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Solvatochromism and halochromism of some furo/pyrazole cyanine dyes

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ABSTRACT

In this study, the electronic absorption spectra of some furo[2,3-b]pyrazole cyanine dyes 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), $CC1_4$ (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 study covers different types of cyanine dyes, it includes monomethine cyanine dyes (simple cyanine dyes), dimethine cyanine dyes and tetramethine cyanine dyes.

Capsule Summary: Solvatochromism and halochromism for a series of cyanine dyes have been investigated. The study proved the suitability of the examined cyanine dyes to acts as solvatochromic and/or halochromic materials.

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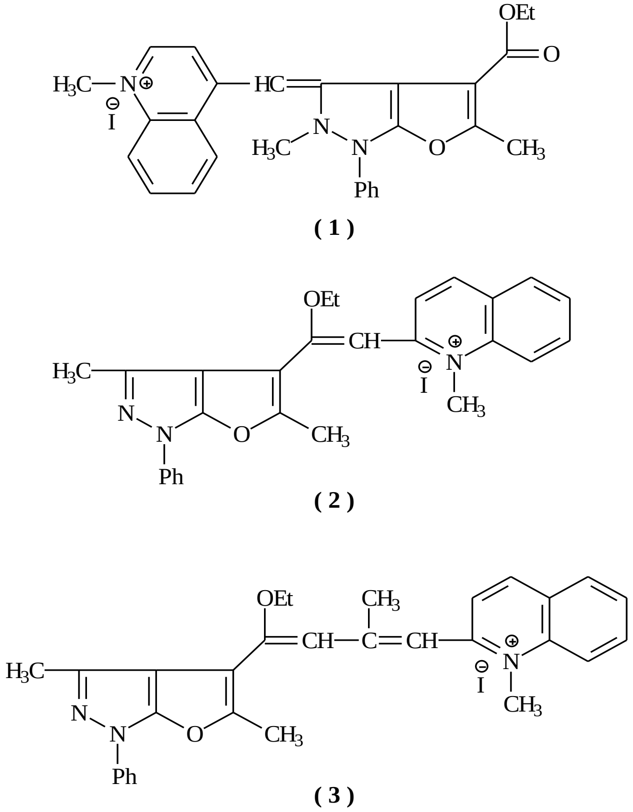
INTRODUCTION

Cyanine dyes (Shindy, 2016; Shindy, 2017; Shindy, 2018; Shindy, 2018a; Shindy, et al., 2019; Gorka and Schnermann, 2016; Liu, et al., 2017; Borisova, et al., 2018; Sha, et al., 2018; Cha, et al., 2011) are suitable compounds for studies of the colour of organic substances and fundamental principles exist relating colour to chemical structure and nature of the solvent (Venkataraman, 2012; West and Geddes, 1964; Derevyanko, et al., 1983; Ishchenko, et al., 1984; Ishchenko, et al., 1989). The pyrazole compounds find various industrial uses and applications (Shindy, et al., 2018). In the biological and pharmaceutical field, pyrazoles have been used as pesticides (Min, et al., 2006), fungicides (Hassan, et al., 1997), antihypertensives (Aly, 2006) and anticancer activity inhibitors (Shindy, et al., 2018). In addition, furan substituted compounds (Chandrashekarachar and Kesagudu, 2017) placed an important role in asthma, rheumatism and ulcers. Immune nanoparticle of furan based polymeric graft co-polymer to provides functional group for coupling of antibodies through Diels-Alder chemistry. Besides, solvatochromism (Park, H. and Chang, S., 2015; Suppan and Ghoneim, 1997; Marini, et al., 2010) is commonly used in many chemical and biological fields, such as probes for determining solvent polarity, sensors and signaling for water content in organic solvents and to investigate the bulk or local polarities of macrosystems (a macro-environment, membranes, etc.) or to probe conformational changes, binding proteins and intermolecular interactions. Furthermore, halochromism (Ren, et al., 2012; Bussemer, et al., 2009; Mazieeres, et al., 2009) have a wide uses and applications as acidity indicators in chemistry, biology and medicine.

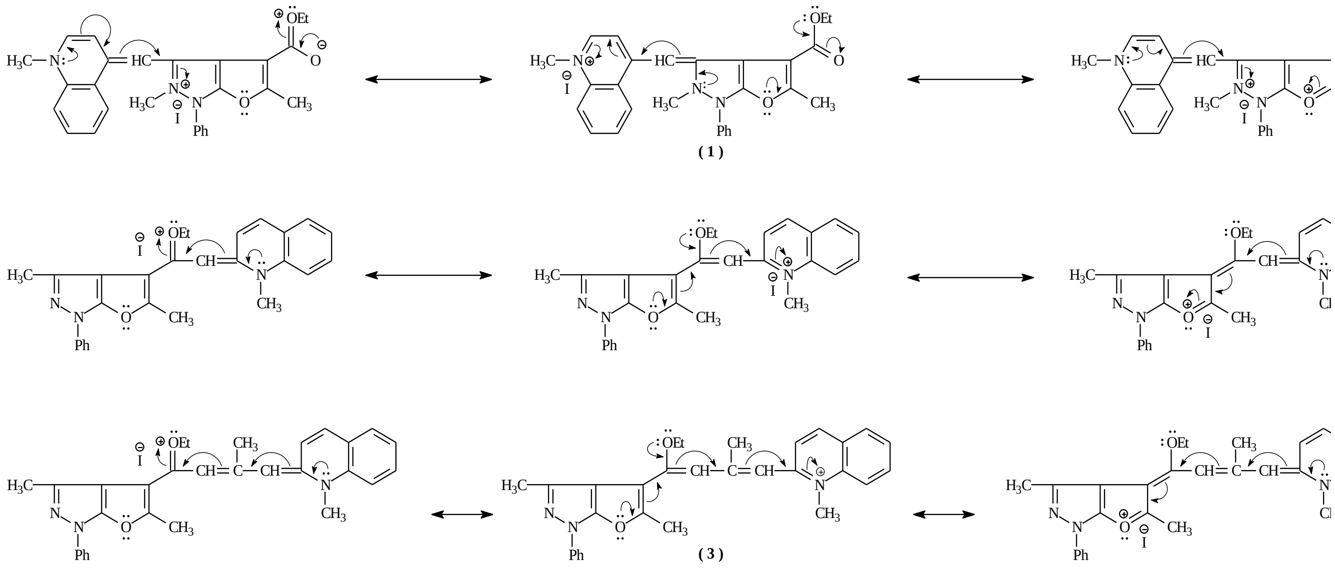
Table 1: Electronic Absorption Spectra of some furo[2,3-b]pyrazole cyanine dyes (1), (2) and (3) in pure solvents (Solvatochromism) (ε_{max} = cm^2mole^{-1})

