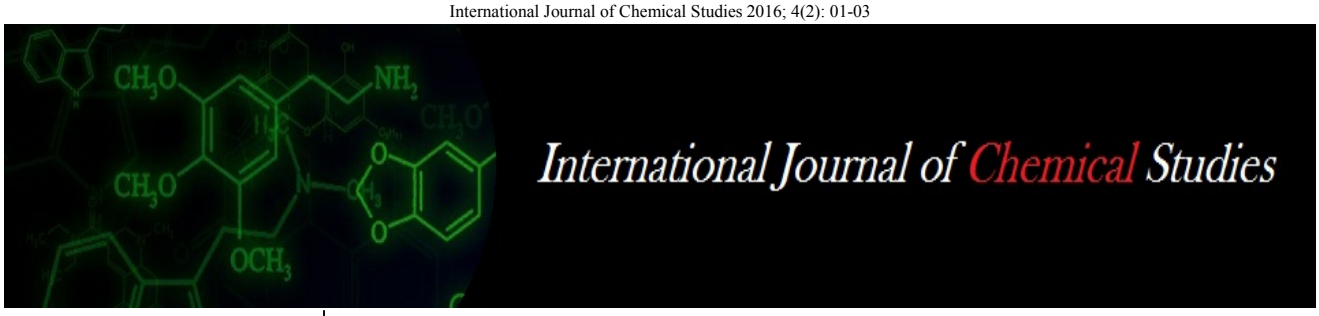

P-ISSN2349–8528
E-ISSN 2321–4902
IJCS 2016; 4(2): 01-03

Received: 10-12-2015
Accepted: 12-01-2016

Hamad M Idres Hasan
Chemistry Department,
Omar El–Mukhtar University,
Libya.

Ahalm M Ali Idres
Chemistry Department,
Omar El–Mukhtar University,
Libya.

Correspondence
Hamad M Idres Hasan
Chemistry Department,
Omar El–Mukhtar University,
Libya.

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

Hamad M Idres Hasan, Ahalm M Ali Idres

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 –π*, π – π*. Also the results showed that there is effect of the studied solvents on the λ 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 ϕ(D) [2], where: *f(D) = 2(D-1) / (2D+1) and ϕ(D) = (D-1)/(D+2)*
The plots of (D-1)/(D+1), f(D) and ϕ(D) against the wave number ν_{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 λ 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 λ_{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 λ_{max} occurs with increasing solvent polarity. This explains the shift of n—π* transition on hydrogen bonding, relative to hydrocarbon solvents. In general, the functional groups with high bond moments are involved in H-bond formation [4].
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 [5].

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 *et al* [7] had undertaken a comprehensives study of the effectiveness of the better known solvent polarity parameters over a wide variety of solvent – 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 (H_2O, 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 hydroxylic solvents to be at 212 and 190 nm (ethanol and H_2O, 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 H_2O 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 hydroxylic solvents ethanol and H_2O, 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 H_2O, 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 many 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 $\phi(D)$, where :-

$$\phi(D) = \frac{2(D-1)}{2(D+1)}$$

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

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.

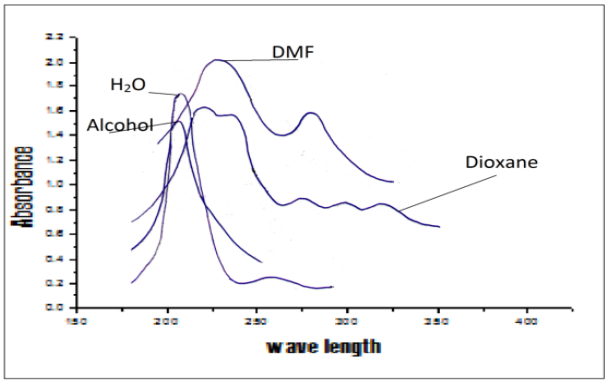

Fig 1: Effect of solvent on the electronic spectra of cysteine.

