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Solvation studies of some tailor made α-N,N-dimethylaminostyryl-N-alkyl pyridinium dyes in binary solvent mixtures containing alcohols, hexane, 1,4-dioxane, DCM and acetone

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ABSTRACT

Solvation of some α-N,N-dimethylaminostyryl-N-alkyl pyridinium dyes has been studied in binary solvent mixtures of alcohol–hexane, alcohol–1,4-dioxane, acetone–hexane, acetone–1,4-dioxane, DCM–hexane, DCM–1,4-dioxane and 1,4-dioxane–hexane to analyze the preferential solvation of any of the solvent in the binary mixture. Due to solvent–solvent interaction, hyper and hypo-polarity in the solvent complex is observed, which is reflected from the bathochromic and hypsochromic shifts of the absorption maxima of the dye molecules. The solvent cage around the dye is influenced by polar–polar and apolar–apolar interactions as well as a proper balance between both the types of interactions.

1. Introduction

Chemical and biochemical practices of various natures involve many types of solvent mixtures and their modifications during chromatographic separation, organic synthesis, reaction kinetics, or protein folding–unfolding processes. Solvent mixtures used for solubilizing substrates lead to their differential physical and chemical properties compared to the bulk of a pure solvent due to differential solvent–solvent and solute–solvent interaction [1]. Gibbs energy of solvation becomes more negative by the effect of solute being preferentially surrounded by one of the solvents [1,2], leading to a difference between the composition of the solvent shell around the solute and the macroscopic ratio, a phenomenon referred to as “preferential solvation (PS)”. Preferential solvation signifies the induction of a change by the solute in its environment with respect to the situation in the bulk solvent, whether through nonspecific solute–solvent interactions (dielectric enrichment) or through specific solute–solvent association. Dielectric enrichment describes the solvatochromic shifts of the UV–vis absorption and fluorescence spectra of dipolar solute molecules in binary solvent mixtures [3,4]. The phenomenon requires the diffusion of the polar and nonpolar solvent molecules near the solute to reach a thermodynamic equilibrium and the approach implies a new distribution of the solvent molecules in the vicinity of the solute dipole by a process of preferential solvation. The present communication deals with the preferential solvation of some α-styrylpyridinium dyes in various binary solvent mixtures of different polarities.

Styrylpyridinium dyes are a class of cyanine dyes having large electronically interacting environment due to the existence of mobile π-electrons showing strong optoelectronic properties, with a history of being exploited in various industrial and medical applications [5–12]. The dyes involve π–π* and n–π* transitions and charge transfer absorptions involving the formation of electron pair donor/electron pair acceptor (EPD/EPA) complexes with various solvent molecules wherein they are dissolved. It is generally accepted that the characteristic long-wavelength absorptions of these EPD/EPA complexes are associated with an electron transfer from donor to acceptor molecule [13–15], thus influencing the optoelectronic behavior of these solvated dye molecules. Such behavior of the dyes depends on the nature of their environment, i.e. the intensity, shape, and maximum absorption wavelength in solution, which depends strongly on the solute–solvent interactions and nature of solvent [16–19].

Solvent-sensitive styrylpyridinium dyes show strong solvatochromic effects due to the influences of solvent polarities directly on the position of their UV–vis absorption band, undergoing negative or positive solvatochromic changes with the increase in the solvent polarity. According to Franck and Condon, solvatochromism occurs due to the differential solvation of the electronic ground and excited states of the solvated solute in the UV–vis region. A better stabilization of the ground state due to solvation by solvents of increasing polarity than the excited state leads to negative solvatochromism and vice versa. According to the Franck–Condon principle [20], the time required for molecules to be excited

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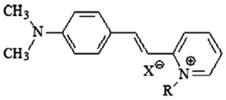


C1: R = CH_3, X = I; **C4**: R = C_4H_9, X = Br; **C16**: R = $C_{16}H_{33}$, X = Br

Chart 1. Molecular structures of α-styrylpyridinium dyes **C1**, **C4**, **C16**.