Comp.	Water		Ethanol		D.M.F		Chloroform		CCl_4		Dioxane	
No.	λ_{max} (nm)	ε_{max}	λ_{max} (nm)	ε_{max}	λ_{max} (nm)	ε_{max}	λ_{max} (nm)	ε_{max}	λ_{max} (nm)	ε_{max}	λ_{max} (nm)	ε_{max}
1	465	15040	479	11880	507	18700	510	14440	513	4630	509	11470
	—	—	—	—	384	16980	400	15580	416	693	403	13500
2	490	11010	525	11100	531	18350	—	—	—	—	—	—
	392	13130	417	12030	427	11270	429	17410	437	6990	422	16910
3	495	18040	509	17680	522	17710	516	19370	—	—	520	14890
	399	13360	412	114200	407	13330	523	19190	437	8280	422	20610

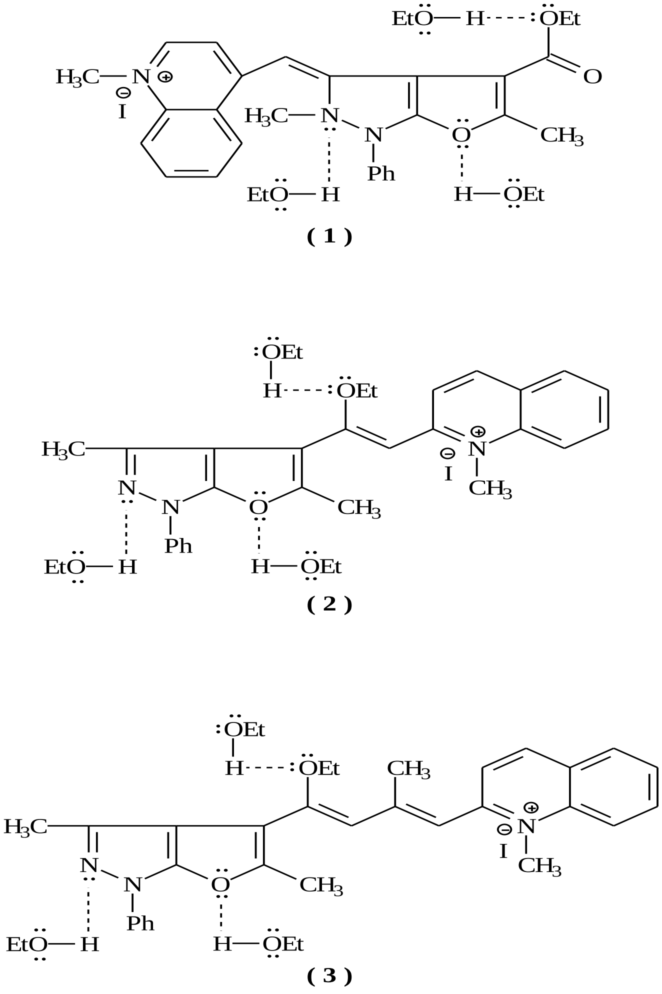


Scheme 1: Chemical structures of the monomethine cyanine dye (1), dimethine cyanine dye (2) and tetramethine cyanine dye (3)

This point of view encouraged us and directed our attention to study the solvatochromism and haolochromism (acid-base properties) of some furo [2,3-b] pyrazole cyanine dyes with the hope that a combination of the favourable properties of both pyrazole, furan 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 hetergenous fields, such as chemistry, biology and medicine.



Scheme 2: Electronic transitions pathways illustration of the monomethine cyanine dye (1), dimethine cyanine dye (2) and tetramethine cyanine dye (3)



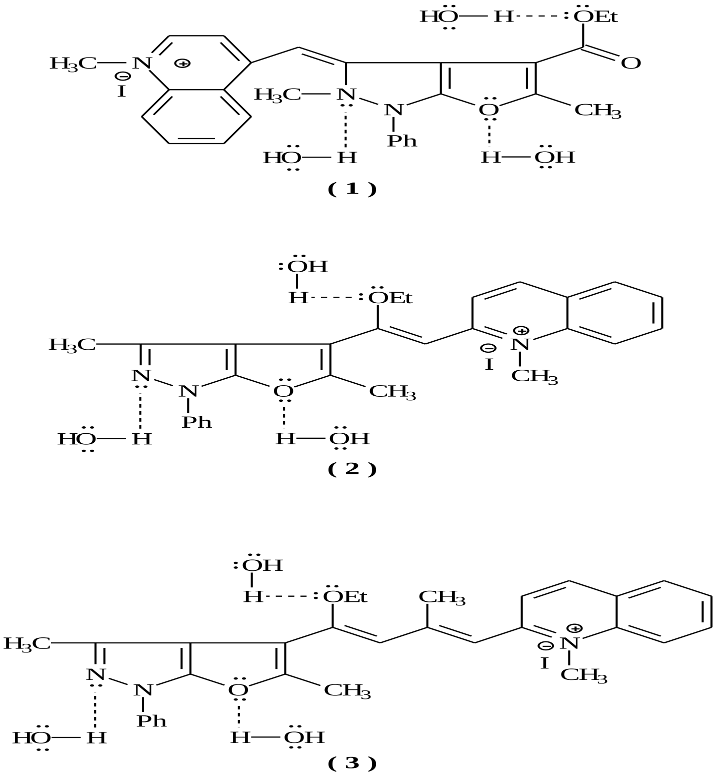
Scheme 3: Hydrogen bond formation between the monomethine cyanine dye (1), dimethine cyanine dye (2), tetramethine cyanine dye (3) and ethanol molecules (specific solvent effect)

Table 2: Commutative data obtained for some furo[2,3-b]pyrazole cyanine dyes (1), (2) and (3) in Mixed Solvents (D.M.F -H_2O mixture)

Comp. No.	Excitation Energy in Pure Solvents (kcal./mol.)		Excitation Orient Energy	Excitation H-bond Energy	Total Excitation Energy
	D.M.F.	H_2O	(kcal./mol.)	(kcal./mol.)	(kcal./mol.)
1	56.10	61.11	1.26	0.87	2.13
2	55.32	60.59	0.56	1.39	1.95
3	54.80	57.66	1.09	0.45	1.54

Table 3: The variation of absorbance with pH at fixed λ for some furo[2,3-b]pyrazole cyanine dyes (1), (2) and (3) in aqueous universal buffer solutions

pH	Absorbance		
	(1) λ = 468 (nm)	(2) λ = 472 (nm)	(3) λ = 496 (nm)
1.65	0.47	0.62	0.64
2.32	0.63	0.68	0.95
4.62	0.63	0.79	0.96
5.85	0.64	0.795	0.965
6.41	0.96	0.80	1.2
7.82	0.855	0.83	1.05
9.61	0.82	0.84	1.0
11.63	0.76	1.02	1.1
pKa	2.4; 7.8	3; 8.8	1.8; 8



Scheme 4: Hydrogen bond formation between the monomethine cyanine dye (1), dimethine cyanine dye (2), tetramethine cyanine dye (3) and water molecules (specific solvent effect)

