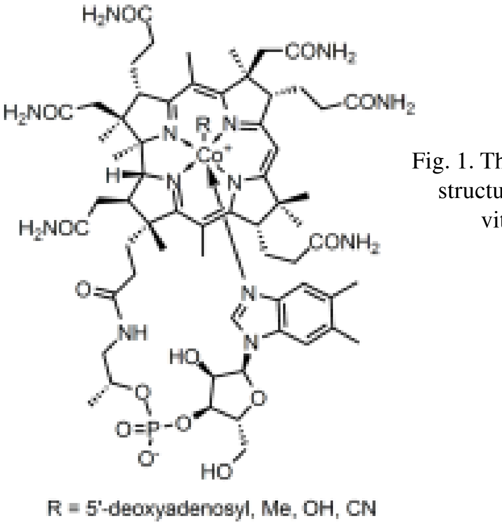

Fig. 1. The Molecular structure of B12 vitamin

The solvent influence on the electronic spectra of B12 vitamin was studied by estimating the contribution of each type of interaction (dispersive, inductive and polarization) to the total spectral shifts registered by passing the spectral active molecule from ground state (gaseous) into solution state achieved in solvents.

Experimental part

Materials and methods

The absorbtion electronic spectra was registred with UV-Vis Shimadzu UV-1700 spectrophotometer.

B12 vitamin has 98% powder and it was purchased from Sigma Aldrich Company.

Theoretical background

In liquids the universal interactions shift the molecular electronic spectra. For estimation of each type of interaction between the spectral molecule and the solvent molecules there are used some theories which regarding the solvent influence on the electronic spectra shifts a function of the electro – optical parameters of the solvent (ε, n) and some microscopic parameters of the spectrally active molecules (the dipole moment, polarizability, ionization potential).

The binary solution can be approximated to a system formed by a "spectrally active" molecule noted by "u" surrounded in the molecular attraction sphere by the solvent molecules, noted "v". The concentrations of the binary solution are very low.

The basic hypotheses of the cell model are [1]:

-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 and the excited state corresponds to the case when the spectrally active molecules are in the excited state and the solvent molecules are in the ground state;

-the distance between the center of spectrally active molecule and the center of solvent molecule from the "p" solvatation sphere is [2]:

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

When the spectrally active molecule is passing from the gaseous state into binary liquid solution it is observed the shift of the maximum electronic band corresponding to the transition between electronic levels:

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

We take into account that in the zero approximation for the ideal gaseous state of the system the energies of the solvent and solute molecules are:

$$\begin{aligned} W_g^0 &= W_g^0(u) + W_g^0(v) \\ W_e^0 &= W_e^0(u) + W_g^0(v) \end{aligned} \qquad (3)$$

---

*email: crina.rusu@yahoo.com

where $W_g^o(v)$ is the total energy of the N type “v” molecules which not interacting between them and $W_g^o(u)$ is the energy of the type “u” isolated molecule.

In the liquid state the molecules interacting between them [3]:

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

Results and discussions

We calculated the radii of the spectrally active molecule and the solvent molecules by using relations:

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

Table 1

Solvent	r_v (10^{-8} cm)
Water	1.925
Methanol	2.523
ethanol	2.85
Acetic acid	2.831
Buthilic alcohol	3.324
NN-DMFA	3.127
Isoamilic alcohol	3.507

The radius of the spectrally active molecules (B12 vitamin) is r_u=3.433(10^{-8} cm).

The values of the radius of the first and the second solvatation sphere calculated by using (1) equation are shown in table 2.

Table 2
THE RADIUS OF THE FIRST AND SECOND SOLVATATION SPHERE

Solvent	$R_{uv(1)}$ (10^{-8} cm)	$R_{uv(2)}$ (10^{-8} cm)
water	5.358	9.208
methanol	5.956	11.002
ethanol	6.283	11.983
Acetic acid	6.264	11.926
Butilic alcohol	6.757	13.405
NN-DMFA	6.553	12.814
Isoamilic alcohol	6.94	13.954

In the “p” solvatation sphere are N(p) molecules [3]:

$$N(p) = \frac{4\pi \cdot R_{uv(p)}^2}{(2r_v)^2} \qquad (6)$$

By using (6) eq. it is obtained the number of molecules from the first solvatation sphere N(1):

Table 3

Solvent	N(1)	N(2)	N=N(1)+N(2)
Water	24	62	86
Methanol	17	60	77
Ethanol	16	58	74
Acetic acid	14	56	70
Butilic alcohol	12	51	63
NN-DMFA	13	53	66
Isoamilic alcohol	12	50	62

