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

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The aim of this paper is the study of the influence of some solvents on the electronic absorbption spectra of B12 vitamin by using the cell model of pure liquid proposed by Takehiro Abe. The radius of the first and second solvation sphere, the number of particles from the first two solvation 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 absorbption 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 C₆₃H₈₈CoN₁₄O₁₄P

The molecular structure of B12 vitamin is:

![Molecular structure of B12 vitamin](image)

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 spectrally 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]:

\[ R_{uv(p)} = r_u + (2p - 1) \cdot r_v \] (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:

\[ h \nu (\tilde{\nu}_r - \tilde{\nu}_e) = W_e(u) - W_g(u) \] (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:

\[ W_0^g = W_0^g(u) + W_0^g(v) \]

\[ W_0^e = W_0^e(u) + W_0^e(v) \] (3)
where $W^N(v)$ is the total energy of the $N$ type $v$ molecules which not interacting between them and $W^g_u(u)$ is the energy of the type $u$ isolated molecule.

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

\[
W_g = W^g_0 + W^g(u) + W^g(v)
\]

\[
W_e = W^e_0 + W_e(u) + W_e(v)
\]

(4)

**Results and discussions**

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

\[
r_u = \sqrt[3]{\frac{3}{4\pi N_A}} \cdot \frac{M_u}{\rho_u}
\]

\[
r_v = \sqrt[3]{\frac{3}{4\pi N_A}} \cdot \frac{M_v}{\rho_v}
\]

(5)

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

\[
N = N(1)+N(2)
\]

(7)

**Table 1**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$r_u$ (10^4 cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1.925</td>
</tr>
<tr>
<td>Methanol</td>
<td>2.523</td>
</tr>
<tr>
<td>Ethanol</td>
<td>2.85</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>2.831</td>
</tr>
<tr>
<td>Butyl alcohol</td>
<td>3.324</td>
</tr>
<tr>
<td>NN-DMFA</td>
<td>3.127</td>
</tr>
<tr>
<td>Isoamyl alcohol</td>
<td>3.507</td>
</tr>
</tbody>
</table>

The radius of the spectrally active molecules (B12 vitamin) is $r_u$=3.433(10^4 cm).

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

**Table 2**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$R_{w(1)}$ (10^4 cm)</th>
<th>$R_{w(2)}$ (10^4 cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>5.358</td>
<td>9.208</td>
</tr>
<tr>
<td>methanol</td>
<td>5.956</td>
<td>11.002</td>
</tr>
<tr>
<td>ethanol</td>
<td>6.283</td>
<td>11.983</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>6.264</td>
<td>11.926</td>
</tr>
<tr>
<td>Butyl alcohol</td>
<td>6.757</td>
<td>13.405</td>
</tr>
<tr>
<td>NN-DMFA</td>
<td>6.553</td>
<td>12.814</td>
</tr>
<tr>
<td>Isoamyl alcohol</td>
<td>6.94</td>
<td>13.954</td>
</tr>
</tbody>
</table>

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

\[
N(p) = \frac{4\pi \cdot R^2_{w(v)}(p)}{(2r_u)^2}
\]

(6)

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

\[
N(1) = \frac{4\pi \cdot R^2_{w(v)}(1)}{(2r_u)^2}
\]

**Table 3**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>N(1)</th>
<th>N(2)</th>
<th>N=N(1)+N(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>24</td>
<td>62</td>
<td>86</td>
</tr>
<tr>
<td>methanol</td>
<td>17</td>
<td>60</td>
<td>77</td>
</tr>
<tr>
<td>Ethanol</td>
<td>16</td>
<td>58</td>
<td>74</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>14</td>
<td>56</td>
<td>70</td>
</tr>
<tr>
<td>Butyl alcohol</td>
<td>12</td>
<td>51</td>
<td>63</td>
</tr>
<tr>
<td>NN-DMFA</td>
<td>13</td>
<td>53</td>
<td>66</td>
</tr>
<tr>
<td>Isoamyl alcohol</td>
<td>12</td>
<td>50</td>
<td>62</td>
</tr>
</tbody>
</table>