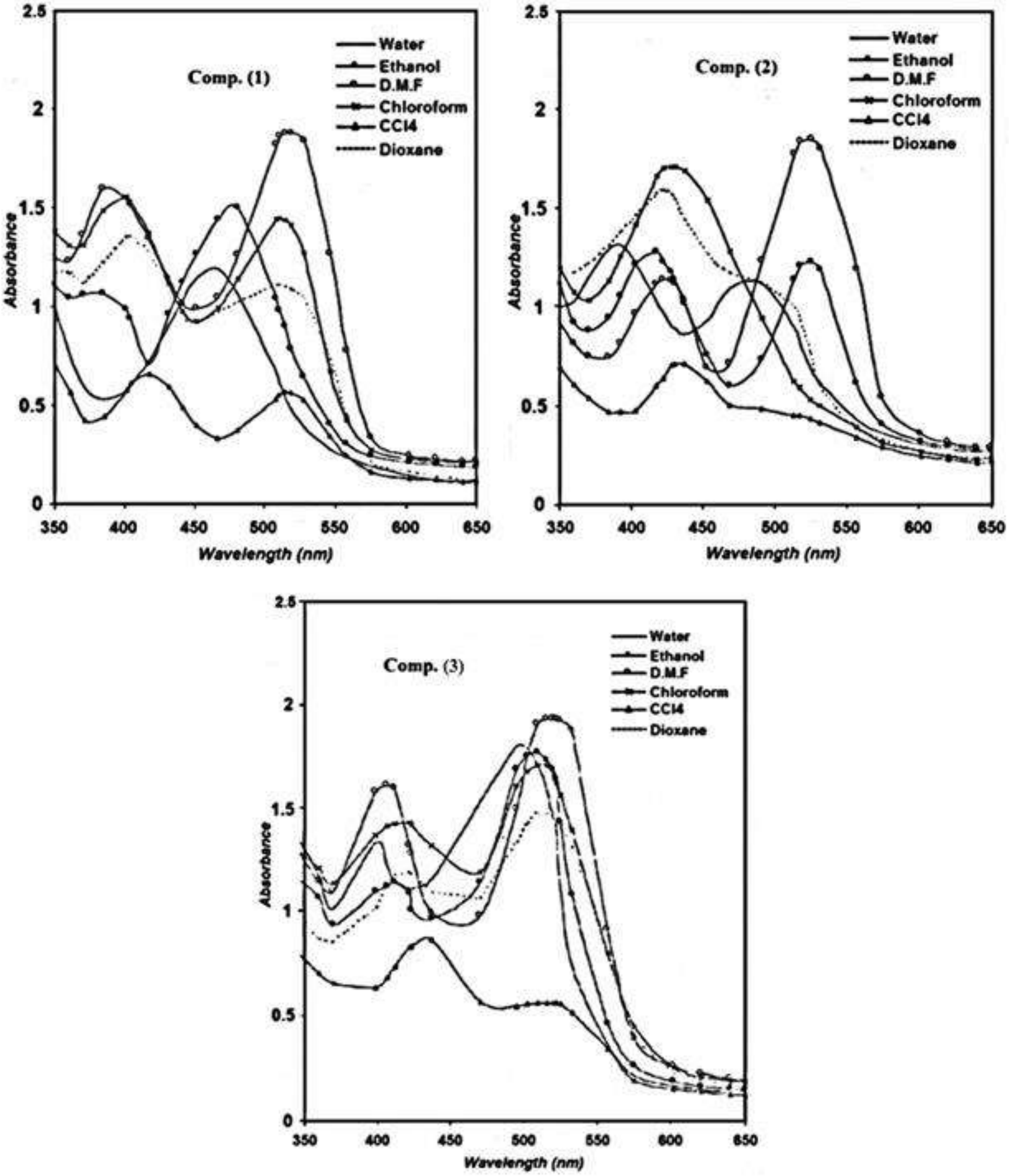


Fig. 1: Solvatochromism of the monomethine cyanine dye (1), dimethine cyanine dye (2) and tetramethine cyanine dye (3) in pure solvents

MATERIAL AND METHODS

The investigated cyanine dyes were prepared in a way that described earlier (Shindy, et al., 2002; Shindy, et al., 2006). The chemical structures of the examined cyanine dyes [monomethine cyanine dye (1), dimethine cyanine dye (2) and tetramethine cyanine dye (3)] are given 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).

