Effect of solvents on the electronic spectra of the amino acids (methionine, cysteine and cystine)

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Abstract

The effects of some solvents (Ethanol, Dioxane, DMSO, DMF and Water) on the U.V spectra were studied by used spectrophotometer from the wave length ranges (190 – 800 nm). The results showed that most of the absorptions were occurred in the U.V region, and that main electronic transitions are related to $n-\pi^*$, $\pi-\pi^*$. Also the results showed that there is effect of the studied solvents on the $\lambda_{max}$ of the amino acids.

Keywords: solvents, electronic spectra, amino acids

1. Introduction

The absorption values in various solvents are influences by solvation and/or dielectric constants of the solvents [1]. The maximum absorption of each ligand at UV region was found in different solvents with different polarities (ethanol, DMF, dioxane, DMSO, and chloroform).

The dielectric constant ($D$) is the factor which has a substantial influence on the transition energy, or more precisely $f(D)$ or $\phi(D)$ [2], where: $f(D) = 2(D-1)/(2D+1)$ and $\phi(D) = (D-1)/(D+2)$

The plots of $(D-1)/(D+1)$, $f(D)$ and $\phi(D)$ against the wave number $\nu_{max}$ (in cm$^{-1}$ of the charge transfer (C.T.) band were obtained for each ligand. In order to know whether the dielectric constant ($D$) is the only factor that influence on the transition energy or there are other factors, like hydrogen bond. The aim of this study is to calculate and investigate of the selected solvents on the studied amino acids by measuring the $\lambda_{max}$ of absorption [1].

Effect of solvents on the electronic spectra of the amino acids

The solvent effects on the electronic absorption spectra are used to study the chemical properties of the excited state and to identify the electronic transitions in a molecule. One of the most simple methods for detecting such effects is the shift of the position of the maximum absorption this is related to the various properties of the solute and the solvent [2].

The solvent polarizability tends to move the absorption maximum towards lower energy, due to the stabilization of the excited state by the induced dipole interaction between the transition moment and the solvent molecule. Also, the frequency shift of the spectra bands from the vapors [3] state to solution could be related to salvation stabilization energy of the excited and ground states depending on the various types of intermolecular interaction. The Frank–condon principle [4] explained the spectral shifts when the solute molecule is excited where the most stable arrangement of the solvent molecules in the ground state is not necessarily. The most stable arrangement in the excited state occurred when the excited solute molecule is surrounded by a solvent cage

In polar or hydrogen bonding solvents with permanent dipole moment for polar solute, blue shift occurs of $\lambda_{max}$ with increasing solvent polarity with the presence of "frank Condon " phenomena. If the excited state – dipole moment is less than that of the ground state, blue shift of $\lambda_{max}$ occurs with increasing solvent polarity. This explains the shift of $n-\pi^*$ transition on hydrogen bonding, relative to hydrocarbon solvents. In general, the functional groups with high bond moments are involved in H-bond formation [5].

The non-polar solute in non-polar solvents leading approximate equal salvation energies of both ground and excited state is due to dispersion depending mainly on the solvent refractive index, similar situation was found for the non-polar solute in polar solvents but with more H-bonding molecule with the increase of solvent cage molecules, the behavior of the polar solute
in the non-polar or polar solvent was found to depend on the
dipole moment of the solute (decreased or increased during
excitation).
The process of the reaction in the first case leads to a blue shift
of the maximum absorption and in the second case a red shift
occurs. It is expected that in the presence of polar solvents,
accumulation of H-bonding forces occurs depending on many
factors: -
The magnitude of the charge in dipole moment during the
electronic transitions, the solvent dipole moment value, and
the size of solvent and solute molecules [9].
Many empirical single-solvent polarity parameters have been
introduced and have had varying degrees of success
 correlating solvent-dependant data. These have been discussed
in a review by Richardt and Dimorth [6]. Nevertheless, little
effort has been devoted to studying the various parameters in
relation to each other. Katritzky el et al [7] had undertaken a
comprehensives study of the effectiveness of the better known
solvent polarity parameters over a wide variety of solvent –
de dependent phenomena (spectroscopic, kinetic and equilibrium)
with the aim of determining the most successful measure of
solvent "polarity". Since it transpires that no single parameter
can deal effectively with all the types of phenomenon which vary with sol

Material and Methods
Ligands
Cysteine
10⁻⁴ M stock solution was prepared by dissolving 0.00302 gm of
cysteine in distilled water by gentle heating till complete
dissolution. The solution was cooled and diluted to 250 ml.
More diluted solutions were prepared by diluting the stock.

