Study of Solvent Effects on the Electronic Absorption Spectra of synthesized acrylates in different Solvents

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Abstract

the influence of solvent *polarity on the absorption spectra of synthesized compounds by* using spectrophotometer from wavelenght range(200-400nm). the results showed that most of the absorption happened in the U.V. region. the absorption spectra of the synthesized compounds were studied in three solvents (H_2O, MeOH, $CHCl_3$) to correlate the effect solvent polarity as well as chemical structures on the UV-VIS region. The absorption maximum (ג max) changed from 291to314nm in water, from 304to318nm in chloroform, from 296 to311 in methanol. A multi-parameters regression model for quantitative assessment has been used to explain the solvent effect on synthesized acrylates.

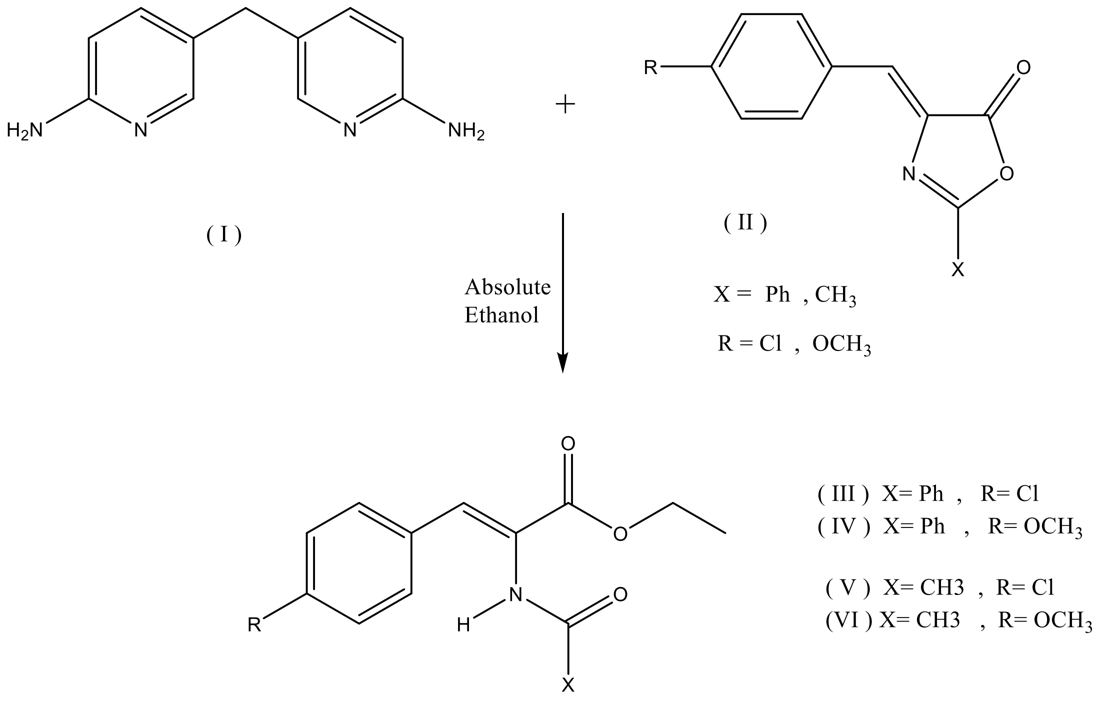
Keywords: electronic absorption, 4-benzylidene-2-phenyloxazol-5(4H)-one, (5,5'-methylene bis (2-amino pyridine), 4-benzylidene-2-methyloxazol-5(4H)-one, solvent effect.

1. Introduction

The study of solvation effect on the structure and spectroscopic behavior of a solute like an organic molecule plays an important role in the development of solution chemistry(Adegoke & Idowu, 2010; Baughman et al., 2009; de Almeida et al., 2011; Kosenkov & Slipchenko, 2010; Sancho et al., 2011; Sıdır et al., 2011) . There are two types of interaction between the solvent and the organic solute, specific and non-specific interaction, which could be accountable for the change in the molecular geometry, electronic structure and dipolar moment of organic molecule (Sancho et al., 2011) . These solute-solvent interactions affect the solute’s electronic absorption spectrum and this phenomenon is well known as solvatochromism (Han et al., 2003; Sancho et al., 2011) . The behavior of a solute in solvents is very different from one to another, and that depends on the polarity index for the solvent (Sancho et al., 2011) . In these kinds of systems, the solute may induce a change in the composition of the solvents in the cybotactic c region compared to that in the bulk leading to preferential solvation (Sancho et al., 2011) .
This situation commonly results from specific, hydrogen bonding, and non-specific, interactions(Sancho et al., 2011) .The polarity measurement is necessary in order to distinguish between these effects. Among all the existing solvent polarity scales (Józefowicz et al., 2005; Kamlet et al., 1983; Sancho et al., 2011; Taft & Kamlet, 1976) .