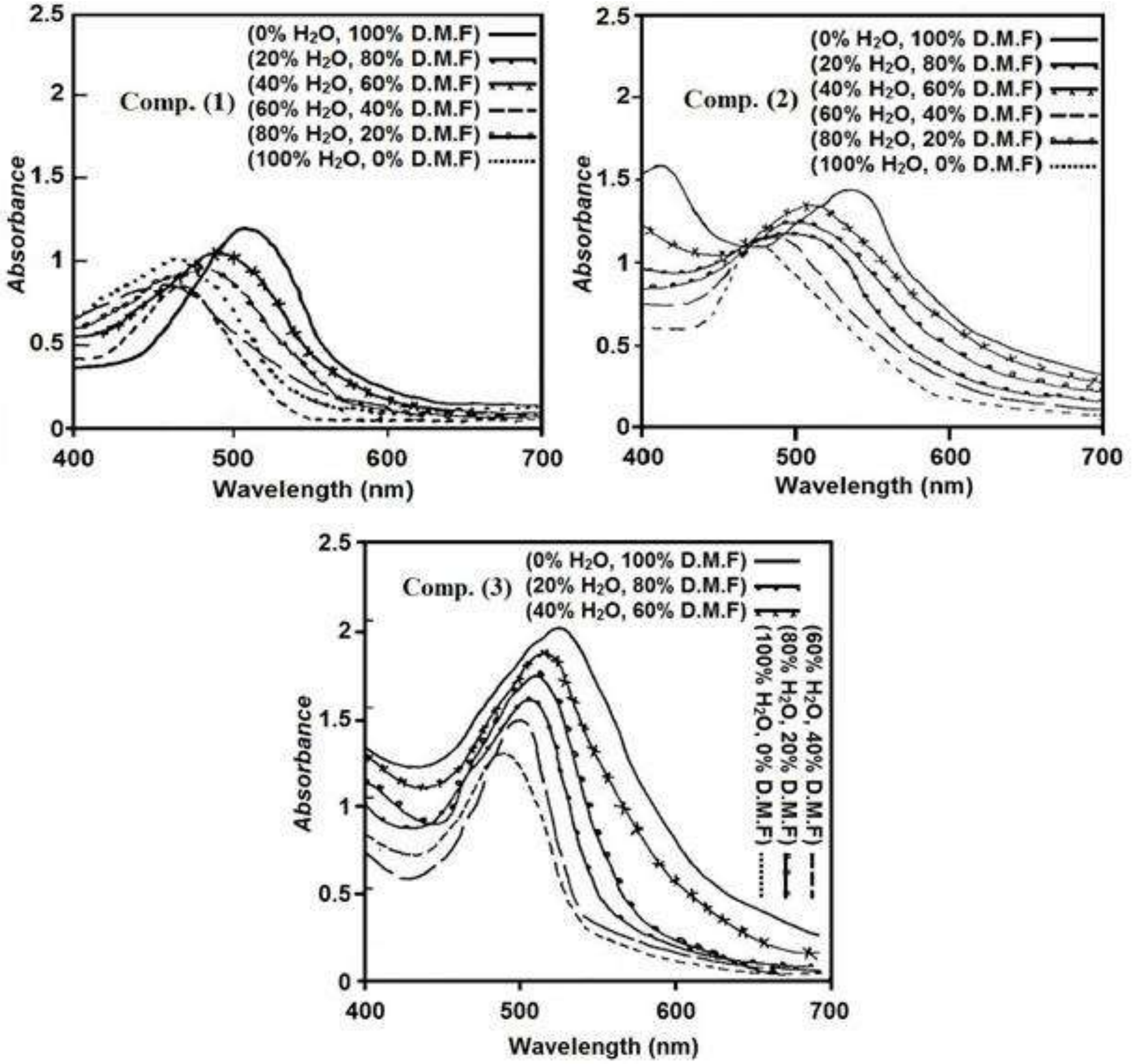


Fig. 2: Solvatochromism of the monomethine cyanine dye (1), dimethine cyanine dye (2) and tetramethine cyanine dye (3) in mixed solvents

The electronic absorption spectra of the dyes were recorded on UV-VIS recording spectrophotometer using l 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.

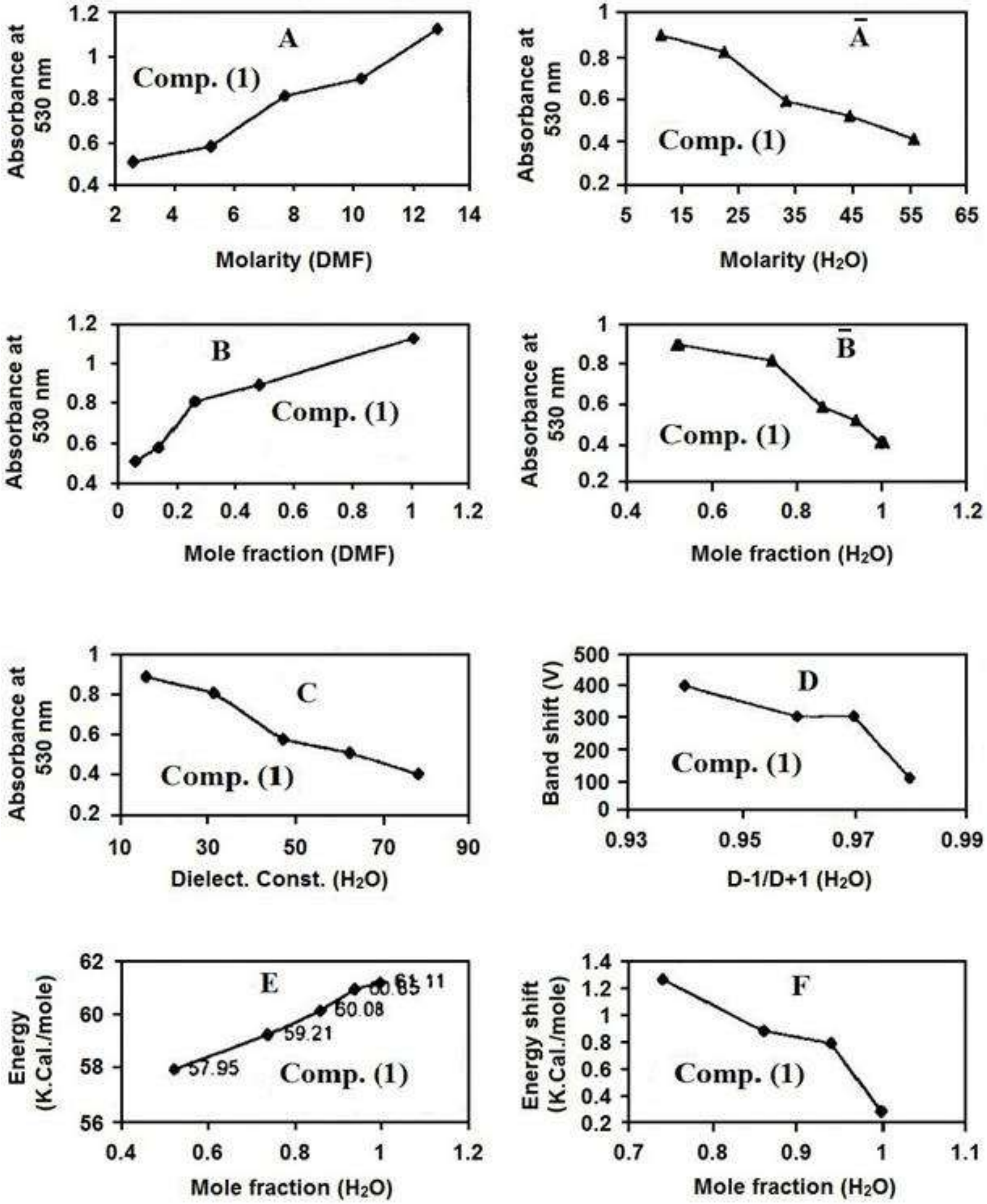


Fig. 3: Various illustration relation curves of the monomethine cyanine dye (1) in mixed solvents