(10^{-15} s) is much smaller than that required to execute vibrations or rotations (10^{-12} to 10^{-10} s), causing no change in the position of the nuclei of the absorbing entity (i.e., absorbing molecule + solvation shell) during electronic transition, which results in a similar solvation pattern of the Franck–Condon excited state as in the corresponding ground state. However, the first Franck–Condon excited state can be more dipolar than the ground state due to intermolecular charge transfer upon excitation. Hence it is assumed that the chemical state of the molecule is the same in different solvents and the response to a polar solvent requires both a permanent dipole moment and a change in dipole moment of the species upon electronic excitation [21].

Various physical forces such as ion–dipole, dipole–dipole, dipole–induced dipole, and hydrogen bonding, tend to alter the energy difference between Franck–Condon ground and excited states of the absorbing species containing the chromophores. Attempts have been made to quantitatively express the influence of solvents of various polarities through various physical solvent properties, mainly relative permittivity, dipole moment, or refractive index. However, these properties alone cannot effectively account for the multitude and specific interactions of solute–solvent on the molecular microscopic level [16]; various solvatochromic indicators and solvent sensitive parameters have been discovered and utilized to study these interactions in an effective way. Brooker [22] and Kiprianov and Petrunkin [23] are the pioneers of the studies on solvatochromism in merocyanine dyes, which possess large negative solvatochromic shifts, second order hyperpolarizability and usefulness in diagnostics and therapeutics [24]. Botrel et al. [25], Jaques [26], Luzhkov and Warshel [27], Morley [28], Da Silva et al. [29], Ishchenko et al. [30], Reichardt et al. [31], and Dähne et al. [32] are some of the excellent workers in this field who have thoroughly studied the impact of solvent on the electronic spectral characteristics of cyanine and other dyes (e.g. betaine dye) and proposed phenomena like positive, negative, and reversal in solvatochromism for these dyes. These propositions were made not only from experimental verifications, but also from theoretical calculations enriching the studies on the optoelectronic properties of various organic dye molecules through solvatochromic modeling.

Recently, Tripathy et al. [33] have reported the influence of solvent polarity on the electronic transition of four classes of α-styrylpyridinium dyes with variable substituents in 21 solvents, wherein Reichardt's $E_T(30)$ scale has been used to propose a quantitative approach towards the relative stability of the electronic ground and excited-state species. Besides, the study also throws some light on the influence of geometry of the dye molecules on solvatochromism from the comparative results with their γ-counter parts [34]. Electron donating/repelling substituents, hydroxy substituent, chloro and nitro substituents influence differently towards the electronic transitions of the substrate molecule due to their difference in inductive and field effects on the substrate. Resonance effect imparted by substituents is also somewhat responsible in the electronic transitions of the substrates, but to a lesser extent compared to inductive and field effects. The dye molecules, except the one with nitro substituent, could show a clear sensing of the difference in their behavior when they are surrounded by solvent cages with solvents of various polarities. The non-polar and polar protic solvents are found to stabilize their excited states whereas the dipolar aprotic solvents stabilize their ground states. The α-styrylpyridinium dye containing nitro substituent could not sense the polarity change in the solvents of various categories due its point-positive charge developed due to an all-pull mechanism within the dye molecule. Existence of an ortho-effect in the α-styrylpyridinium dyes has been proposed to be the reason, which enables these dyes for efficient solvent polarity sensing property.

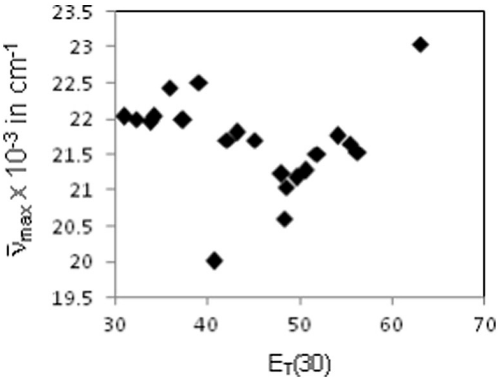


Fig. 2. Plot of $E_T(30)$ vs. $\bar{\nu}_{max}$ of dye **C4** in solvents of various polarities.