Polarity dependence of the electronic states of an organic molecule contains a chromophore could be applied as a sensitive of solute-solvent interactions . .

2. Material and methods



(I)

(II)

X = Ph , CH_3

R = Cl , OCH_3

(III) X= Ph , R= Cl
(IV) X= Ph , R= OCH_3

(V) X= CH3 , R= Cl
(VI) X= CH3 , R= OCH_3

The synthesized compounds(5,5'-methylene bis (2-amino pyridine), (4-(4-chlorobenzylidene)-2-phenyloxazol-5(4H)-one), 4-(4-methoxybenzylidene)-2-phenyloxazol-5(4H)-one 4-(4-chlorobenzylidene)-2-methyloxazol-5(4H)-one, 4-(4-methoxybenzylidene)-2-methyloxazol-5(4H)-one , , were prepared in laboratory .faculty of science Benghazi university. purified and recrystallized .All solvents(water, methanol, and chloroform)were Spectro quality grade. The spectra studies in solution were measured using *Cecil 7400 Double Beam UV/Vis Spectrophotometer in which the absorbance is described as a function of wavelength.* The synthesized compounds were characterized by IR, ^1H NMR and ^{13}C NMR, D_2O exchange, APT spectroscopy.

3. Results and Discussion

Figure 1 shows the variation in the UV-absorption spectra of compound (5,5'-methylene bis (2-amino pyridine) at different solvents. As an overall trend, the absorption spectrum of compound

(I) dissolved in water, methanol and chloroform was distinguishable from that of pure solvents, since the spectral band in all solvent ranged from 280 to 340 nm, but the maximum absorbance (A_{max}=1.55) was recorded when the compound (I) was dissolved in water, Up dissolving in chloroform the absorbance declined to 1.08 Fig 1 also displayed that maximum absorbance of bis molecule reached the maximum at 300 nm in water, 303 nm in methanol, and peaked at 304 nm in chloroform. Also, it can be noted that the intensity band increased by increasing the polarity of solvent. This could be attributed to the formation of hydrogen bonding between the polar solvent and the amine group as was described in details by Zaitseva, Varfolomeev, and Solomonov, 2012(Zaitseva, Varfolomeev, & Solomonov, 2012).