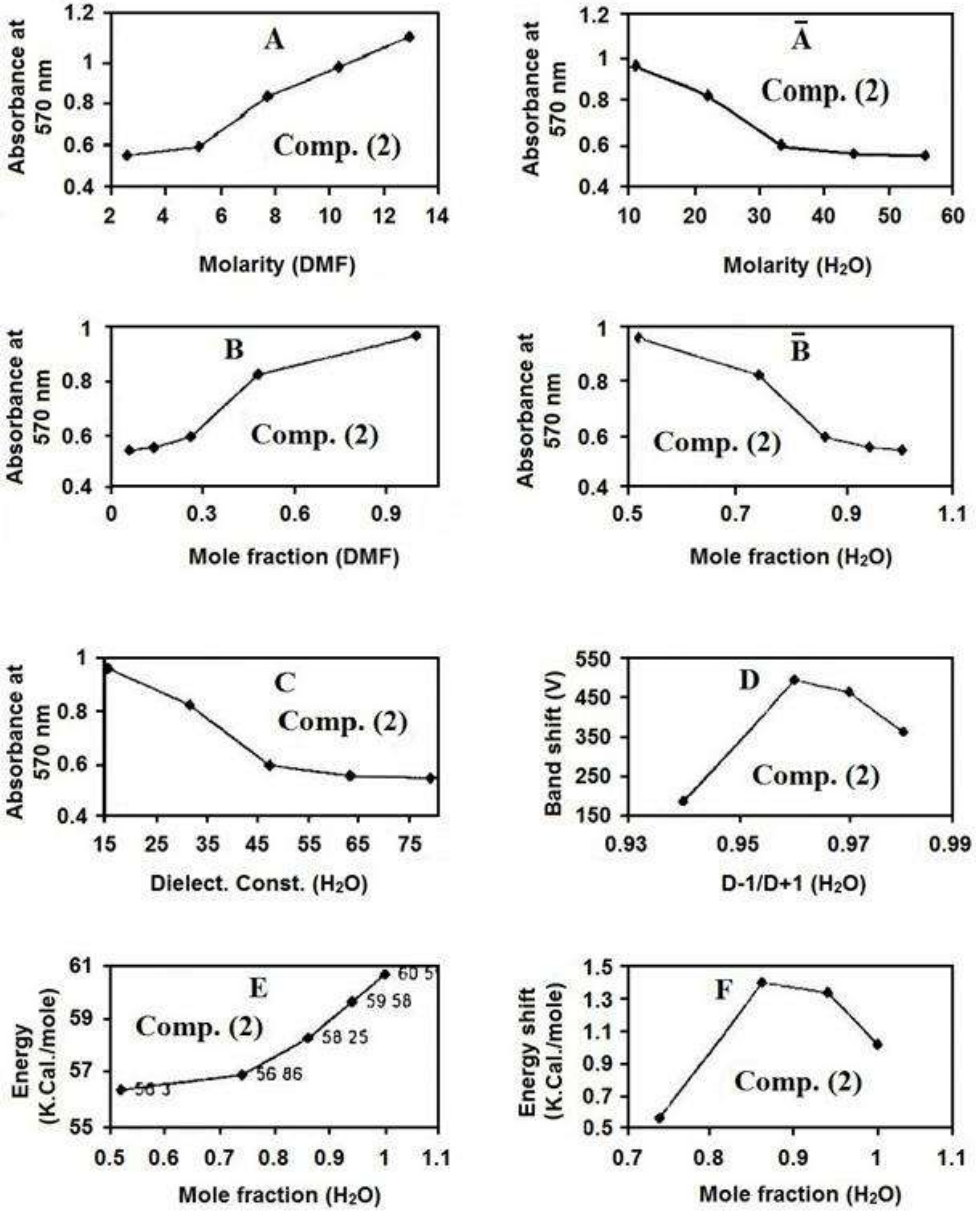


Fig. 4: Various illustration relation curves of the dimethine cyanine dye (2) in mixed solvents

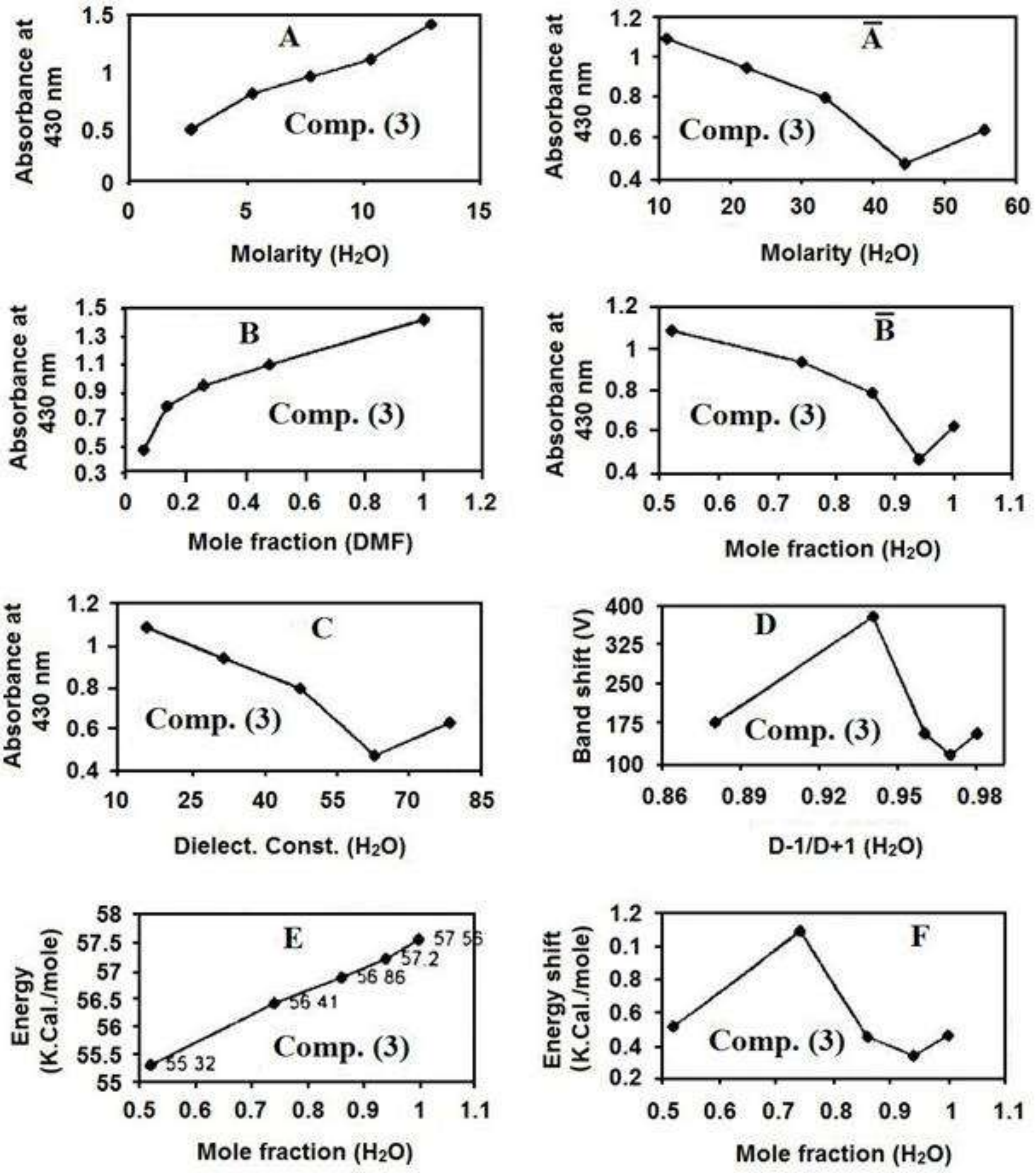


Fig. 5: Various illustration relation curves of the tetramethine cyanine dye (3) in mixed solvents

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.

