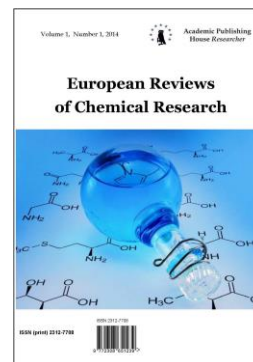


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Solvatochromic and Halochromic Evaluation of Some Biheterocyclic Cyanine Dyes

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Abstract

In the present study, the electronic absorption spectra of some biheterocyclic cyanine dyes having furan and pyrazole nucleus was recorded and investigated in a number of 6 (six) pure solvents having different polarities [water (78.54), D.M.F (36.70), ethanol (24.3), chloroform (4.806), CCl_4 (2.238) and dioxane (2.209)], mixed solvents [DMF- H_2O] and/or in a series of 8 (eight) aqueous universal buffer solutions having varied pH values [1.65, 2.32, 4.62, 5.85, 6.41, 7.82, 9.61 and 11.63 units] to evaluate their solvatochromic and/or halochromic properties, respectively. The dyes were thought to be better solvatochromic dyes when they give strong positive and/or negative solvatochromism in pure solvents having different polarities. Consequently, the solvatochromic of the dyes decrease when they give weak positive and/or negative solvatochromism in pure solvents having different polarities. In addition, the dyes were thought to be better halochromic dyes when they give strong positive and/or negative halochromism in aqueous universal buffer solutions having varied pH values. Consequently, the halochromic of the dyes decrease when they give weak positive and/or negative halochromism in aqueous universal buffer solutions having varied pH values. The study covers two different types of cyanine dyes. It includes, bis dimethine cyanine dyes and di-tri mixed methine cyanine dyes.

Keywords: cyanine dyes, solvatochromic dyes, halochromic dyes, acid-base properties, solvent effects, absorption spectra.

1. Introduction

Cyanine dyes (Shindy, 2012; Shindy, 2016; Shindy, 2017; Shindy, 2018; Shindy, 2019; Shindy, 2020) are important class of functional dyes and possesses an excellent, unique, superior and exceptional photochemical and photophysical properties, such as high molar extinction coefficients (molar absorptivity), tunable fluorescence intensities, narrow absorption bands, moderate quantum yields and absorb light mainly in the visible region, but also include and/or cover UV and NIR regions, larger than any other class of dye system. Therefore, an extensive number of cyanine dyes have been synthesized and developed for numerous applications in photographic processes and more recently as fluorescent probes for bio-molecular labeling and imaging (Mishra, et al., 2000; Pisoni, et al., 2014; Wada, et al., 2015; Hyun, et al., 2014; Hyun, et al., 2015; Njiojob, et al., 2015; Hyun, et al., 2015a; El-Shishtawy, et al., 2010; Henary and Levitz, 2013). On the other side, pyrazole compounds (Perrin, 1972; Eicher and Hauptmann, 2003; Panda and Jena, 2012; Hu, et al., 2012) are reported to possess a wide range of biological activities in literature such as anti-microbial, anti-fungal, anti-tubercular, anti-inflammatory, anti-convulsant,

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anti-cancer, anti-viral, angiotensin converting enzyme (ACE) inhibitory, neuroprotective, cholecystokinin-1 receptor antagonist, and estrogen receptor (ER) ligand activity and others (Katz, et al., 1965; Lango, Valentina, 2007). In addition, furan based substituted compounds (Chandrashekarachar, Kesagudu, 2017) showed very promising biomaterials such as anti-microbial, anti-cancer, anti-hyperglucemic and analgesic. Furan poly substituted compounds are employed as building blocks of synthesis of naturally occurring biomaterials which are important in medicinal chemistry. Besides, solvatochromic (Panigrahi, et al., 2013; Berezin, et al., 2007; Zimmermann, Machado, 2009) compounds attracted much attentions in the application of fluorescent probe, indicator, chromogenic reagent and molecular recognition field. Spectroscopic changes observed when solvatochromic dyes are dissolved in various media have been used to evaluate the polarity, temperature and the viscosity of the microenvironment in solution. Such dyes are useful as optical probes when a small perturbation causes large changes in the spectroscopic properties. Furthermore, halochromic (Zimmermann, Machado, 2009; Mazieres et al., 2009; Bussemer et al., 2009; Puyol et al., 2006) materials are used in chemical indicators, such as universal indicator, which indicates over a pH range of 1-14 with a continuous colour scale. These materials detect alterations in the acidity of substances, like detection of corrosion in metals. They are also suited for use in environments where pH changes occur frequently, or places where changes in pH are extreme.

Based on the former concepts we studied here the solvatochromism and halochromism (acid-base properties) of some biheterocyclic cyanine dyes containing furan and pyrazole nucleus, with the hope that a combination of the favourable properties of both furan, pyrazole and cyanine dyes may be achieved. In addition, this study shed the light on the best practical conditions when these dyes are used and/or applied as photosensitizers. Besides, this study is performed to evaluate the solvatochromic and halochromic properties of the investigated cyanine dyes to may be used and/or applied as solvatochromic and/or halochromic materials in any of the diverse and a broad area of many heterogenous fields, such as chemistry, biology and medicine.

Experimental

The investigated cyanine dyes were prepared in a way that described before (Shindy et al., 2002; Shindy et al., 2006). The molecular structures of the examined cyanine dyes [bis dimethine cyanine dye (1) and di-tri mixed methine cyanine dye (2)] are shown in Scheme 1 (Shindy et al., 2002; Shindy et al., 2006).

The organic solvents were of spectroscopic grade or were purified according to recommended methods (Shindy et al., 2014; Shindy et al., 2014a).

The electronic absorption spectra of the dyes were recorded on UV-VIS recording spectrophotometer using 1 cm cells Quartz. The stock solutions were about 1×10^{-3} M. Lower molarities were obtained by accurate dilution. The spectra were recorded immediately in order to eliminate as much as possible the effect of time.

For mixed solvents studying, an accurate volume of the stock solution (1×10^{-3} M in ethanol) of the dye was placed in 10 ml measuring flask containing the required volume of ethanol, then completed to the mark with the other solvent.

For aqueous universal buffer studying, an accurate volume of the stock solution was added to 5 ml of the buffer solution in a 10 ml volumetric flask, then diluted to the mark with redistilled water. The pH was checked before spectral measurements.

The aqueous universal buffer solution is prepared as a modified buffer series derived from that of Britton (Shindy et al., 2014; Shindy et al., 2014a). The constituents are as follows:

a. 0.4 M solution of phosphoric acid and 0.4 M acetic acid was prepared by dilution of the concentrated stock.

b. A solution of 0.4 M boric acid was obtained by dissolving the recrystallized acid in redistilled water.

c. A stock acid mixture was prepared by mixing equal volumes of the three acids. The total molarity of the acid was thus maintained at 0.4 M.