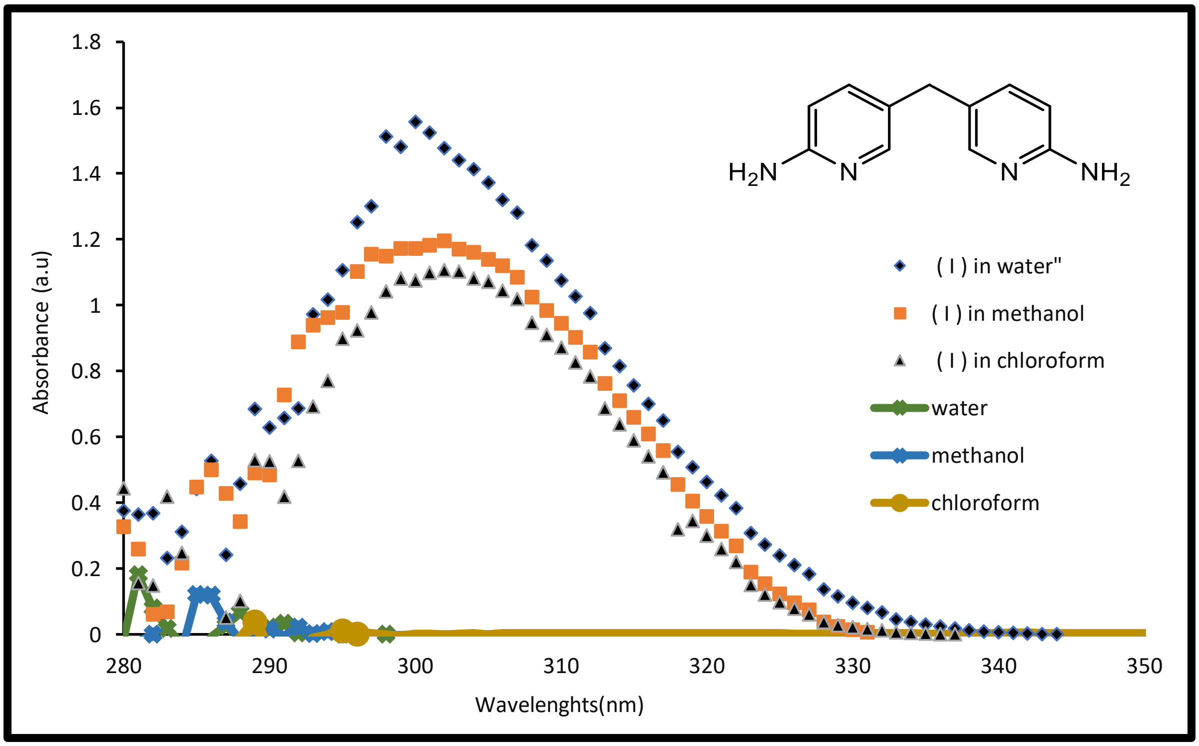


Figure 1. UV-absorbance of (I) as a function of wavelenght at different solvents

Figures 2 and 3 display the change in absorbance relative to the wavelength of compound (III) (Ethyl(Z)-2-benzamido-3-(4-chlorophenyl) acrylate and compound (V) (Ethyl(Z)-2-acetamido-3-(4-chlorophenyl) acrylate compounds in different solvents. In this study, as it can be observed the absorption spectra for these compounds varies from one solvent to another. All of which fall in the range between 280 to 360 nm. Unlike what was noted in case compound (I) Fig 1 The maximum absorption for compounds (III) and (V) were recorded in chloroform and the lowest intensity value was noted when these compounds dissolved in water. Fig 2, exhibits the maximum absorbance of compound (III) at 310 nm in chloroform, 296 nm in methanol, and peaked at 314 nm in water. Fig 3, showed the maximum absorbance of compound (V) approached the maximum at 306 nm in chloroform 296 nm in methanol, and peaked at 299 nm in water. It is important to observe that, there are decreasing in band intensity for these compounds as the polarity increasing.