α-Styrylpyridinium dyes are geometrically different from their γ-isomers due to the difference in the positions of the quaternary nitrogen and the alkyl group present on them. In the former, the N-substituted alkyl groups are present at a position “ortho” and in the later, the groups are present at a position “para” with respect to the styryl unit. As a consequence, the chromophoric unit at the styryl moiety is more influenced by the N-substituted alkyl groups at the pyridinium moiety in the α-isomer than in the γ-isomer. Such a geometrical variation inducts an observable difference in the solvent-polarity sensitivities of both the isomers [35].

It is also important to note that styrylpyridinium dyes have non-linear optical (NLO) properties since they lack center of symmetry and hence are recognized as typical second harmonic generation (SHG) active molecules [36]. They possess strong first hyperpolarizability (β), a factor contributed by the interaction between the substituent and the conjugated system (β_{add}) and the donor–acceptor charge transfer within the system (β_{CT}). In case of the γ-styrylpyridinium dyes, where the donor–acceptor groups are at the opposite ends, maximum non-centrosymmetry and large first hyperpolarizability might be observed compared to the α-isomers where the positions of donor and acceptor moieties are ortho to each other [37]. As a consequence, the direction as well as the extent of electronic movement in both classes of the isomers should be different resulting in a difference in their solvation by neat as well as binary solvent mixture.

The present work involves a meticulous study of the preferential solvation of some α-(*N*,*N*-dimethylaminostyryl)-pyridinium dyes (Chart 1) associated with established donor–acceptor system and variable hydrophobic clefts as the probes in some binary solvent mixtures of

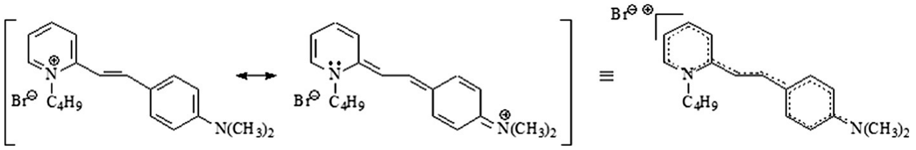


Fig. 1. Push–pull phenomenon in α-styrylpyridinium dyes.