A series of buffer solutions with varied pH values ranging from (1.65-11.63) was prepared by mixing 150 ml of the acid mixture in a 250 ml volumetric flask with an appropriate volume of 1.0 M NaOH and diluted to the mark with redistilled water. The pH's of the buffer solutions were checked using an Orion pH-meter model (60iA) accurate to 0.005 pH units at 25 °C.

3. Results and discussion

3.1. Solvatochromic evaluation

Solvatochromic properties evaluation for the bis dimethine cyanine dye (1) and di-tri mixed methine cyanine dye (2) was carried out via examining of their electronic visible absorption spectra in pure solvents having different polarities. The dyes were thought to be better solvatochromic dyes when they give strong positive and/or negative solvatochromism in pure solvents having different polarities. Consequently, the solvatochromic of the dyes decrease when they give weak positive and/or negative solvatochromism in pure solvents having different polarities. So, we may say that the solvatochromic of one dye is higher than the other one if the positive and/or the negative solvatochromism in pure solvents having different polarities of the former one is stronger than that of the later one. In contrary, we may say that the solvatochromic of one dye is lower than the other one if the positive and/or the negative solvatochromism in pure solvents having different polarities of the former one is weaker than that of the latter one. (Shindy, 2019; Shindy et al., 2020). Positive solvatochromism reveals bathochromic shifted (red shifted) absorption bands with increasing solvent polarity. In contrast, negative solvatochromism discloses hypsochromic shifted (blue shifted) bands with increasing solvent polarity. This study was carried out to select the best solvents to use of these dyes as photosensitizers when there are applied in photosensitive material industry. The other important purpose of this study is to evaluate the solvatochromic properties of these dyes to may be used and/or applied as probes for determining solvent polarity, in physical, physical organic, inorganic and/or in solution chemistry.

The electronic absorption spectra of the bis dimethine cyanine dye (1), di-tri mixed methine cyanine dye (2) in pure solvents of different dielectric constant viz. water (78.54), D.M.F (36.70), ethanol (24.3), chloroform (4.806), CCl_4 (2.238) and dioxane (2.209) (Shindy et al., 2014; Shindy et al., 2014a) are recorded, Figure 1. The λ_{max} and ϵ_{max} values of the absorption bands due to different electronic transitions within the solute molecule in these solvents are represented in Table 1.

From Table 1, it's clearly that the electronic absorption spectra of the dyes in ethanolic medium are characterized by the presence of one essential absorption bands. These bands can be assigned to intramolecular charge transfer transitions (Shindy et al., 2014; Shindy et al., 2014a). These charge transfer is essentially due to transfer of lone pair of electrons from both pyrazole nitrogen atom and furan oxygen atom to the two positively charged quaternary quinolinium salt residue, Scheme 2.

The data given in Table 1 show that the charge transfer band exhibits a hypsochromic shift in ethanol relative to DMF, dioxane, $CHCl_3$ and CCl_4 . This effect may be attributed to the following factors:

a. The bathochromic shift in DMF relative to ethanol is a result of the increase in solvent polarity due to the increasing of dielectric constant of DMF relative to ethanol.

b. The hypsochromic shift occur in ethanol relative to dioxane, $CHCl_3$ and CCl_4 is result of the solute-solvent interaction through intermolecular hydrogen bond formation between ethanol and the lone pair electrons of both the pyrazole nitrogen atom and the furan oxygen atom, Scheme 3. This decreases slightly the electron density on the pyrazole nitrogen atom and furan oxygen atom and consequently decreases to some extent the mobility of the attached π -electrons over the conjugated pathway system to the positively charged heterocyclic quaternary salt residue, and accordingly blue shifts are occurs.

The unexpected hypsochromic shift in the λ_{max} of the longer wavelength charge transfer in water relative to ethanol and the other solvents, as well as it's lower extinction coefficients can be mainly ascribed to the possible interaction of water molecules with the lone pair electrons of pyrazole nitrogen atom and furan oxygen atom through hydrogen bond formation, Scheme 4. This makes difficult the transfer of charge to the quaternary heterocyclic residue and consequently there is observed a hypsochromic shift in water relative to ethanol and the other solvents, Table 1.

3.2. Solvatochromism in mixed solvents

This study is performed to trace the possibility of the formation of a hydrogen bonded solvated complex between the solute and solvent molecules. The complexes which are liable to form in solution are those of compounds capable of forming stable hydrogen bond between solute and solvent.

The electronic absorption spectra of 1.00×10^{-4} M of the bis dimethine cyanine dye (1) and di-tri mixed methine cyanine dye (2) in DMF containing varying amounts of H_2O is shown in

Figure 2. It's shown in the presence of 11.1 M of H₂O the spectrum exhibits bands at 524 nm for (1) and 529 nm for (2), respectively. While in the presence of 22.2 M, 33.3 M, 44.4 M, 55.6 M the bands is blue shifted to 515, 511, 503 and 501 nm for (1); 519, 516, 507 and 505 nm for (2), respectively. Also, a decrease in band intensity at fixed wavelength [550 nm (1); 530 nm (2)] is observed on increasing of H₂O concentration, See [Figures \(3, 4\)A, A](#).

The decreases in absorbance as well as the gradual blue shift in the maximum absorption wavelength on increasing the H₂O content can be ascribed to the gradual formation of the complex species through intermolecular hydrogen-bonding.

The graphical representation of absorbance at 550 nm for (1); 530 nm for (2) against the mole fraction of H₂O results that the absorbance decreases gradually with increasing the mole fraction of H₂O. See [Figures \(3, 4\)B, B](#).

To investigate the effect of the dielectric constant of the medium on the band shift (γ), on plotting versus $D-1/D+1$ ([El-Ezaby et al., 1970](#); [Gangaly, Banerjee, 1978](#)), broken line was obtained. See [Figures \(3, 4\)D](#).

Furthermore another broken line was obtained on plotting the absorbance against the dielectric constant of the medium. See [Figures \(3, 4\)C](#). Such behavior indicates that factors other than the change in the dielectric constant of the medium are responsible for the shift of λ_{\max} at lower and higher percentage of H₂O. These factors mainly include the solute solvent interaction through intermolecular hydrogen bonding which leads to the formation of some molecular complexes.

On plotting the excitation energy (E) versus the mole fraction of H₂O, See [Figures \(3, 4\)E](#), a broken line with three segments was obtained. The first segment represents the orientation of the solvent molecules around the solute. The second segment corresponds to the molecular complex formation, where is the third one represents the steady state of energy attained after complete of the molecular complex. From the above relation, it is clear that the position of the band and consequently the excitation energy depends not only on the mole fraction of H₂O, but also on the followings:

- a. Solvation energy.
- b. Orientation of the solvent molecule around the solute molecule in the ground and excited states.
- c. Dipole moment of the solute in both ground and excited states.
- d. Dipole-Dipole interaction between the solute and the solvent.
- e. The strength of the hydrogen bonding between the solute and the solvent in both the ground and the excited states.