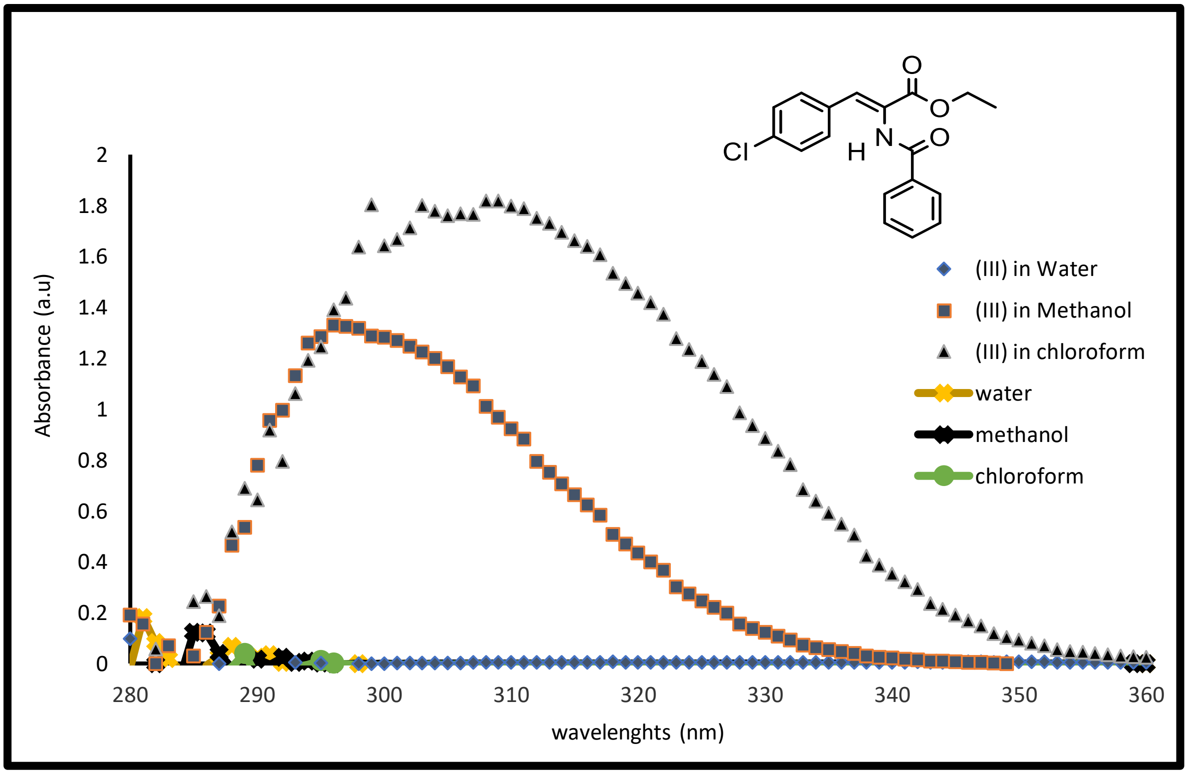


Figure 2. UV-absorbance of (III) as a function of wavelenght at different solvents