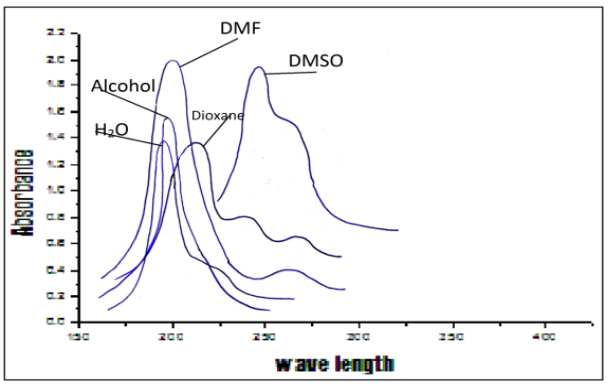

Fig 2: Effect of solvent on the electronic spectra of Cystine.

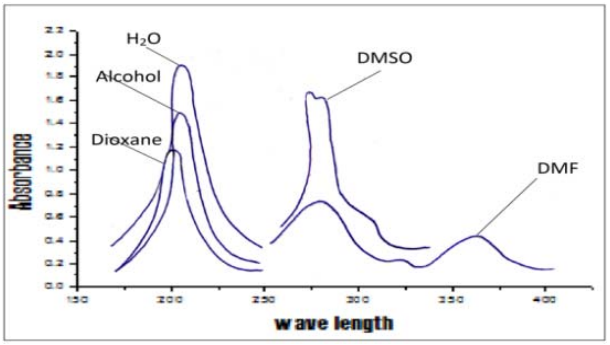

Fig 3: Effect of solvent on the electronic spectra of Methionine.

Table 3: Effect of solvents on the electronic spectral properties of the ligands.

Compounds	λ_{max}				
	H_2O	**Ethanol**	**Dioxane**	**DMF**	**DMSO**
Cysteine	190	212	214	234	–
	246	–	295	278	–
	–	–	316	–	–
	–	–	346	–	–
Cystine	192	208	206	238	260
	246	–	346	286	280
Methionine	196	214	206	278	260
	–	–	–	370	270

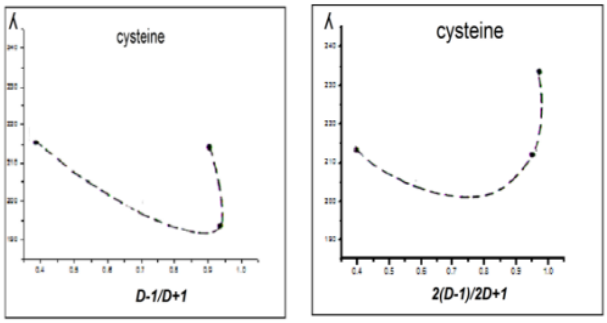

Fig 4a: (D-1/D+1) and 2(D-1)/2D+1, λ_{max} relationship.

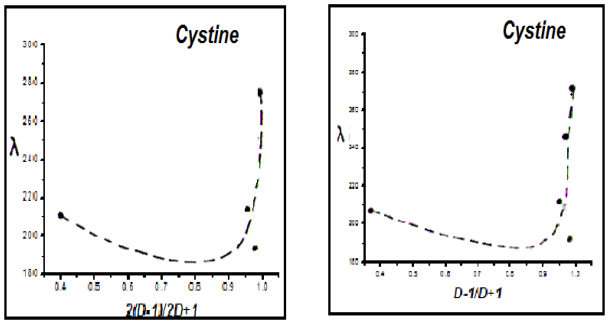

Fig 4b: (D-1/D+1) and 2(D-1)2D+1, λ_{max} relationship.

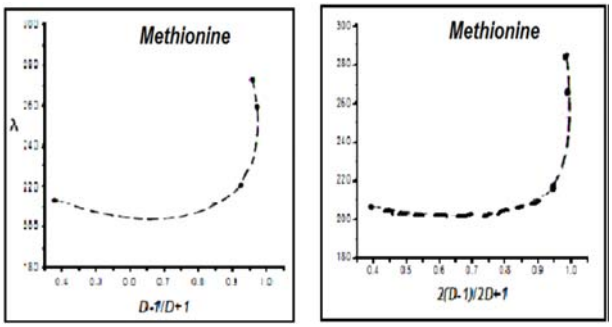

Fig 4c: (D-1/D+1) and 2(D-1)2D+1, λmax relationship

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