In pure DMF solution, the dye molecule forms a solvent cage, which is affected on adding H₂O. At lower H₂O content, H₂O molecules will distribute themselves uniformly on all the solvation sheathes around the molecule. The added molecules may first enter the outer solvation sheathes and then will introduce themselves in the first sheathes as their proportions are increased. This probably due to the fact that addition of H₂O permit the formation of the solvent cage around the solute molecules, through intermolecular hydrogen bonding which is previously discussed.

From [Figures \(3, 4\)E](#) and [Table 2](#) it is possible to evaluate the excitation energy of the solute in the pure H₂O as equal to 57.1 Kcal/mol (comp. 1); 56.6 Kcal/mol (comp. 2), whereas the value in pure DMF amounts to 54.3 K cal/mol (comp. 1); 53.7 K cal/mol (comp. 2). The difference between the excitation energy in pure DMF and that corresponding to the first inflection point amounts to 0.30 Kcal/mol (comp. 1); 0.4 Kcal/mol (comp. 2). This value corresponds to the orientation energy of the solvent molecules around the solute molecules ([El-Ezaby et al., 1970](#); [Gangaly, Banerjee, 1978](#)). See [Figures \(3, 4\)E, Table 2](#).

The plot of E and ΔE against the mole fraction of H₂O results broken lines (see [Figures \(3, 4\)E](#); [\(3, 4\)F, Table 2](#)) indicating that the excitation energy depends on factors other than the mole fraction of H₂O. From the above relation it was observed that the orientation energy is equal to 0.90 Kcal/mol (comp. 1), 1.00 Kcal/mol (comp. 2) and the hydrogen bond energy equal to 0.50 Kcal/mol (comp. 1), 0.30 Kcal/mol (comp. 2), see [Table 2](#).

3.3. Halochromic evaluation

Halochromic properties evaluation for the bis dimethine cyanine dye (1) and di-tri mixed methine cyanine dye (2) was carried out by investigated of their electronic visible absorption

spectra in aqueous universal buffer solutions having varied pH values, [Figure 5](#). The dyes were thought to be better halochromic dyes when they give strong positive and/or negative halochromism in aqueous universal buffer solutions having varied pH values. Consequently, the halochromic of the dyes decrease when they give weak positive and/or negative halochromism in aqueous universal buffer solutions having varied pH values. So, we may say that the halochromic of one dye is higher than the other one if the positive and/or the negative halochromism of the former one in aqueous universal buffer solutions having varied pH values is stronger than that of the latter one. In contrary, we may say that the halochromic of one dye is lower than the other one if the positive and/or the negative halochromism of the former one in aqueous universal buffer solutions having varied pH values is weaker than that of the latter one. ([Shindy, 2019](#); [Shindy et al., 2020](#)). Positive halochromism means occurrence of a bathochromic shifted (red shifted) absorption bands with changing solution pH of the buffer solution. In contrast, negative halochromism means occurrence of a hypsochromic shifted (blue shifted) absorption bands with changing the pH of the buffer solution.

The solutions of the bis dimethine cyanine dye (1) and di-tri mixed methine cyanine dye (2) have a permanent cationic charge in basic media which then discharged on acidification. This prompted our attention and encouraged us to study their spectral behavior in different buffer solutions in order to select a suitable pH for use of these dyes as photosensitizers. The other important purpose of this study is to evaluate the halochromic properties of these dyes to may be used and/or applied as indicators in operations of acid/base titrations in analytical chemistry. The acid dissociation or protonation constants of these dyes have been determined. The effect of the compounds as photosensitizers increase when they are present in the ionic form, which has a higher planarity ([Shindy et al., 2014](#); [Shindy et al., 2014a](#)), and therefore more conjugation.

The electronic spectra of the bis dimethine cyanine dye (1) and di-tri mixed methane cyanine dye (2) in aqueous universal buffer of varying pH values (ranging from 1.65 to 11.63 units) showed bathochromic shifts with intensification of their absorption bands at high pH (alkaline media) and hypsochromic shifts with quenching the intensity of the absorption bands at low pH (acidic media), [Figure 5](#).

So, the mentioned dyes which have free lone pairs of electrons on the pyrazole nitrogen atom and furan oxygen atom undergo protonation in low pH (acidic media). This leads to a criterion of positive charge on pyrazole nitrogen atom and furan oxygen atom and consequently the electronic charge transfer pathway to the quaternary heterocyclic quinolinium salt residue will be difficult resulting a hypsochromic shifts for the absorption bands.

On increasing the pH of the media, the absorption bands are intensified and bathochromically shifted due to deprotonation of the pyrazole nitrogen atom and furan oxygen atom and consequently the electronic charge transfer pathways to the quaternary heterocyclic quinolinium salt residue will be easier and facilitated resulting a bathochromic shifts for the absorption bands.

The charge transfer of the dyes is attributed to electronic transitions from both pyrazole nitrogen and furan oxygen atoms to the positively charged quinolinium 2-yl salt moiety, [Scheme 2](#). This electronic transitions are responsible for intensification of the absorption bands and the mesomeric interactions with the rest of the molecule, consequently the charge transfer band interaction within the free base is facilitated, [Scheme 2](#).

Several methods have developed for spectrophotometric determination of the dissociation constants of weak acids. The variation of absorbance with pH can be utilized ([Shindy et al., 2014](#); [Shindy et al., 2014a](#)). On plotting the absorbance at the λ_{\max} vs. pH, an S-shaped curves are obtained, [Figure 6](#), [Table 3](#).

An all of the S-shaped curves obtained, the horizontal portion to the left corresponds to the acidic form of the indicator, while the upper portion to the right corresponds to the basic form, since the pka is defined as the pH value for which one half of the indicator is in the basic form and the other half in the acidic form. This point is determined by intersection of the curve with a horizontal line midway between the left and right segments ([Shindy et al., 2014](#); [Shindy et al., 2014a](#)). The acid dissociation or protonation constants values of the dyes are summarized in [Table 3](#).

3. Conclusion

Following are major conclusions were drawn from the results discussed in this study:

1. The solvatochromism of the bis dimethine cyanine dye (1) and di-tri mixed methine cyanine dye (2) in pure solvents having different polarities underwent displacements to give positive solvatochromism (occurrence of a bathochromic shift with increasing solvent polarity) and/or negative solvatochromism (occurrence of a hypsochromic shift with increasing solvent polarity) depending upon the following factors:

a. Increasing and/or decreasing the polarity (the dielectric constant) of the solvent (general solvent effect).

b. Hydrogen bond and/or molecular complex formation between the solute (dyes molecules) and the solvent used (specific solvent effect).