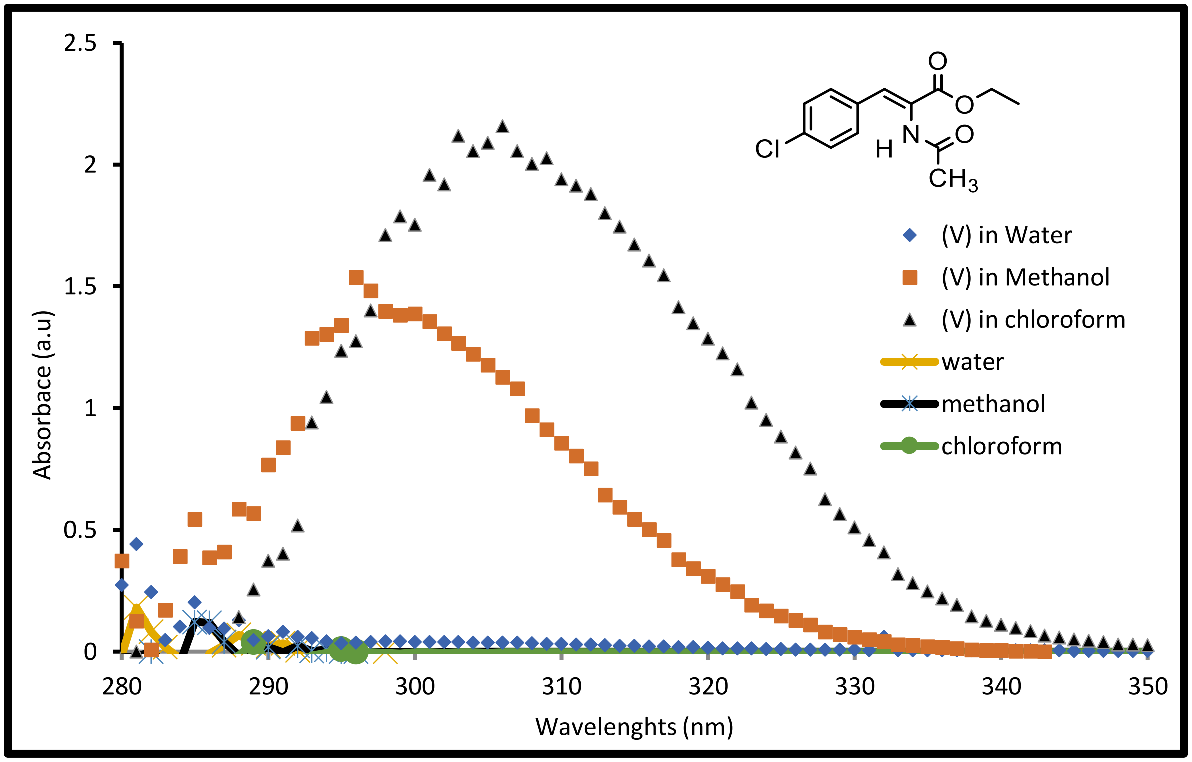


Figure 3. UV-absorbance of (V) as a function of wavelenght at different solvents

Figures 4 and 5 present the variation in the UV-absorption spectra of Ethyl-2-benzamido-3-(4-methoxyphenyl) acrylate (IV) and Ethyl-2-acetamido-3-(4-methoxyphenyl) acrylate (VI) compounds in different solvents. The spectral bands of both compounds at all solvent ranged from 280 upto 370 nm. Fig 4, Shows the maximum absorbance (A_{max}=1.89) was recorded when the compound (IV) was dissolved in methanol. Upon dissolving in water, the absorbance descends to 0.021. Fig 4, also displayed the maximum absorbance of compound (IV) reach the maximum at 311 nm in methanol, 318 nm in chloroform, and peaked at 308 nm in water. Fig 5, exhibit the maximum absorbance (A_{max}=2.43) was observed when the (VI) compound was dissolved in water, and the minimum absorbance recorded in methanol (A_{max} = 0.168). Fig 5, showed the maximum absorbance of (VI) compound at 309 nm in water, and lowest absorbance peaked at 311 nm in methanol.

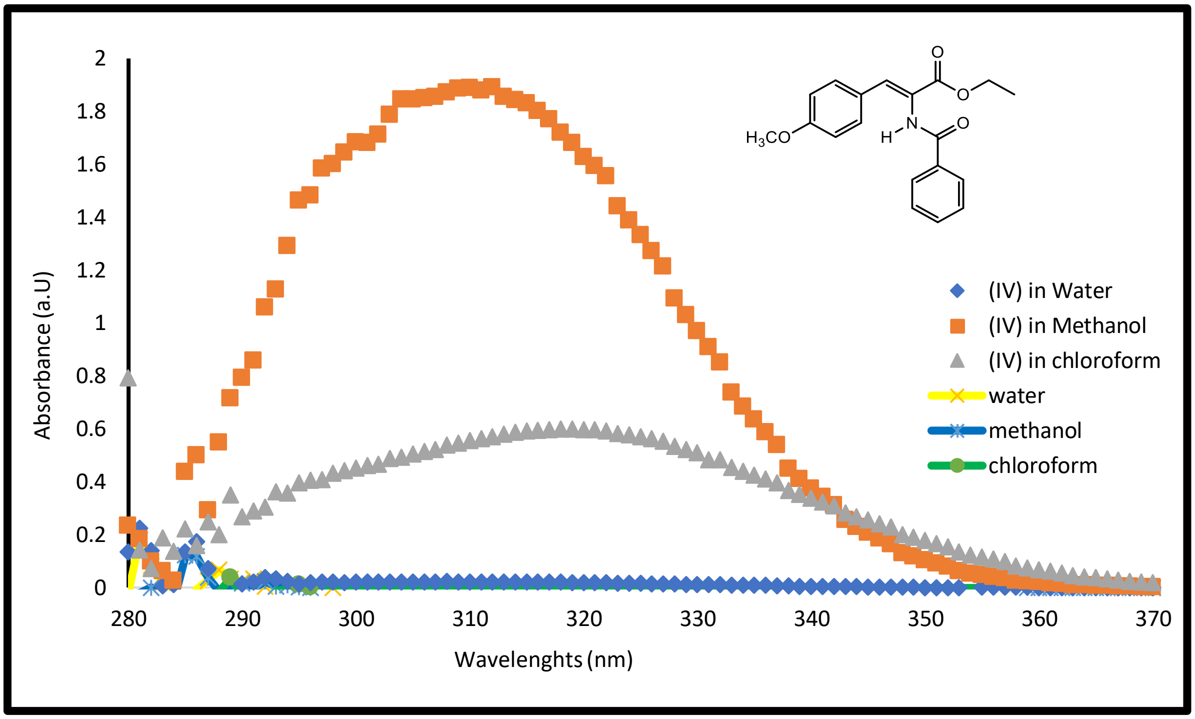


Figure 4. UV-absorbance of (IV) as a function of wavelenght at different solvents