RESULTS AND DISCUSSION

Solvatochromison in pure solvents:

The term solvatochromism is used to describe the pronounced change in position (and sometimes intensity) of an UV/V of absorption band, accompanying a change in the polarity of the medium. A hypsochromic (or blue) shift, with increasing solvent polarity, is usually called negative solvatochromism. In contrast, the corresponding bathochromic (or red) shift with increasing solvent polarity is termed positive solvatochromism. When absorption spectra are measured in solvents of different polarity it is found that not only the position but also the intensity and shape of the absorption band can vary, depending on the nature of the solvent

This study was carried out to select the best solvents to may use of these dyes as photosensitizers when they 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. In addition, solvatochromic evaluation study is very important in the case of cyanine dyes because the extensive uses and applications of these dyes in textile industry

The electronic absorption spectra of the monomethine cyanine dye (1), dimethine cyanine dye (2) and tetramethine cyanine dye (3) in pure solvents of different dielectric constant viz. water (78.54), D.M.F (36.70), ethanol (24.3), chloroform (4.806), $CC1_4$ (2.238) and dioxane (2.209) (Shindy, et al., 2014; Shindy, et al., 2014a) are recorded, Fig. (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 or two 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 either from the pyrazole nitrogen atom (dye 1) or from the furan oxygen atom (dyes 2, 3) to the 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 $CC1_4$. 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).

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 monomethine cyanine dye (1); dimethine cyanine dye (2); and tetramethine cyanine dye (3) in DMF containing varying amounts of H_2O is shown in Fig. (2). It's shown in the presence of 11.1 M of H_2O the spectrum exhibits bands at 493.5 nm for (1); 508 nm for (2) and 517 nm for (3) respectively. While in the presence of 22.2 M, 33.3 M, 44.4 M, 55.6 M the bands is blue shifted to 483, 476.5, 470 and 468 for (1); 503, 491, 480 and 472 nm for (2) and 507, 503, 500 and 496 nm for (3) respectively. Also, a decrease in band intensity at fixed wavelength [(530 nm (1); 570 nm (2),); 430 nm for (3)] is observed on increasing of H_2O concentration, see Figs. (3, 4, 5) A, A^-.

The decreases in absorbance as well as the gradual blue shift in the maximum absorption wavelength on increasing the H_2O content can be ascribed to the gradual formation of the complex species through intermolecular hydrogen-bonding.

The graphical representation of absorbance at 530 nm for (1); 570 nm for (2); 430 for (3) against the mole fraction of H_2O results that the absorbance decreases gradually with increasing the mole fraction of H_2O. See Figs. (3, 4, 5)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 and Banerjee, 1978), broken line was obtained. See Figs (3, 4, 5)D.

Furthermore another broken line was obtained on plotting the absorbance against the dielectric constant of the medium. See Figs. (3, 4, 5)C. Such behaviour 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 H_2O. These factors mainly include the solute solvent interaction through intermolecular hydrogen bonding which leads to the formation of some molecular complexes.

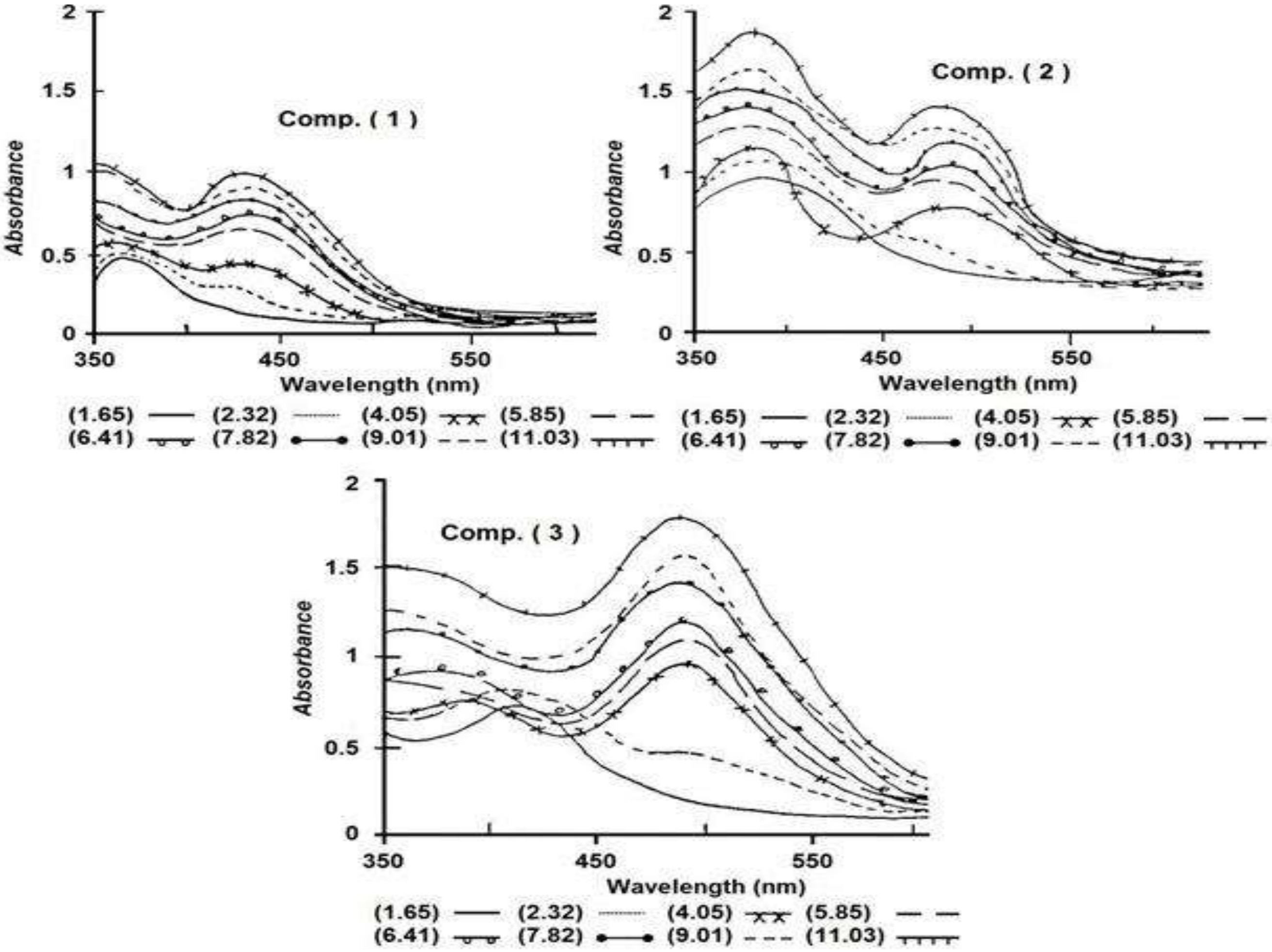


Fig. 6: Halochromism of the monomethine cyanine dye (1), dimethine cyanine dye (2) and tetramethine cyanine dye (3) in aqueous universal buffer solutions

On plotting the excitation energy (E) versus the mole fraction of H_2O (Figs. 3, 4, 5)E, a broken line with three sigments was obtained. The first sigment represents the orientation of the solvent molecules around the solute. The second sigment corresponds to the molecular complex formation, where, as 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 H_2O, 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 boding 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 H_2O. At lower H_2O content, H_2O 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 H_2O permit the formation of the solvent cage around the solute molecules, through intermolecular hydrogen bonding which is previously discussed.