2. The halochromism of the bis dimethine cyanine dye (1), di-tri mixed methine cyanine dye (2) in aqueous universal buffer solutions having varied pH values underwent displacements to give hypsochromic shifted and lower intensity bands in the lower pH media (acidic media). This is can be related to the protonated structures of the dyes in this media. In contrast, the bands of these dyes are intensified and bathochromically shifted in high pH media (basic media). This can be attributed to the deprotonated structures of the dyes in this media.

3. Solvatochromic evaluation of cyanine dyes can be determining through investigating their electronic absorption spectra in pure solvents having different polarities.

4. Halochromic evaluation of cyanine dyes can be made via examining their electronic absorption spectra in aqueous universal buffer solutions having varied pH values.

5. The trace of the possibility of the formation of a hydrogen bonded solvated complex between the solute (cyanine dyes) and solvent molecules can be performed by investigating the electronic absorption spectra of solute (cyanine dyes) in mixed solvents.

6. These cyanine dyes can be used as probes for determining solvent polarity in solution chemistry due to their solvatochromic properties.

7. These cyanine dyes can be used as acid-base indicators in analytical chemistry due to their halochromic properties.

8. Because cyanine dyes have multi purposes uses and applications in various fields and different research area, this research paper is recommended not only for heterocyclic and/or cyanine dyes chemists but also for other scientists in many and many heterogenous fields like biology, biotechnology, biochemistry, physics, engineering, pharmacology, medicine as well as environment and clinical analysis.

9. Furthermore, this study is recommended for all whom interested in the light absorbing systems in their research, labeling of biomolecules and/or in the synthesis and characterization of complex organic compounds

4. Conflict of interest

There is no conflict of interest.

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Appendix

Table 1. Electronic Absorption Spectra of some biheterocyclic cyanine dyes (1) and (2) in pure solvents (Solvatochromism).

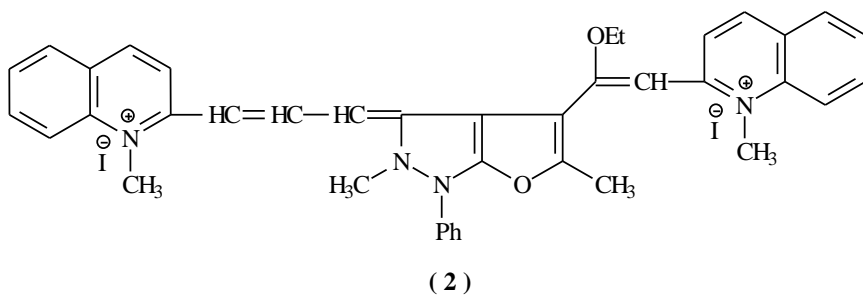
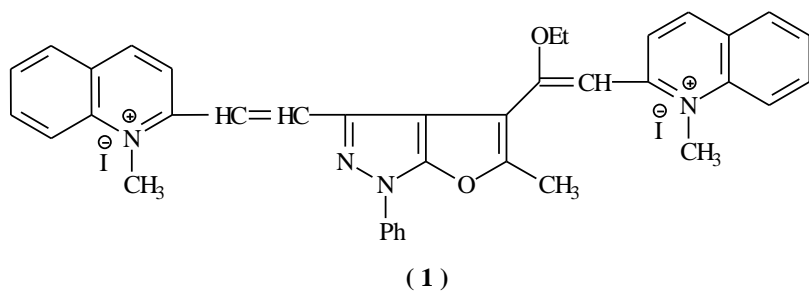
Comp. No.	Water		Ethanol		D.M.F		Chloroform		CCl ₄		Dioxane	
	λ_{\max} (nm)	ϵ_{\max} (cm ² mole ⁻¹)	λ_{\max} (nm)	ϵ_{\max} (cm ² mole ⁻¹)	λ_{\max} (nm)	ϵ_{\max} (cm ² mole ⁻¹)	λ_{\max} (nm)	ϵ_{\max} (cm ² mole ⁻¹)	λ_{\max} (nm)	ϵ_{\max} (cm ² mole ⁻¹)	λ_{\max} (nm)	ϵ_{\max} (cm ² mole ⁻¹)
1	496	16060	502	7890	513	19630	512	18560	503	11040	502	11580
	—	—	—	—	396	16460	514	14730	425	10770	420	10700
2	493	18170	508	14220	518	12630	513	15750	515	12930	513	18240
	—	—	—	—	396	7910	411	12860	519	14100	411	16140

Table 2. Commutative Data Obtained for some biheterocyclic cyanine dyes (1) and (2) in Mixed Solvents (D.M.F.-H₂O mixture)

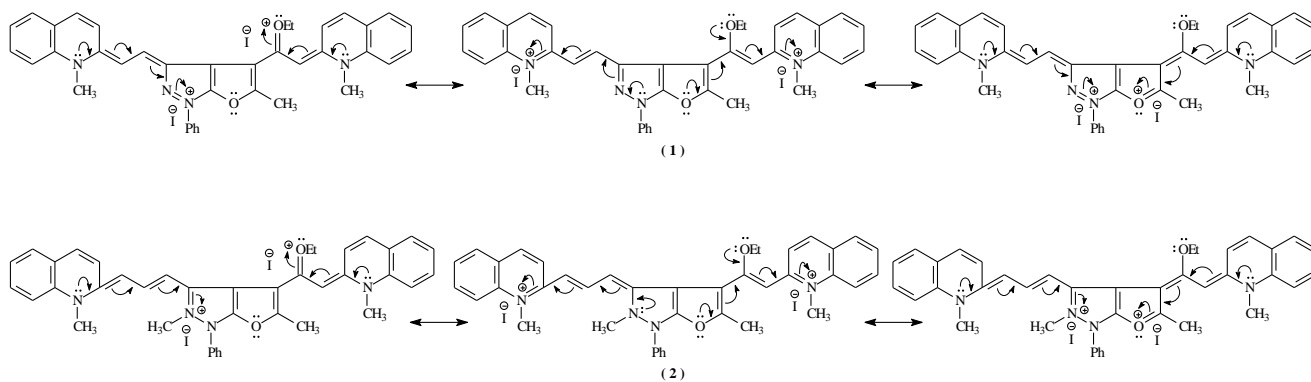
Comp. No.	Excitation Energy in Pure Solvents (kcal./mol.)		Excitation Orient Energy (kcal./mol.)	Excitation H-bond Energy (kcal./mol.)	Total Excitation Energy (kcal./mol.)
	D.M.F.	H ₂ O			
1	54.30	57.10	0.90	0.50	1.40
2	53.70	56.40	1.00	0.30	1.30

Table 3. The variation of absorbance with pH at fixed λ for some biheterocyclic cyanine dyes (1) and (2) in aqueous universal buffer solutions