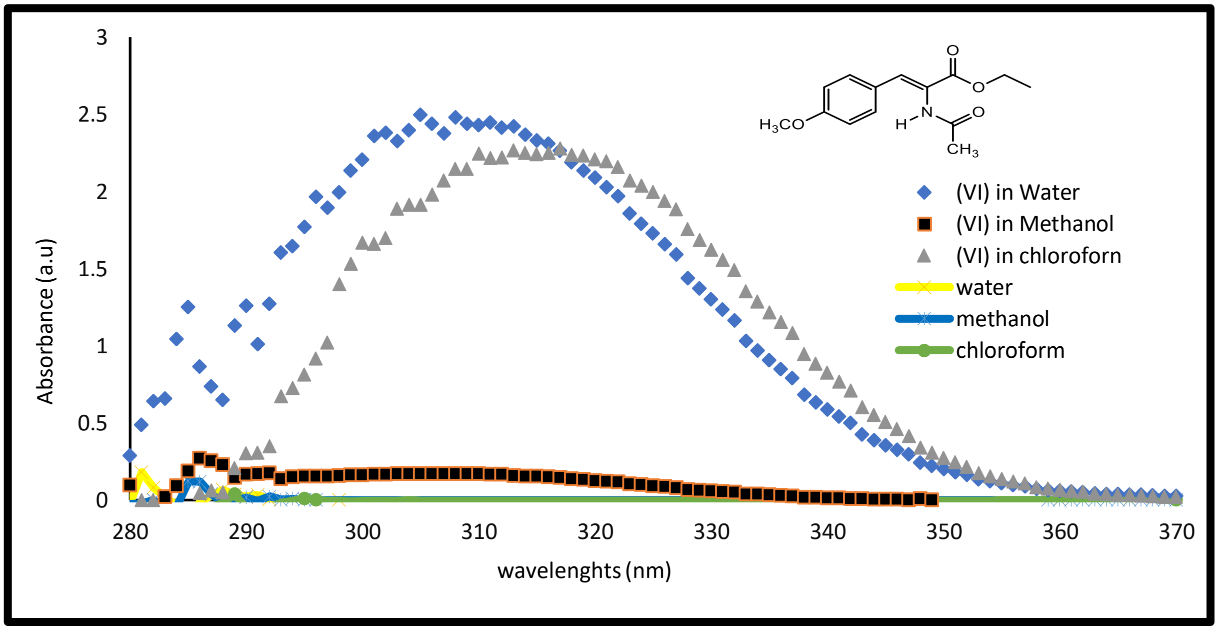


Figure 5. UV-absorbance of (VI) as a function of wavelenght at different solvents

Table (1) presents the maximum absorption wavelength (λ_{max}) of the studied organic compounds (I, III, IV, V, VI) in different solvents. The UV-absorption spectra show absorbance maxima can be found in (291-318) nm depending on the used solvent, are summarized. For compound (I) (A_{max}=1.55 in water, 1.17 in methanol, 1.08 in chloroform). As was observed the decreasing in wavelength corresponding to increasing in absorbance and increasing in polarity of solvent. For compound (III) (A_{max} =1.79 in chloroform ,1.39 in methanol, 0.005 in water). The maximum absorbance recorded when compound (III) dissolved in chloroform. With decreasing the polarity of solvent, the absorbance increase. For compound (V) (A_{max} =0.08 in water, 1.35 in methanol, 2.15 in chloroform). As was noted the increasing in wavelenght with decreasing in polarity of solvent and increase in absorbance. In compound (IV) (A_{max}= 0.021 in water, 1.89 in methanol, 0.6 in chloroform). Finally, for compound (VIII) (A_{max} = 2.43 in water, 2.24 in chloroform, 0.16 in methanol). In the case of (IV) and (VI) compounds there is no clear trend between the solvent polarity, absorbance and wavelenght values.

Table 1. Absorption maxima of studied organic compounds in different solvents, λ_{max} values are expressed in nm.

Com.NO	**Solvent**	**λ (nm)**	**$\tilde{V}$ (nm^{-1})**	***A* (a.u)**	**$\mathcal{E}$ (M^{-1} cm^{-1})**
I	**Water**	**300**	**0.00333**	**1.557**	**18.317**
	Methanol	**303**	**0.0033**	**1.171**	**13.776**
	Chloroform	**304**	**0.00329**	**1.082**	**12.729**
III	**Water**	**314**	**0.00318**	**0.005**	**96.89**
	Methanol	**296**	**0.00338**	**1.39**	**26.937**
	Chloroform	**310**	**0.00323**	**1.798**	**34.844**
IV	**Water**	**308**	**0.00316**	**0.021**	**401.5**
	Methanol	**311**	**0.00322**	**1.89**	**35.946**
	Chloroform	**318**	**0.00314**	**0.6**	**11.472**
V	**Water**	**291**	**0.00334**	**0.08**	**645.6**
	Methanol	**296**	**0.00338**	**1.536**	**24.189**
	Chloroform	**306**	**0.00327**	**2.157**	**33.968**
VI	**Water**	**309**	**0.00324**	**2.438**	**37.740**
	Methanol	**311**	**0.00326**	**0.168**	**2678**
	Chloroform	**315**	**0.00317**	**2.24**	**52.093**