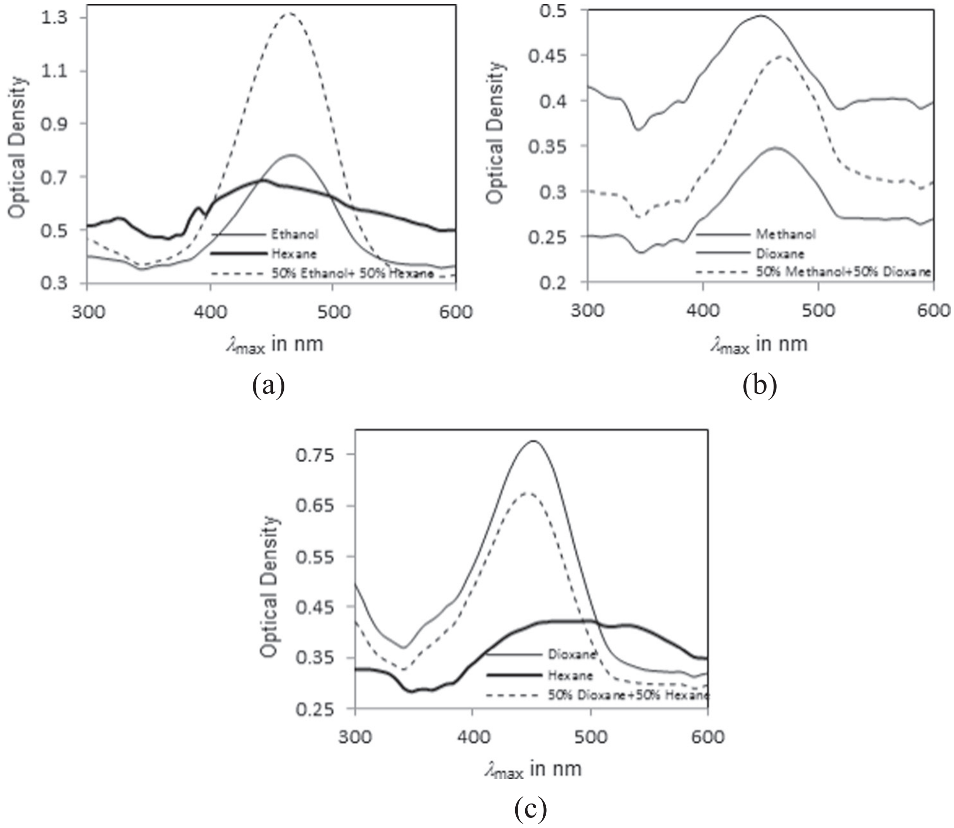


Fig. 3. Absorption maxima of **C1** in ethanol–hexane (a), methanol–dioxane (b) and dioxane–hexane (c) binary solvent mixtures.

variable polarities. The solvent mixtures leading to preferential solvation of these probes may be utilizing various solvating factors, which have been analyzed in the present communication.

2. Experimental section

α-Styrylpyridinium dyes (**C1**, **C4**, and **C16**) were prepared by the sequential reaction of 2-methylpyridine with alkyl halide (methyl iodide, n-butyl bromide, and hexadecyl bromide), followed by condensation with N,N-dimethylamino benzaldehyde in the presence of piperidine in ethanol medium [38]. The purity of the compounds was checked by thin-layer chromatography. The various solvents used in the study, such as methanol, ethanol (Qualigens), 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-octanol, 1,4-dioxane (Merck), hexane, acetone, and dichloromethane (Spectrochem) were purified by standard procedures and were distilled just before use [39]. Spectroscopic measurements were carried out at 298 K in a Hitachi U-3010 recording UV–vis spectrophotometer fitted with thermostatic cell holders. The mixtures of dye solutions were prepared by mixing the dye solutions in different solvents with appropriate dye concentration.