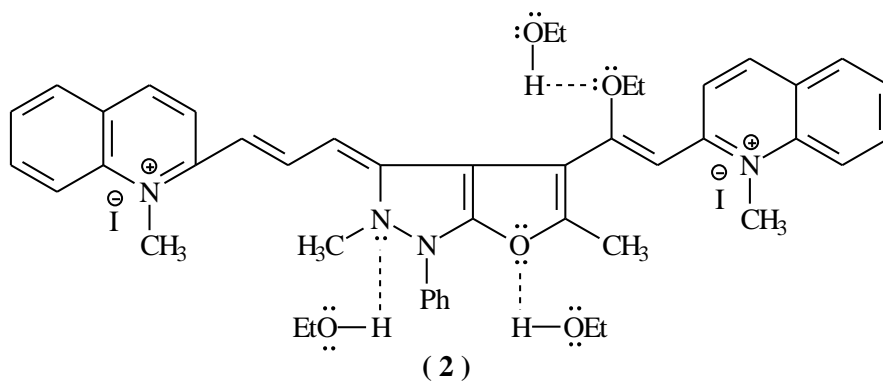
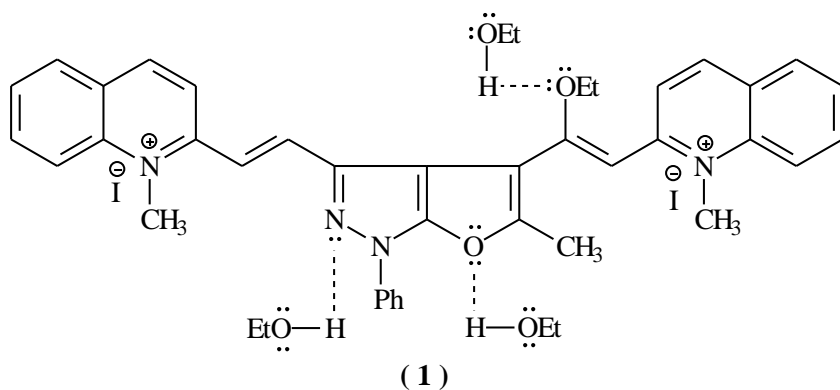
pH	Absorbance	
	(1)	(2)
	$\lambda = 510$ (nm)	$\lambda = 585$ (nm)
1.65	0.35	0.31
2.32	0.71	0.48
4.62	0.86	0.62
5.85	0.82	0.57
6.41	0.82	0.55
7.82	0.82	0.66
9.61	0.87	0.65
11.63	0.89	0.64
pKa	2; 9	2.6; 8.4



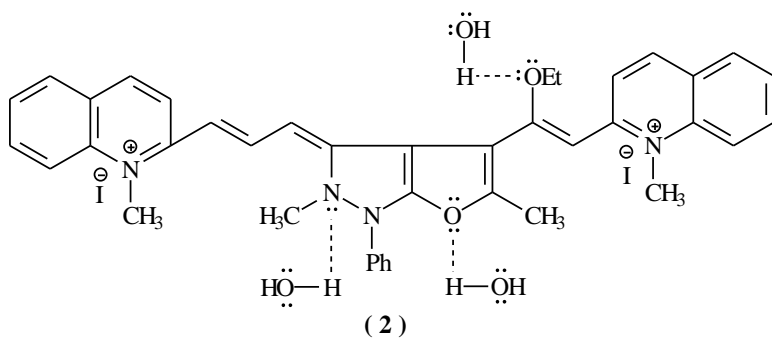
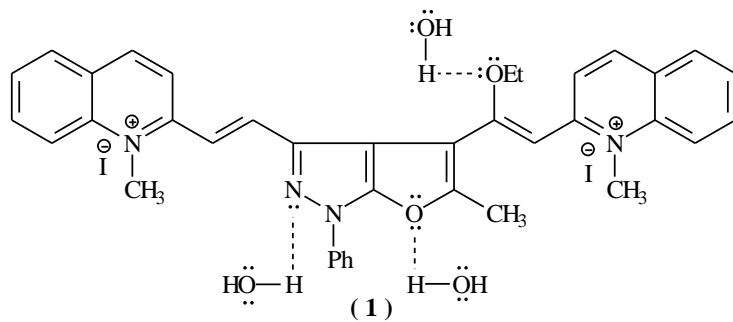
Scheme 1. Molecular structures of the bis dimethine cyanine dye (1) and di-tri mixed methine cyanine dye (2)



Scheme 2. Electronic transitions pathways illustration of the bis dimethine cyanine dye (1) and di-tri mixed methine cyanine dye (2)



Scheme 3. Hydrogen bond formation between the bis dimethine cyanine dye (1), di-tri mixed methine cyanine dye (2) and ethanol molecules (specific solvent effect)



Scheme 4. Hydrogen bond formation between the bis dimethine cyanine dye (1), di-tri mixed methine cyanine dye (2) and water molecules (specific solvent effect)

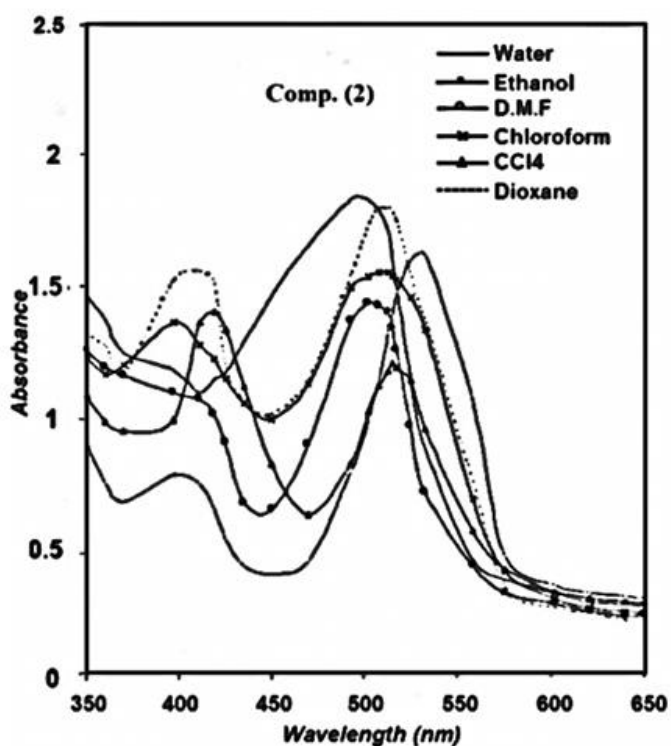
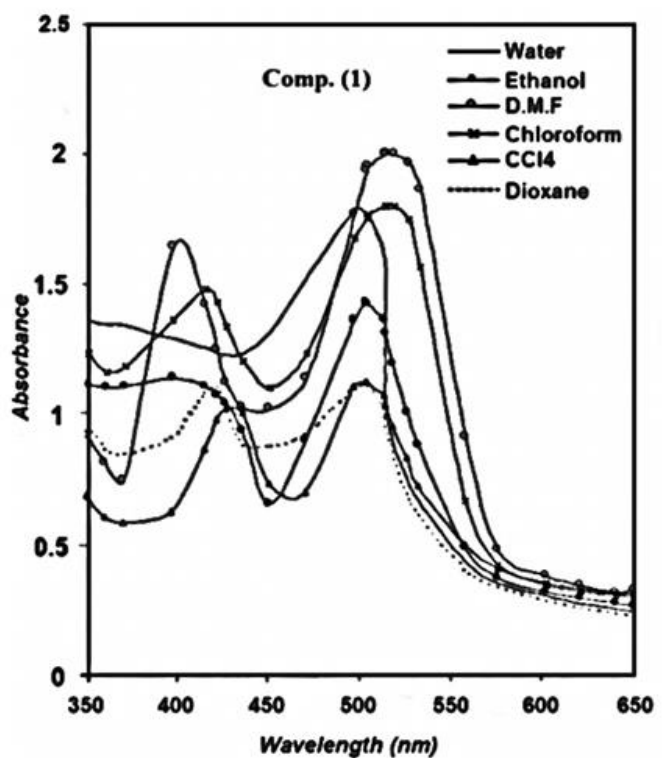