The molar absorptivity, also known as molar extinction coefficient, at a selected wavelenght ($\mathcal{E}_\lambda$) was determined by using the absorbance (A_λ) read at that wavelenght according to the following equation(Cataldo et al., 2013) :

$$\mathcal{E}_\lambda = A_\lambda (bc)^{-1} \ldots\ldots (1)$$

Table (1) summarized the result of molar extinction coefficient. From the data it is evidenced that the ($\mathcal{E}_\lambda$) of all synthesized compounds were extremely high. According to the Lambert and Beer law, the absorbance is directly proportional to the thickness "b" (or optical path length) and the concentration "c" of the absorbing molecules in the UV spectra. As shown in equation (1), the proportionality constant linking absorbance
with the optical path length and with concentration is "ε" , known as molar absorptivity
or more commonly known in the literature as molar extinction coefficient whose typical
physical dimensions are $L \bullet cm^{-1} \bullet mol^{-1}$ (Cataldo et al., 2013; Clothup et al., 1990).

The molar absorptivity coefficient ($\mathcal{E}$) for esters in different solvents evaluated show the trend that the molar absorptivity coefficient increased as the polarity of the solvent decreased. The decrease of molar absorptivity ($\mathcal{E}$) with increasing polarity shows that as the energy gap between two states (ground and excited state) increasing, possibility of transition becomes less, hence decreases molar absorptivity
coefficient ($\mathcal{E}$). The influence of nonpolar solvent addition is generally attributed to the differential polarity of the ground- and excited state orbitals.
Relative polarities of n, π, and π^* orbitals: $\pi < \pi^* < n$.
n orbitals interact the most strongly with polar solvents, followed by π^*, then by π.

This could be attributed to, so that it's more favorable to determine ($\mathcal{E}_\lambda$) in organic solvent instead of water.

To sum up, we have investigated the effect of different solvents on the spectral parameters of organic compounds prepared at laboratory by using UV-vis spectroscopy. This technique offers a means to study and understand polarity and solvation dependences on absorbance and its related parameters. Table (2) The increase of solubility lead to increase in solvation as a result decrease in molar extinction coefficient as we observed in the cases of compounds (III), (V) and (IV) in water.

But the remainder compounds in all solvents the results were satisfactory the absorbance spectrophotometry of different solvents is influenced by the physical properties of the solvent, the most important of which are: dipole moment, dielectric constant and refractive index, the difference in solvation energy from one solvent to another, the change in polarity and bipolar of dissolved during the excitation process. Thus, the solvent effect is the sum of many factors that can get together with each other or cancel each other.

Table 2. **Some physical properties of solvents used in this work.**

Solvents	**Dielectric Constant (κ)**	**Dipole moment (μ)**	**Refraction index (n)**
Water	80.1	1.82	1.33
Methanol	23.7	1.7	1.32
Chloroform	4.8	1.15	1.45

4. Conclusion

According to the literature Oxazolones react with amines to give imidazolone· In this work more than two types of Oxazolones, 4-Arylidene-2-methyloxazol-5(4H)-one, 4-Arylidene-2-phenyloxazol-5(4H)-one. Were reacted with 5,5'-methylene bis(2-aminopyridine) using different techniques, in the presence of Absolut ethanol, the acrylic esters were produced, four novel acrylic esters (III-VI) with different yields (5-86%) was prepared. this method is a new method for synthesis of acrylic ester

The effect of different solvents on the spectral parameters of organic compounds prepared at laboratory was investigated by using UV-vis spectroscopy. Where This technique offers a means to study and understand polarity and solvation dependences on absorbance and its related parameters. the result was the increasing of solubility lead to increasing in solvation as a result decreasing in molar extinction coefficient as observed in the cases of compounds (III), (V) and (IV) in water. The absorption spectrophotometry of different solvents is influenced by the physical properties of the solvent, the most important of which are: dipole moment, dielectric constant and refractive index, the difference in solvation energy from one solvent to another, the change in polarity and bipolar of dissolved during the excitation process. Thus, the solvent effect is the sum of many factors that can get together with each other or cancel each other.

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