3. Results and discussion

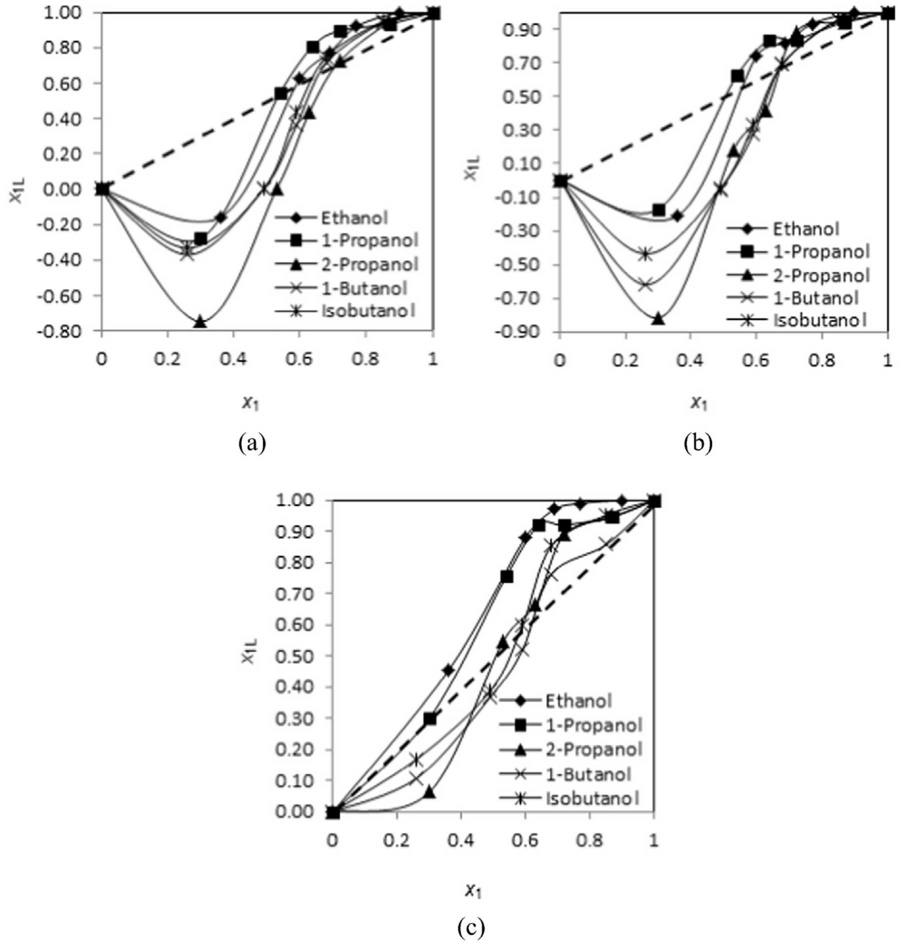
3.1. Solvatochromism in pure solvent

Absorption maxima (λ_{max}) of **C4** dye recorded in 21 solvents undergo an ordered change with the polarities of the solvents [33]. The difference in the values of absorption maxima due to change in solvent ($\Delta\lambda_{max}$) from highest to lowest dielectric constants gets good contributions from both field and resonance effects; however the field effect has a higher contribution. A perfect push–pull mechanism operates between the electron-repelling/donating *N*,*N*-dimethylamino moiety as the substituent at the styryl unit and the electron-withdrawing pyridinium moiety (Fig. 1).

The $\overline{\nu}_{max}$ values exhibit a linear relationship with the polarity scale in nonpolar and polar protic solvents (Fig. 2) with almost similar significances. The $\overline{\nu}_{max}$ values decrease with the polarity of the dipolar aprotic solvents (λ_{max} increases) which suffers a reversal (λ_{max} decreases) with the polarity of the polar protic solvents at an $E_T(30)$ value of approximately 48.0. In addition, there also exists a reversal at an $E_T(30)$ value of approximately 37.0 during change over from nonpolar to dipolar aprotic media.

Variation of λ_{max} with the change in the polarity of solvents ranges from 454 nm in hexane to 496 nm in dichloromethane (DCM). The stability of the ground and Franck–Condon excited states can be envisaged from the change in the λ_{max} values with solvent polarity. For instance, the decrease in the λ_{max} values with increasing polarity reflects the stability of the ground state, whereas, increase in the λ_{max} values with polarity reflects the stability of the Franck–Condon excited state. With the increase in the polarity of solvents, the λ_{max} values decrease in nonpolar and polar protic class of solvents and increase in the dipolar aprotic class of solvents (Fig. 2). In other words, the non-polar and polar protic solvents tend to stabilize the ground state of the dye molecule and the dipolar aprotic solvents tend to stabilize its Franck–Condon excited state. The contributions towards the stabilities of the excited states of the dye by the nonpolar and polar protic solvents are 41.6% and 47.1% respectively and 11.3% by dipolar aprotic solvents. In other words, the nonpolar and polar protic solvents contribute about 35–40% more towards the stability of its ground state than the dipolar aprotic solvents.