Fig. 1. Solvatochromism of the bis dimethine cyanine dye (1) and di-tri mixed methine cyanine dye (2) in pure solvents

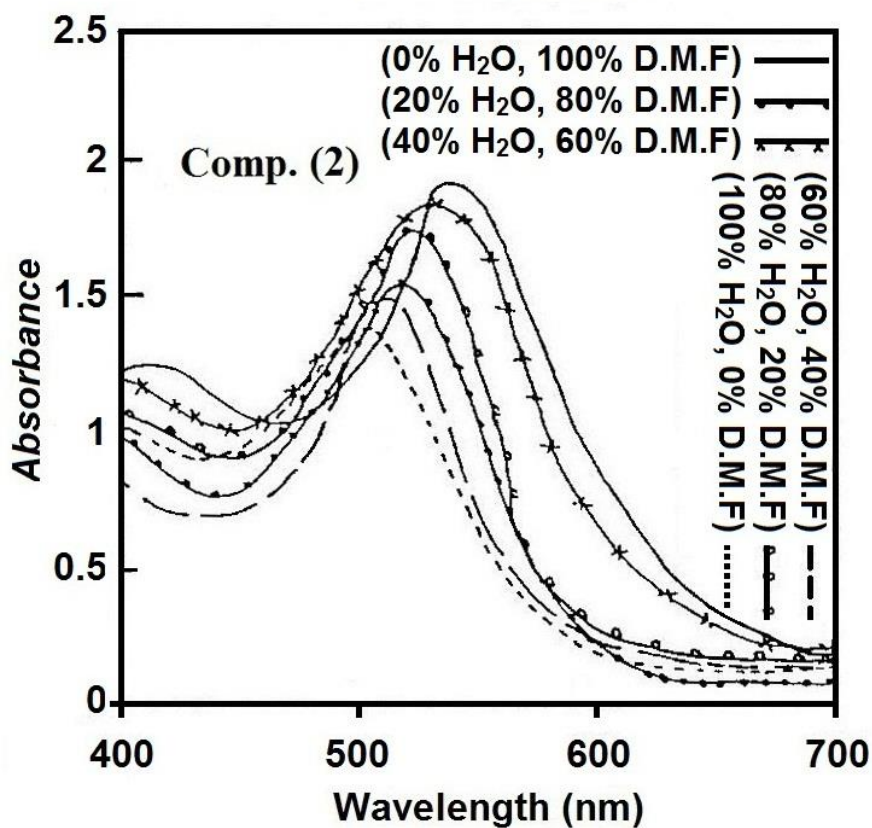
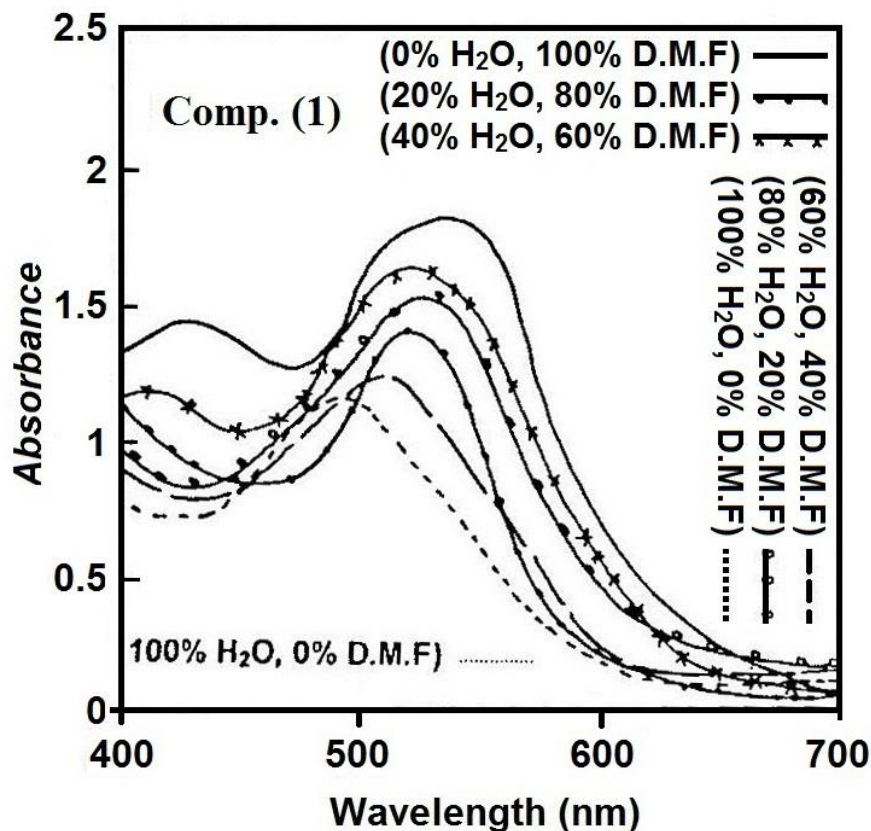


Fig. 2. Solvatochromism of the bis dimethine cyanine dye (1) and di-tri mixed methine cyanine dye (2) in mixed solvents