From Figs. (3, 4, 5) E and Table (2) it is possible to evaluate the excitation energy of the solute in the pure H_2O as equal to 61.11 Kcal/mol (comp. 1); 60.59 Kcal/mol (comp. 2); 57.66 Kcal/mol (comp. 3), where, as the value in pure DMF amounts to 56.1 K cal/mol (comp. 1); 55.32 K cal/mol (comp. 2); 54.8 K cal/mol. (comp. 3). The difference between the excitation energy in pure DMF and that corresponding to the first inflection point amounts to 1.85 Kcal/mol (comp. 1); 0.98 Kcal/mol (comp. 2); 0.52 Kcal/mol (comp. 3). This value corresponds to the orientation energy of the solvent molecules around the solute molecules (El-Ezaby, et al., 1970; Gangaly and Banerjee, 1978) See Figs. (3, 4, 5)E, Table (2).

The plot of E and ΔE against the mole fraction of H_2O results broken lines [See Figs. (3, 4, 5)E; (3, 4, 5)F, Table (2)] indicating that the excitation energy depends on factors other than the mole fraction of H_2O. From the above relation it was observed that the orientation energy is equal to 1.26 Kcal/mol (comp. 1), 0.56 Kcal/mol (comp. 2), 1.09 Kcal/mol (comp 3) and the hydrogen bond energy equal to 0.87 Kcal/mol (comp. 1), 1.39 Kcal/mol (comp. 2), 0.45 Kcal/mol (comp. 3), See Table (2).

Halochromism (acid-base properties in aqueous universal buffers)

Halochromism means the colour change, which occurs on addition of acid or base or salt to a solution of a compound. A chemical reaction such as ion formation transforms a colourles compound into a coloured one. Halochromic compounds are compounds, which change their colour when pH changes occur. The term chromic is defined as a material that can change colour reversibly with the presence of a factor, and in this case the main factor is pH. The pH indicators, therefore have this property.

The solutions of the monomethine cyanine dye (1), dimethine cyanine dye (2), and tetramethine cyanine dye (3) 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 the monomethine cyanine dye (1), dimethine cyanine dye (2), and tetramethine cyanine dye (3) 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

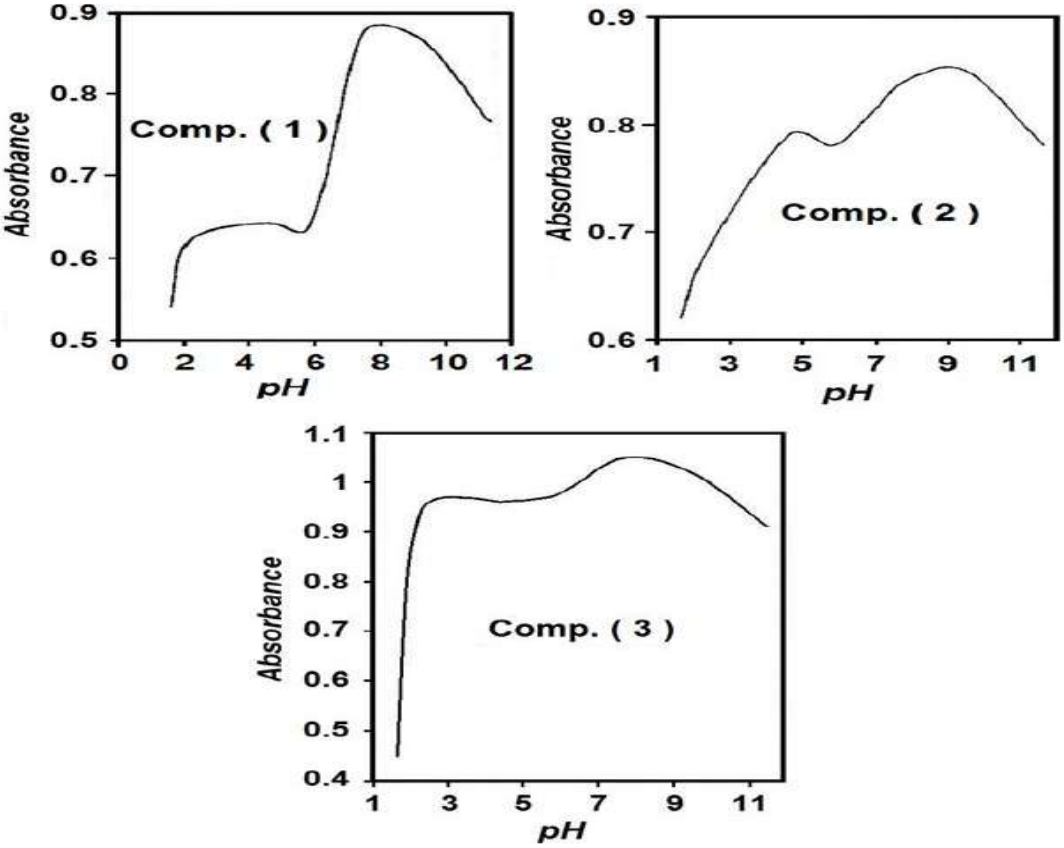


Fig. 7: Acid-base S-Curves of the monomethine cyanine dye (1), dimethine cyanine dye (2) and tetramethine cyanine dye (3)

absorption bands at low pH (acidic media), Figs. (6). 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 pathways 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 pathway 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 either the pyrazole nitrogen atom (dye 1) or furan oxygen atom (dyes 2, 3) to the positively charged quinolinium 4-yl salt moiety (dye 1)) and/or to the positively charged quinolinium 2-yl salt moiety (dyes 2 and 3), 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, Figs. (7), 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 medway 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).

CONCLUSION

From the results discussed in this study we could conclude that:

(1) The electronic visible absorption spectra of the monomethine cyanine dye (1), dimethine cyanine dye (2), and tetramethine cyanine dye (3) in pure solvents having different polarities (solvatochromism) underwent displacements to give positive solvatochromism (occurrence of a bathochromic shift with increasing solvent polarity) and / or negative solvatochromism (occurance 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 electronic visible absorption spectra of the monomethine cyanine dye (1), dimethine cyanine dye (2) and tetramethine cyanine dye (3) in aqueous universal buffer solutions having varied pH values (Halochromism) 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. Inversely, 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) These cyanine dyes can be used as:

a-Probes for determining solvent polarity in solution chemistry due to their solvatochromic properties.

b-Acid-base indicators in analytical chemistry due to their halochromic properties.