The solvent cage formed around **C4** might be showing various types of interactions with it. For instance, the non-polar solvent cage might be interacting with the electronically rich dye molecule through some van der Walls type of interactions, whereas the dipolar aprotic solvents and polar protic solvents might be interacting through H-bonding as well as



(a)

(b)

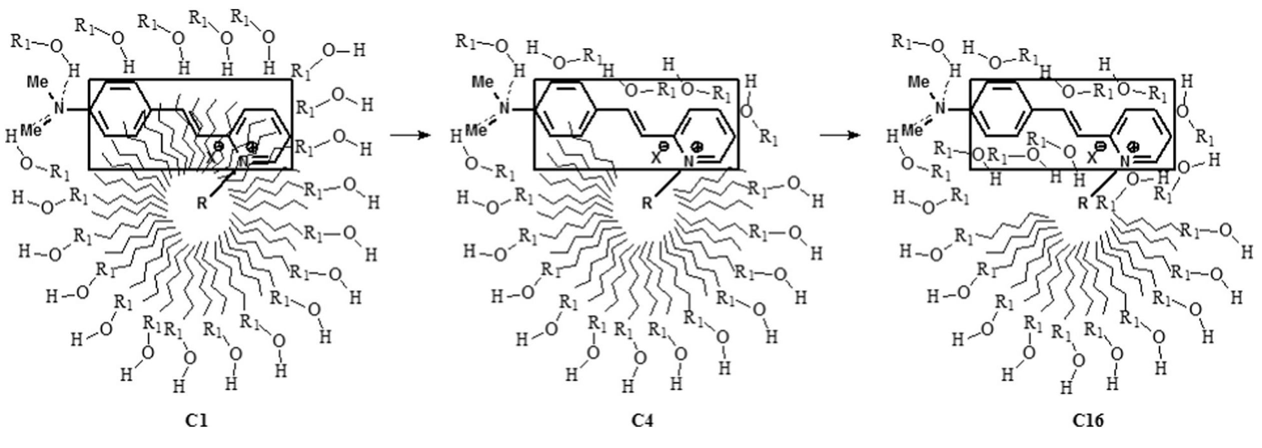
(c)

Fig. 4. Plot of local mole fraction (x_{1L}) vs. mole fraction (x_1) of alcohols in alcohol–hexane binary mixture in the solvation of dyes **C1** (a), **C4** (b) and **C16** (c).

dipole–dipole modes. However, the directions of H-bonding with these solvents are opposite to each other.

3.2. Solvatochromism in binary solvent mixture

Solvation of the dyes **C1**, **C4**, and **C16** with variable hydrophobic clefts, acting as solvatochromic indicators, in some binary solvent mixtures of different polarities has been carried out where the binary solvent mixtures have been chosen from their $E_T(30)$ polarity values. Seven polar protic alcohols with various $E_T(30)$ values in parentheses such as methanol (55.5), ethanol (51.9), 1-propanol (50.7), 2-propanol (48.4), 1-butanol (49.7), isobutanol (48.6), and 1-octanol (48.1) have been used as the parent solvents and hexane (31.0), a non-polar solvent, and 1,4-dioxane (36.0), a dipolar aprotic solvent, have been taken as the cosolvents with each of the parent solvent to prepare the binary solvent mixtures at different proportions. Besides, some polar solvents such as dichloromethane (DCM: 40.7) and acetone (42.2) also have been employed as parent solvents, each with the cosolvents hexane and dioxane to study the impact of binary solvent mixture on the absorption of the dyes. The dyes have also been treated with a mixture of dioxane and hexane with dioxane as the parent solvent.



Scheme 1. Schematic representation of solvation of **C1**, **C4** and **C16** dyes in alcohol–hexane binary mixtures.

Table 1
Absorption maxima of **C1** in different alcohol–hexane binary mixtures and disorder.