The total number of molecules from the first and second sphere of solvatation is:

$$N=N(1)+N(2) \qquad (7)$$

Table 4
THE WAVE NUMBERS OF THE ELECTRONIC ABSORBTION UV SPECTRA

Solvent	λ(nm)	$\tilde{\nu}(cm^{-1})$
Water	361	27701
Methanol	360.8	27716
Ethanol	361.4	27670
Acetic acid	361.2	27685
Buthilic alcohol	361.5	27663
NN-DMFA	361.6	27655
Isoamilic alcohol	361.5	27663

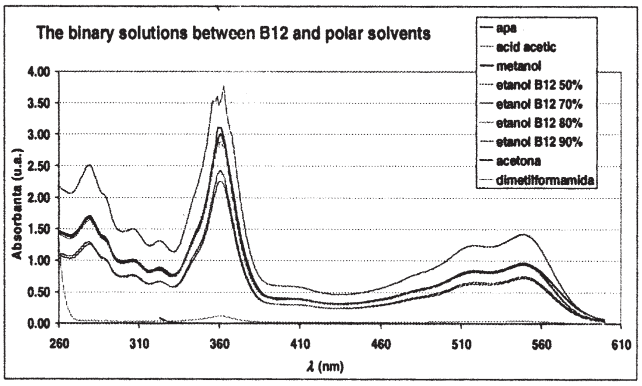

Fig. 2. The electronic absorbtion spectra of B12 in polar solvents

In the liquid state, the molecules interact through forces which can not be neglected. The interactions from liquid state can be classified in two categories [3]:

- the local interactions which are specific to the hydrogen bond formation and they occur between two or three molecules;
- the universal interactions which occurs between a great numbers of molecules and can be classified into: orientation, induction and dispersion interactions.

The universal forces manifest in the sphere of molecular attraction.

The interaction potential by dispersion forces can be expressed by the relation:

$$U_{dsip} = -\frac{3}{2}\cdot\frac{I_u \cdot I_v}{I_u + I_v}\cdot\frac{\alpha_u}{r_u^3}\cdot\frac{n^2-1}{n^2+2} \qquad (8)$$

In the equation (8) α_u, r_u are the polarizability and the radius of the “u” molecule; 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” molecule in the ground state.

By using HyperChem 8.0 molecular program QSAR application - it was calculated the polarizability of “u” molecule (i.e. α_u=130.75 A^3) [4].

The ionization potentials (table 5) of the solvent molecules in the ground state can be approximated by using the Koopman theorem:

$$I \cong -E_{HOMO}(eV) \qquad (9)$$

The ionization potential in the excited state of the “u” can be calculated from the maximum wave number of the electronic spectra by using relation:

Table 5
THE CALCULATED IONIZATION POTENTIAL
OF POLAR SOLVENTS

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	11.44
Butilic alcohol	1.399	0.241	10.887
NN-DMFA	1.431	0.258	9.296
Isoamilic alcohol	1.407	0.246	10.782

$$I_g(u) - I_e(u) = hc\tilde{\nu}_l \tag{10}$$

Table 6
THE VALUES OF DISPERSION
POTENTIAL

Solvent	U_{dsip} (eV)
Water	-2.78
Methanol	-2.79
Ethanol	-3.05
Acetic acid	-3.06
Buthilic alcohol	-3.27
NN-DMFA	-3.5
Isoamilic alcohol	-3.33

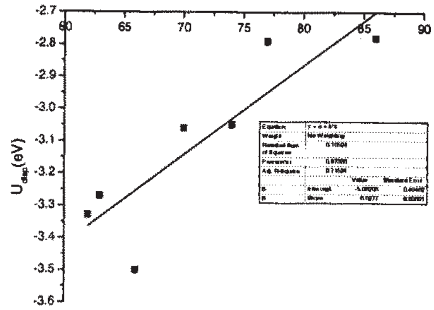

Fig. 3. The dispersion potential vs. number of molecules from the first two solvatation sphere

It can be seen that as the number of the molecules increases when the dispersion potential in absolute value increases.

There were considered as the first approximation only the dispersion forces acting in the solutions formatting by B12 vitamin and polar solvents.

By using notation [5]:

$$X = \frac{3}{2} \cdot \frac{I_e(u) \cdot I_g(v)}{I_e(u) + I_g(v)} \cdot \frac{8066}{r^3(u)} \cdot \frac{n^2 - 1}{n^2 + 2} \tag{11}$$

it can be represented the linear correlation between the wave number in the maximum electronic spectra and term X, ν = f(X).