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REFERENCES

Aly, A.A., 2006. Synthesis of polyfunctionally substituted pyrazolonaphthyridine, pentaazanaphthalene, and heptaazaphenanthrene derivatives. Phosphorous Sulfur Silicon 181, 2395-2409.

Borisova, I.A., Zubarev, A.A., Rodinovskaya, A., Shestopalov, A.M., 2018. Synthesis and properties of aza analogs of merocyanine dyes based on N-substituted 2- and 4-aminopyridinium salts. Russian Chemical Bulletin 67, 168–171.

Bussemer, B., Dreiling, I., Grummt, U., Mohr, G. J., 2009. Spectroscopic and quantum chemical study of the bronestedacid cites in zeolite L channels with acidochromic cyanine dyes.Journal of Photochemistry and Photobiology A: Chemistry 204, 90-96.

Cha, S., Choi, M.G., Jeon, H.R., Chang, S., 2011. Negative solvatochromism of merocyanine dyes: Application as water content probes for organic solvents. Sensors and Actuators B: Chemical 157 (1),14-18.

Chandrashekarachar, D., Kesagudu, D., 2017. Impotrtance of furan based compounds and their biomedical applications: An overview. Indo American Journal of Pharmaceutical Research 7(1), 7541-7549.

Derevyanko, N.A., Dyadyusha, G.G., Ishchenko, A.A., Tolmachev, A.I., 1983. Theoretical and Experimental Chemistry 19, 169-178.

El-Ezaby, M.S., Salem, I.H., Zewail, A.H., Issa, R.M., 1970. Spectral studies of some hydroxy-derivatives of anthraquinones. Journal of the Chemical Society 13, 1293-1926.

Gangaly, T., Banerjee, S.B., 1978. Effect of hydrogen bonding on the electronic absorption spectra of xylenols. Spectrochimica Acta A 34, 617-623.

Gorka, A.P., Schnermann, M.J., 2016. Harnessing cyanine photooxidation: from slowing photobleaching to near-IR uncaging. Current Opinion in Chemical Biology 33, 117-125.

Hassan, A.E., Abdella, M.M., Ahmed, A.I., 1997. Studies on the synthesis and cyclization reactions of 2-(5-Amino-3-arylpyrazol-1-yl)-3-methylquinoxalines. Journal of Chemical Research S, 322-323.

Ishchenko, A.A., Svidro, V.A., Derevyanko, N.A., 1989. Solvatofluorochromy of cationic cyanine dyes. Dyes and Pigments 10, 85-96.

Ishchenko, A.A., Derevyanko, N.A., Zubarovski, V.M., Tolmachev, A.I., 1984. Theoretical and Experimental Chemistry 20, 443-451.

Liu, H., Zhang, Y., Mei, L., Guo, Q., Li, H., Liao, L., 2017. Tetrahedral substitution to induce tunable luminescent properties in apatite structural solid-solution phosphors $Ca_9La(PO_4)_5[(Si,Ge)O_4]F_2:Ce^{3+}$. Dyes and Pigments 145, 514-517.

Marini, A., Muñoz-Losa, A., Biancardi, A., Mennucci, B., 2010. What is solvatochromism?. The Journal of Physical Chemistry B 114, 17128-17135.

Mazieeres, M.R., Duprat, C., Wolf, J.G., Roshal, A.D., 2009. pH dependent spectral properties and electronic structure of benzothiazole containing cyanine dyes. Dyes and Pigments 80, 355-360.

Min, G., Eric, C., Lihu, Y., 2006. A general method for the preparation of 3-acyl-4-cyano-5-amino-pyrazoles. Tetrahedron Letters 47, 5797-5799.

Park, H., Chang, S., 2015 .Signaling of water content in organic solvents by solvatochromism of a hydroxynaphthalimide-based merocyanine dye. Dyes and Pigments 122, 324-330.

Ren, Z., Qin, C., Tang, R., Chen, G., 2012. Study on the dyeing properties of hemicyanine dyes. II. Cationic dyeable polyester. Coloration Technology 128,147-152.

Sha, X., Xiao, J., Yin, D., Sun, R., Xu, Y., Ge, J., 2018. Preparation of a photostable tribrachia cyanine dye and its high chemical activity towards hydrosulfide. Dyes and Pigments 149, 505-511.

Shindy, H.A., 2016. Characterization, Mechanisms and Applications in the Chemistry of Cyanine Dyes: A Review. European Journal of Molecular Biotechnology 14, 158-170.

Shindy, H.A., 2017. Fundamentals in the Chemistry of Cyanine Dyes: A Review. Dyes and Pigments 145, 505-513.

Shindy, H.A., 2018. Structure and solvent effects on the electronic transitions of some novel furo/pyrazole cyanine dyes. Dyes and Pigments 149, 783-788.

Shindy, H.A., 2018a. Novel polyheterocyclic cyanine dyes: synthesis, photosensitiztion and solvent/electronic transitions correlation. European Reviews of Chemical Research 5, 30-39.

Shindy, H.A., El-Maghraby, M.A., Eissa, F.M., 2014a. Effects of Chemical structure, solvent and solution pH on the visible spectra of some new methine cyanine dyes. European Journal of Chemistry 5, 451-456.

Shindy, H.A., El-Maghraby, M.A., Eissa, F.M., 2002. Novel Cyanine Dyes: Synthesis, Characterization and Photosensitization-Structure Correlation. Journal of the Chinese Chemical Society 49, 1061-1068.

Shindy, H.A., El-Maghraby, M.A., Eissa, F.M., 2006. New photosensitizers cyanine dyes: Synthesis and properties. Indian Journal of Chemistry 45B, 1197-1203.

Shindy, H.A., El-Maghraby, M.A., Eissa, F.M., 2014. Synthesis and sprctral properties of novel hemicyanine dyes. Russian Chemical Bulletin (in Russian) 63(3), 707-715.

Shindy, H.A., El-Maghraby, M.A., Goma, M.M., Harb, N.A., 2019. Polynuclear heterocyclic monomethine and trimethine cyanine dyes: synthesis and various absorption spectra studies. European Journal of Molecular Biotechnology 7, 25-39.

Shindy, H.A., El-Maghraby, M.A., Goma, M.M., Harb, N.A., 2018. Synthesis, electronic transitions and antimicrobial activity evaluation of novel monomethine and trimethine cyanine dyes. European Journal of Molecular Biotechnology 6, 83-95.

Suppan, P., Ghoneim, N., 1997. Solvatochromism. The Royal Society of Chemistry, Cambridge.

Venkataraman, K., 2012. The chemistry of synthetic dyes, V4, Elsevier.

West, W., Geddes, A.L., 1964. The effects of solvents and of solid substrates on the visible molecular absorption spectrum of cyanine dyes. The Journal of Physical Chemistry 68, 837-847.

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