Hexane (vol.%)	Absorption maxima (nm)					Disorder
	EtOH	1-PrOH	2-PrOH	1-BuOH	iso-BuOH	
0	467	469	468	471	473	0
20	467	468	467.2	470	472	0.022
40	466	467.4	464	466	468	0.622
50	464	466	460	460	462	0.918
60	462	462	454	454	454	0.633
80	452	450	444	448	448	0.967
100	454	454	454	454	454	0

In the presence of binary solvent mixtures, solvation of a dye probe (D) is contributed by solute–solute (DD), solute–solvent (DS), and solvent–solvent (SS) interactions. However, DS interactions play a more vital role during the preferential solvation of the probe molecules, though other interactions are also important. During the solvation of an entity in presence of a mixture of binary solvents S1 and S2, a part of each solvent might be undergoing some mutual interactions producing a new class of solvent S12, which also participates in the solvation of the entity, besides the pure solvents S1 and S2. As a consequence, the solvatochromic indicator interacts to a different extent with the solvents of the mixture and hence the composition of the solvation sphere is different from the composition of the bulk solvent. Such a phenomenon has been explained successfully by Skwierczynski and Connors [40], who proposed a two-step solvent-exchange model (Eqs. (1), (2)) where the entity solvated by S1, S2 and S12 is represented by BM(S1)2, BM(S2)2 and BM(S12)2, respectively.

$$\mathrm{BM(S1)2} + \mathrm{2S2} \rightleftarrows \mathrm{BM(S2)2} + \mathrm{2S1} \tag{1}$$

$$\mathrm{BM(S1)2} + \mathrm{S2} \rightleftarrows \mathrm{BM(S12)2} + \mathrm{S1}. \tag{2}$$

The interaction of both the solvents in each case yields a common structure S12 with particular properties different from S1 and S2. It has been suggested that solvophobic interactions contributing to the formation of the solvent complexes (S12) are responsible for the observed synergistic effects in the preferential solvation of the dyes, an effect by virtue of which greater than individual effects of each solvent is observed. In the present case, the λ_{max} values of the dyes in various solvent mixtures at their different proportions are found to be shifted bathochromically or hipsochromically compared to their λ_{max} values in the neat solvents, reflecting preferential solvation of the probes due to the charge of their chromophores or the length of their hydrophobic clefts (Fig. 3).

The λ_{max} value in ethanol–hexane binary mixture remains in between that of neat solvent (Fig. 3a), shows a bathochromic shift in methanol–dioxane binary mixture (Fig. 3b) and a hypsochromic shift in dioxane–hexane binary mixture (Fig. 3c) confirming the existence of preferential solvation phenomena with the solvent mixtures.

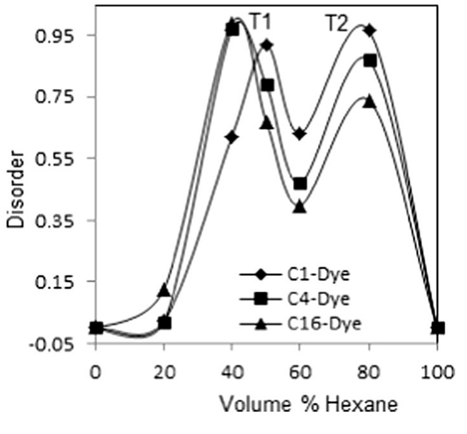


Fig. 5. Plot of disorder vs. volume percent hexane for the solvation of **C1**, **C4**, and **C16** dyes in alcohol–hexane binary mixture.

Charged chromophore lowers down the solubility of the probe in highly nonpolar solvent like hexane and increases its solubility in highly polar solvents like alcohols, whereas the apolar hydrophobic clefts induce the reverse effects. Hence, the solubility of the probes in solvent mixtures of various polarities is definitely because of a proper balance between these two factors and accordingly solvent cages due to each of the solvent in the binary mixture should be formed around the chromophore as well as the apolar hydrophobic clefts of the dye molecules.