The slope of this dependence gives the polarizability of spectrally active molecule in the excited state by using equation [7]:

$$\nu = \nu_l + \left[\alpha_g(u) - \alpha_e(u)\right] \cdot X \tag{12}$$

The slope of the straight line represents the difference of the polarizabilities in the two states participating to the transition. By using equation (12) from the slope of the linear dependence is obtained the polarizability of spectrally active molecules :

$$\alpha_e(u) = 131.91 \cdot 10^{-24}\, cm^3$$

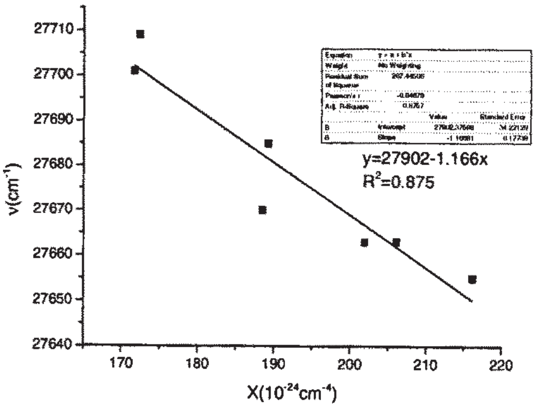

Fig. 4. Spectral shifts vs. dispersion function

Knowing the values of the polarizability in the excited state of the spectrally active molecule it can be calculated the dipole moment of the molecule in the excited state by using equation (13) [6]-[8]:

$$\left[\mu_e^2(u) - \mu_g^2(u)\right] + a \cdot \alpha_e(u) = b \tag{13}$$

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

$$a = \frac{\frac{3}{2} I_g(v)\alpha_g(v) \cdot \frac{I_g(u) - hc\nu_l}{I_g(v) + I_g(u) - hc\nu_l}}{\frac{3}{4\pi N_A} \cdot \frac{M_v}{\rho_v} \cdot \left[\frac{\left(\varepsilon_v - n_v^2\right)\cdot\left(2\varepsilon_v + n_v^2\right)}{\varepsilon_v\left(n_v^2 + 2\right)^2} + \frac{n_v^2 - 1}{n_v^2 + 2}\right]}$$

$$b = \frac{-\frac{\nu_l - \nu_v}{C} + \frac{3}{2}\alpha_g(v) \cdot \alpha_g(u) \cdot \frac{I_g(u) \cdot I_g(v)}{I_g(v) + I_g(u)}}{\frac{3}{4\pi N_A} \cdot \frac{M_v}{\rho_v} \cdot \left[\frac{\left(\varepsilon_v - n_v^2\right)\cdot\left(2\varepsilon_v + n_v^2\right)}{\varepsilon_v\left(n_v^2 + 2\right)^2} + \frac{n_v^2 - 1}{n_v^2 + 2}\right]} \tag{14}$$

The intercept gives the difference between the square of the dipol moments of the two states participating to transition:

$$\left[\mu_e^2(u) - \mu_g^2(u)\right] = 16.06D^2$$
$$\mu_g(u) = 8.33D \tag{15}$$

The dipole moment in the excited state is μ_e=9.24Debye.

By using molecular dynamics calculations we can simulate the movement of the molecules [9-10]. These calculations include studying equilibrum properties and kinetic behaviour. Equilibrum simulations can predict thermodynamic properties of a molecular system [4].

Langevin simulation was used to futher explore the properties of the investigated system: B3 vitamin – water molecule. Similar results on the analized dynamics of the polimers were presented in [11] and [12].

The Langevin simulation was made for a friction coefficients 0.05 ps^{-1}; previous average values -1295.483;

There can be seen lower values of these parameters after Langevin dynamic modeling.

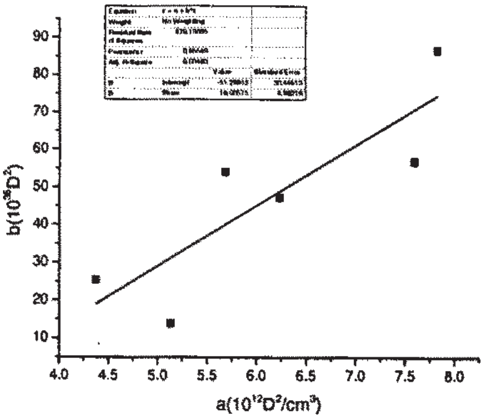

Fig. 5. The linear dependence b vs. a Abe coefficients

Table 7
THE PROPERTIES OF THE INVESTIGATED SYSTEM

Properties	B3+water (ground state)	B3+water (after Langevin dynamic)
Total energy (kcal/mol)	-42948.951	-1788.04
Binding Energy (kcal/mol)	-1795.893	-1791.466
Heat of Formation (kcal/mol)	-114.162	-109.735
E_{HOMO} (eV)	-10.926	-10.418
E_{LUMO} (eV)	-1.123	-0.754
Dipole moment (Debye)	2.748	-1.575
Polarizability (Å^3)	13.75	13.75
Charge on nitrogen atom	-0.098	-0.087

Conclusions

The Abe theory is applied in order to verify the influence of the solvent on the visible vibronic spectra of B12 vitamin.