Cystine
10⁻⁴ M stock solution was prepared by dissolving 0.0060 gm of
cystine in distilled water by gentle heating till complete
dissolution. The solution was cooled and diluted to 250 ml.
More diluted solutions were prepared by diluting the stock.

Methionine
10⁻³ M stock solution was prepared by dissolving 0.0373 gm of
methionine in 250 ml distilled water, more diluted solutions
were prepared by diluting the stock.

Different solvents with different polarities: - (ethanol, DMF,
dioxane, DMSO, and chloroform).

Results and Discussion
The absorption spectra of the three amino acid compounds in
different solvent (H₂O, dioxane, ethanol, DMF and DMSO)
are illustrated in figures (1, 2 and 3), and the values of λ max are
collected in table (3).
The electronic spectra of cysteine in dioxane gave four bands
at 214,295,316, and 346 nm. These are due to n-π* electronic
transitions [8]. The first band is blue shifted in presence of
hydroxylc solvents to be at 212 and 190 nm (ethanol and H₂O,
respectively). Such band is strongly red shifted to be at 234
nm in presence of DMF. The second band (295 nm) is strongly
blue shifted to be at 246 and 278 nm in presence of H₂O and
DMF solvents while the third and fourth bands are disappeared
in all solvents Figure (1).
On the other hand, the electronic spectra of Cystine in
presence of different solvents are illustrated in Figure (2) and
Table(3) two band are appeared in dioxane with λ max at 206
and 342 nm, due to n-π* type electronic transition. the first
band is slightly red and blue shifted to 208 and 192 nm in
presence of the hydroxylc solvents ethanol and H₂O,
respectively, but strongly red shifted to 238 and 260 nm in
presence of the basic solvents DMF and DMSO, respectively.
The second band 342 nm is highly blue shifted to 246, 286, and
280 nm in presence of H₂O, DMF, DMSO, respectively.
The electronic spectra of Methionine in presence of different
solvents are illustrated in figure (3). Only one main band is
observed in ethanol, dioxane, and water solvents λ max located
at 214, 206, and 196 nm, respectively. This band may
be assigned as being of the n-π* type electronic transition. The
change in the electronic spectral bands from ethanol to water is
a strong indication to the presence of an internal hydrogen
bonds [9]. Such bands in basic solvents become at 278 - 370
nm and 260 – 270nm in presence of DMF and DMSO,
respectively.
The property of the solvent shows a reasonable degree of
correlation with the transition energy is the dielectric constant
[10], λ max is related to f(D) or ϕ(D), where :-

ϕ(D) = \frac{2\(D-1\)}{2\(D+1\)}

f(D) = \frac{\(D-1\)}{\(D+1\)}

For non-polar solvent, four interaction mechanisms are possible: -
1- The dispersion forces between the solute and solvent
molecules.
2- Solvent permanent dipole-solute induced dipole.
3- Solute permanent dipole-solvent induced dipole.
4- Permanent dipole permanent dipole interactions.
The data represented in Figures (4) are in favors to suggest
that all these compounds exist in associated picture in presence
of solvents under investigation.
Table 3: Effect of solvents on the electronic spectral properties of the ligands.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>λ_{max}</th>
<th>H_{2}O</th>
<th>Ethanol</th>
<th>Dioxane</th>
<th>DMF</th>
<th>DMSO</th>
</tr>
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<tbody>
<tr>
<td>Cysteine</td>
<td></td>
<td>190</td>
<td>212</td>
<td>214</td>
<td>234</td>
<td>–</td>
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<td></td>
<td></td>
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<td>295</td>
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<td>–</td>
<td>316</td>
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<td></td>
<td></td>
<td>–</td>
<td>–</td>
<td>346</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Cystine</td>
<td></td>
<td>192</td>
<td>208</td>
<td>206</td>
<td>238</td>
<td>260</td>
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<tr>
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<td>286</td>
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<td>Methionine</td>
<td></td>
<td>196</td>
<td>214</td>
<td>206</td>
<td>278</td>
<td>370</td>
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<tr>
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<td>246</td>
<td>–</td>
<td>346</td>
<td>286</td>
<td>270</td>
</tr>
</tbody>
</table>

Fig 3: Effect of solvent on the electronic spectra of Methionine.

Fig 4a: (D-1/D+1) and 2(D-1)/2D+1, λ_{max} relationship.

Fig 4b: (D-1/D+1) and 2(D-1)/2D+1, λ_{max} relationship.

Fig 4c: (D-1/D+1) and 2(D-1)/2D+1, λ_{max} relationship

References