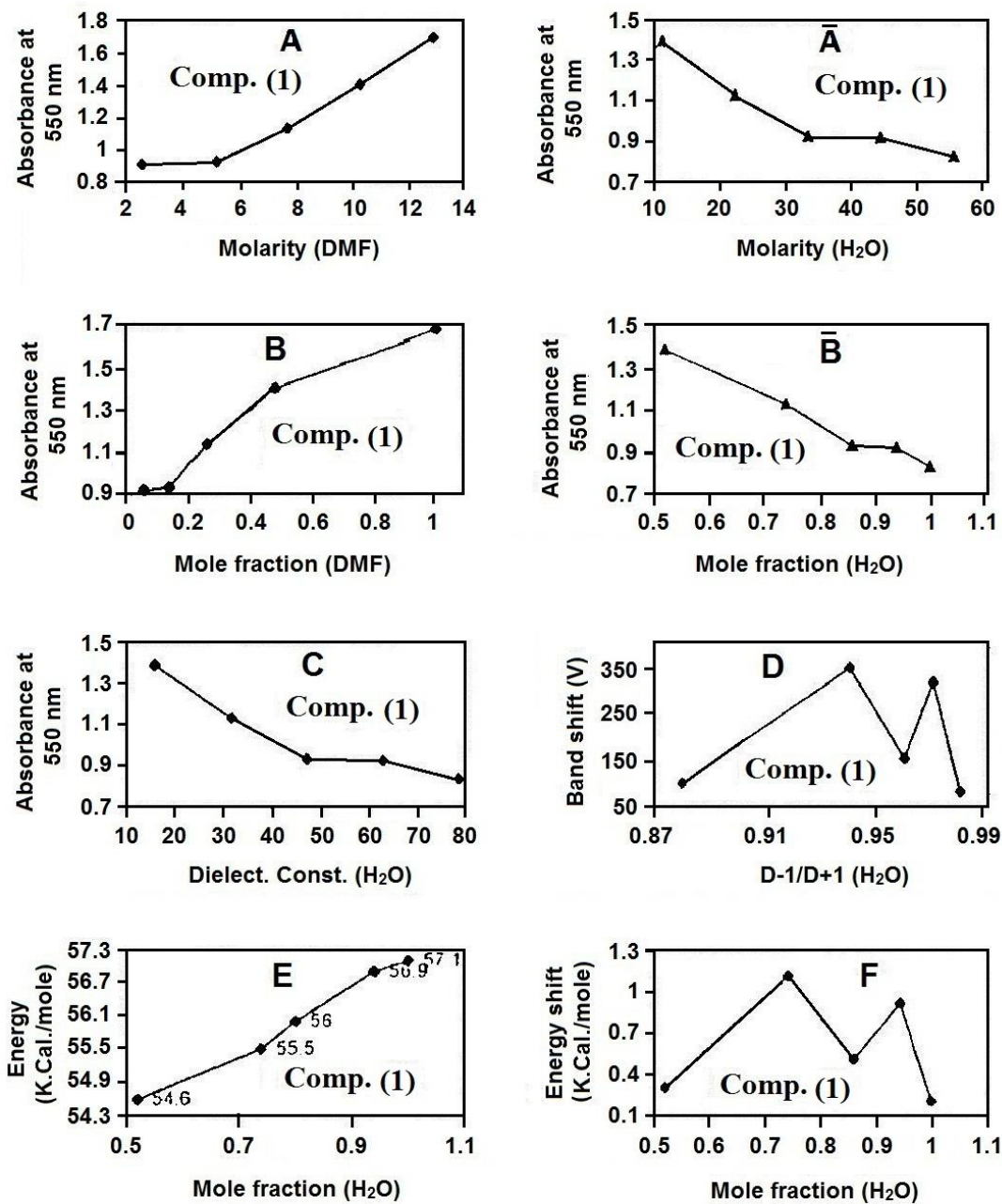


Fig. 3. Various illustration relation curves of the bis dimethine cyanine dye (1) in mixed solvents

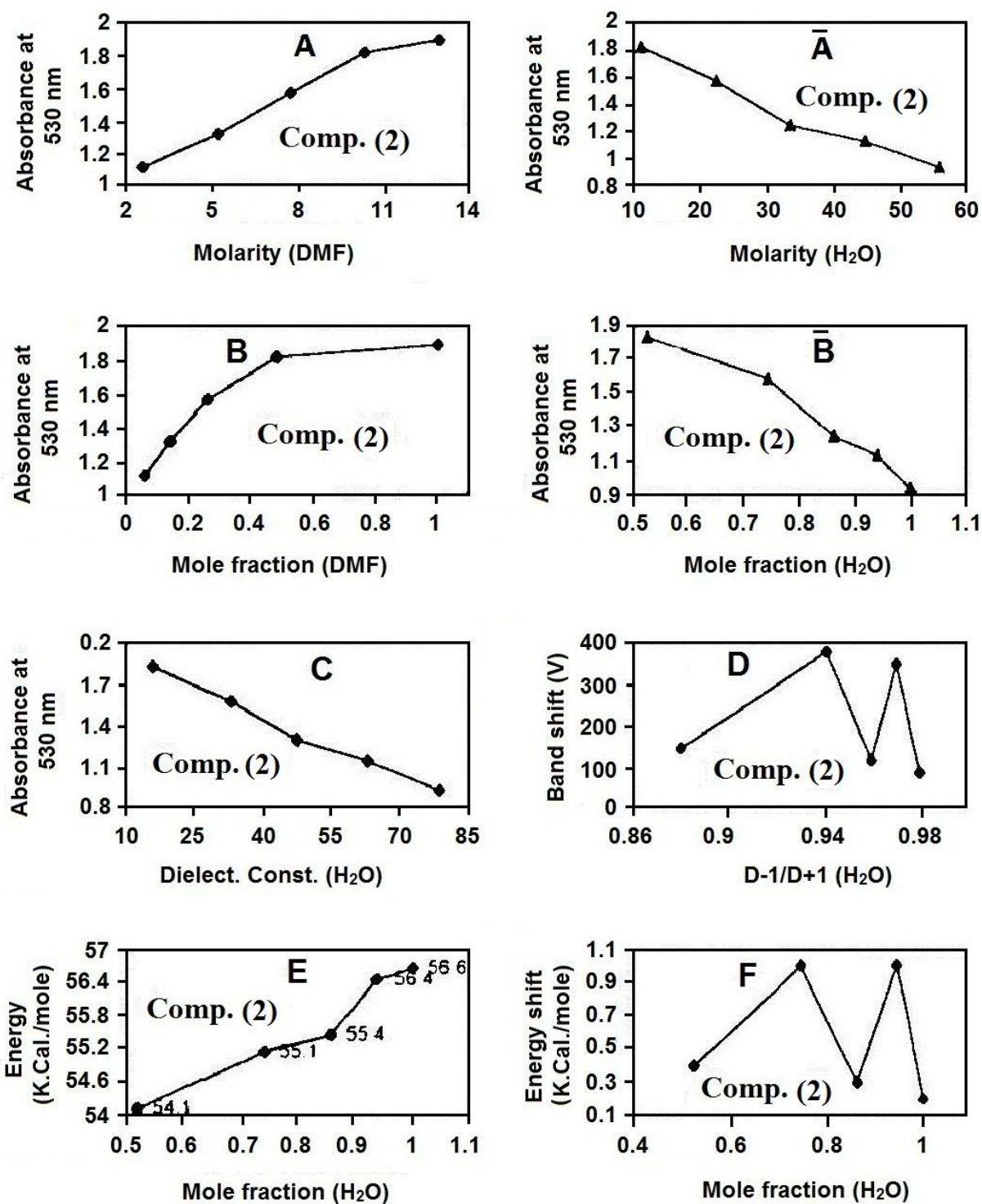


Fig. 4. Various illustration relation curves of the di-tri mixed methane cyanine dye (2) in mixed solvents