A linear dependence between a and b coefficients was obtained. The slope of the straight line represents the polarizability of spectrally active molecules in the excited state α_e(u).

The cut to origin corresponding to the linear dependence represents the difference between the square of the dipol moments of „u” molecule in the excited and ground state.

If the dipol moment of the ground state is known by using other method (i.e. from HyperChem program) the dipol moment of the excited state can be estimated by using equation (15).

Comparing the results between the values of the polarizability and the dipol moment of spectrally active molecule in the excited state and the ground state it results an increase both the polarizability and the dipol moment by excitation.

Some electro - optical properties are determined by the universal and specific interactions which act between the solut molecule (B12 vitamin) and the solvent molecules.

The cell model applied to the binary solutions between B12 vitamin and polar solvents permits to estimate the dispersion potential according the basic hypotheses.

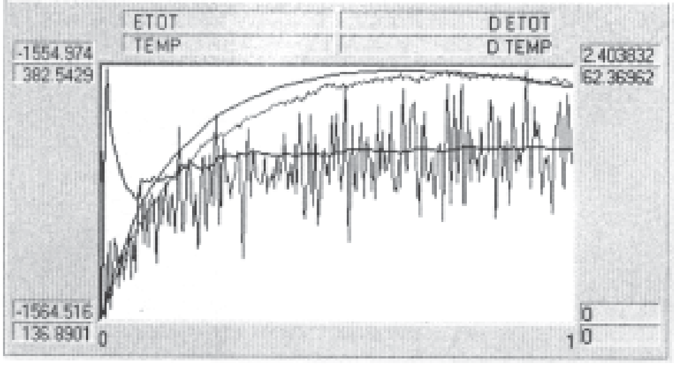

Fig. 6. The Langevin Simalation for B3 vitamin

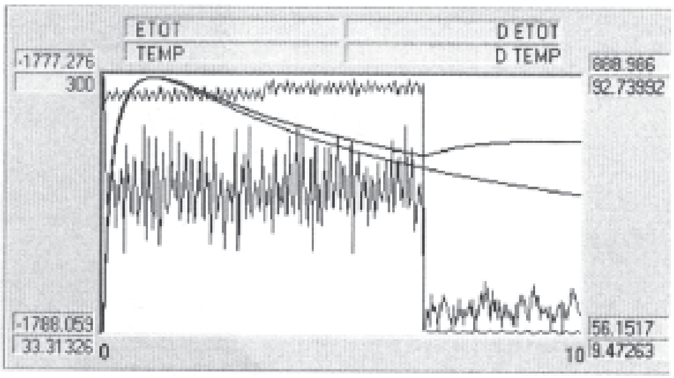

Fig. 7. The Langevin Simulation for molecular system B3 vitamin – water molecule

From Abe model applied to the solution between B12 vitamin and some polar solvents can be estimated the values of microscopic parameters like the polarizability and the dipol moment in the excited state.

References

1. ABE, T., Bull. Chem. Soc. Jap., **38**, 1965, p.1314
2. ABE, T., Bull. Chem. Soc. Jap., **39**, 1966, p. 936
3. DOROHOI, D.O., Liquids State Physics –Models and Experiments, Editura Gama, B.C.U., Iasi, Romania
4 HyperChem, Molecular Visualization and Simulation Program Package, Hypercube, Inc. Gainesville, Floride 32601
5. DIMITRIU, M., „Spectral and Molecular Methods for Estimating of the Electro – Optical and Structural Parameters of the Organic Molecules”, Editura Pim, Iasi, 2009
6. DIMITRIU, M., ROGOJANU, A. , DULCESCU, M., DOROHOI, D.O., Annals of Suceava University-Food Engineering, **1**, 2008, p.74
7. DOROHOI, D.O., J.Mol. Struct., **792**, SI, 2006, p. 86
8. TIGOIANU, I. R., AIRINEI, A., DOROHOI, D.O., Bulletin of the Transilvania University of Brasov, **4**, 2007, p. 289
9. PAUN, V.-P., Mat. Plast., **44**, no. 1, 2007, p. 393
10. PAUN, V.-P., PAUN, M.-A., TOMA, A.,CIUCU, C., POPENTIU, F., Mat. Plast., **45**, no. 1, 2008, p. 57
11. PAUN, V.-P., Rev. Chim. (Bucharest), **57**, no.2, 2006, p. 221
12. COLOTIN, M., POMPILIAN, G. O., NICA, P., et al., ACTA PHYSICA POLONICA A, **116**, nr. 2, 2009, p. 157

Manuscript received: 27.07.2013