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

\[
N = N(1)+N(2)
\]

Table 4

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda$(nm)</th>
<th>$\nu$(cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>361</td>
<td>27701</td>
</tr>
<tr>
<td>Methanol</td>
<td>360.8</td>
<td>27716</td>
</tr>
<tr>
<td>Ethanol</td>
<td>361.4</td>
<td>27670</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>361.2</td>
<td>27685</td>
</tr>
<tr>
<td>Butyl alcohol</td>
<td>361.5</td>
<td>27663</td>
</tr>
<tr>
<td>NN-DMFA</td>
<td>361.6</td>
<td>27655</td>
</tr>
<tr>
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<td>361.5</td>
<td>27663</td>
</tr>
</tbody>
</table>

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<td>27663</td>
</tr>
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</table>

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\[
N = N(1)+N(2)
\]

Table 5

**Table 5**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$I_u$ [eV]</th>
<th>$I_v$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>1.30</td>
<td>1.75</td>
</tr>
<tr>
<td>methanol</td>
<td>1.29</td>
<td>1.74</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.30</td>
<td>1.74</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>1.31</td>
<td>1.76</td>
</tr>
<tr>
<td>Butyl alcohol</td>
<td>1.32</td>
<td>1.77</td>
</tr>
<tr>
<td>NN-DMFA</td>
<td>1.33</td>
<td>1.78</td>
</tr>
<tr>
<td>Isoamyl alcohol</td>
<td>1.34</td>
<td>1.79</td>
</tr>
</tbody>
</table>

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:

\[
U_{disp} = -\frac{3}{2} \left( \frac{I_u + I_v}{r_u} \right) \frac{\alpha_u}{r_u^3} \frac{n^2 - 1}{2n^2 + 2}
\]

(8)

In the equation (8) $\alpha$, $r$, $I$ are the polarizability and the radius of the “u” molecule; $I$ 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. $\alpha_u = 130.75$ A$^3$) [4].

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

\[
I = -E_{HOMO}(eV)
\]

(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:
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]:

\[ I_g(u) - I_e(u) = h \nu v \] (10)

The slope of this dependence gives the polarizability of spectrally active molecule in the excited state by using equation (11) [6]-[8]:

\[ a = \frac{3}{2} \frac{I_g(v) \alpha_g(v)}{I_g(v) + I_e(u) - h \nu v} \left( \frac{1}{n_v^2} - \frac{1}{n_v^2 + 2} \right) \]

The slope of the straight line represents the difference of the polarizabilities in the two states participating to the transition.

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]:

\[ \left[ \mu_e^2(u) - \mu_g^2(u) \right] + a \cdot \alpha_e(u) = t \]

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

\[ a = \frac{3}{2} \frac{I_g(v) \alpha_g(v)}{I_g(v) + I_e(u) - h \nu v} \left( \frac{1}{n_v^2} - \frac{1}{n_v^2 + 2} \right) \]

\[ b = \frac{3}{2} \frac{M_v}{n_v^2} \left( \frac{1}{n_v^2 + 2} - \frac{1}{n_v^2} \right) \]

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

\[ \left[ \mu_e^2(u) - \mu_g^2(u) \right] = 16.06 \cdot D^2 \]

The dipole moment in the excited state is \( \mu_e = 9.24 \text{Debye} \).

By using molecular dynamics calculations we can simulate the movement of the molecules [9-10]. These calculations include studying equilibrium properties and kinetic behaviour. Equilibrium 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.
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 \( \alpha(e) \).

The cut to origin corresponding to the linear dependence represents the difference between the square of the dipolar moments of \( \mu \) molecule in the excited and ground state. If the dipole moment of the ground state is known by using other method (i.e. from HyperChem program) the dipole moment of the excited state can be estimated by using equation (15).

Comparing the results between the values of the polarizability and the dipole moment of spectrally active molecule in the excited state and the ground state it results an increase both the polarizability and the dipole 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 some polar solvents permits to estimate the dispersion potential according the basic hypotheses.

**References**

4 HyperChem, Molecular Visualization and Simulation Program Package, Hypercube, Inc. Gainesville, Floride 32601

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