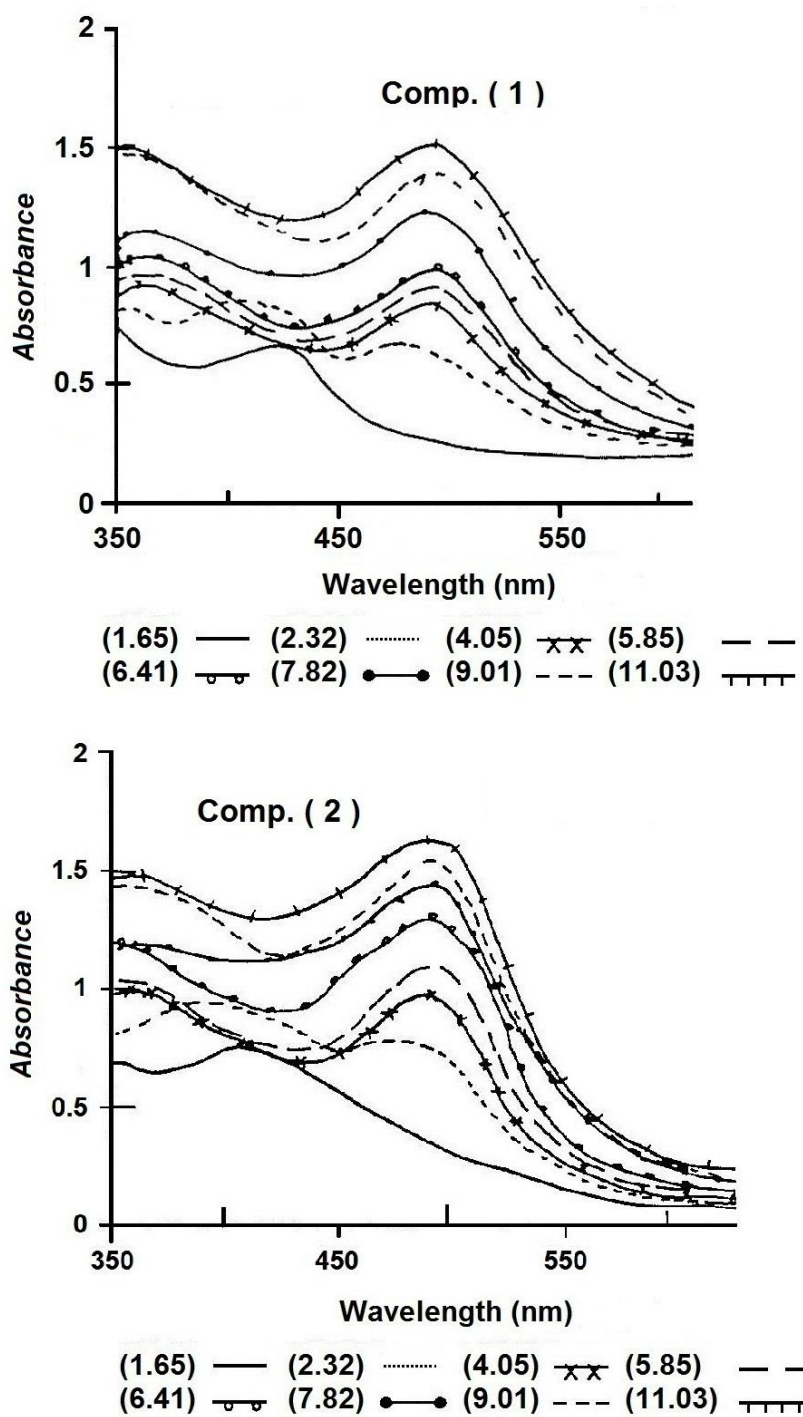


Fig. 5. Halochromism of the bis dimethine cyanine dye (1) and di-tri mixed methine cyanine dye (2) in aqueous universal buffer solutions

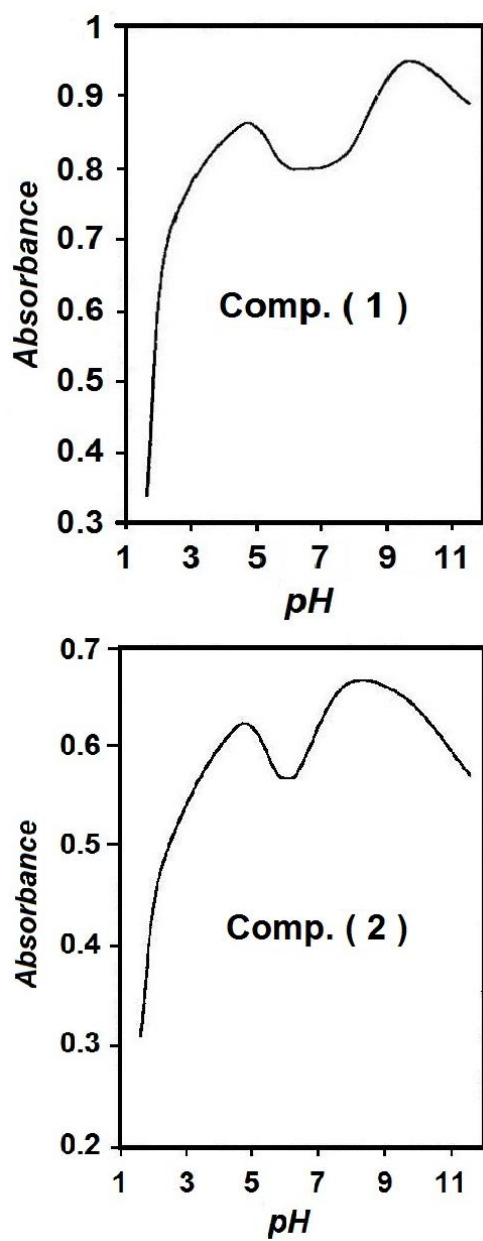


Fig. 6. Acid-base S-Curves of the bis dimethine cyanine dye (1) and di-tri mixed methine cyanine dye (2)