Such a discussion leads to the fact that in addition to solute–solvent interaction, solvation characteristics in the binary solvent mixtures also depend on solvent–solvent interaction, that is, solvent non-ideality as well, since solvent–solvent interaction creates a mixture with characteristics different from those of the individual parent solvents. During ideal solvation, any observed property (P) of a probe in the solvent mixture is the average of contributions of the component solvents (Eq. (3)) [41]. Deviation from Eq. (1) indicates the existence of preferential solvation (PS) of the probe:

$$P = \sum x\mathrm{i}P\mathrm{i}. \tag{3}$$

Maitra and Bagchi [42] have extensively studied the preferential solvation of some ketocyanine dyes by binary and ternary solvent mixtures using electronic transition energy (E_T) obtained from the relationship,

$$E_T = 28951/\lambda_{max}. \tag{4}$$

From the deviation from ideality of the solvent mixture, they proposed a two-phase solvation model consisting of local region or solvation shell and outside the local region, or bulk. The solvent molecules present in the solvation shell experience the field due to solute molecules. The solvent composition in the solvation shell is different from that of the bulk. If the contribution of both the solvents to the E_T of the probe in the binary mixture is assumed to be a linear combination, then the mole fraction of the solvents in the solvation shell, otherwise termed as local mole fraction (x_{1L}) of S_1 in the binary mixture of S1 and S2 can be calculated from Eq. (5):

$$x_{1L} = \left[E_{T(S12)} - E_{T(S2)}\right] / \left[E_{T(S1)} - E_{T(S2)}\right] \tag{5}$$

where, $E_{T(S1)}$, $E_{T(S2)}$, and $E_{T(S12)}$ refer to the electronic transition energy of the probe in S1, S2, and solvent mixture (S1 + S2) respectively.

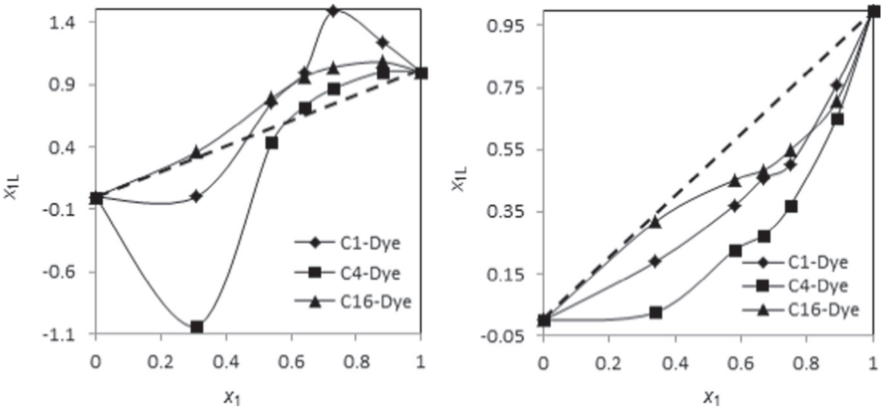
In all the solvent mixtures in the present study, the more polar of the two component solvents is considered as S1 and the other as S2. Analysis of the plot of mole fraction (x_1) of S1 in the S1 + S2 solvent mixture versus the local mole fraction of S1 (x_{1L}) provides some useful information: (i) positive deviation from ideality, referring to PS by S1; (ii) negative deviation from ideality, referring to PS by S2; and (iii) collinearity of the plot with ideality, indicating similar composition of the binary solvents in the solvation shell as well as bulk. The x_{1L} values of various solvents in the binary mixtures were determined by using Eqs. (3) and (4) (Supplementary Tables S1–S45).

3.2.1. Preferential solvation in alcohols–hexane, acetone–hexane and DCM–hexane binary mixtures

In presence of **C1**, **C4** and **C16** dyes taken as probes in alcohol–hexane binary mixtures, the plots of mole fraction of alcohols (x_1) with their local mole fractions (x_{1L}) show an initial negative deviation from

$$\mathrm{D} \xrightarrow{\mathrm{S_1}} \mathrm{DS_1} \xrightarrow[\mathrm{T1}]{\mathrm{S_2}} \mathrm{DS_1S_2} \xrightarrow[\mathrm{T2}]{\mathrm{S_2}} \mathrm{DS_2}$$

Scheme 2. Solvation of probes in binary solvent mixtures.

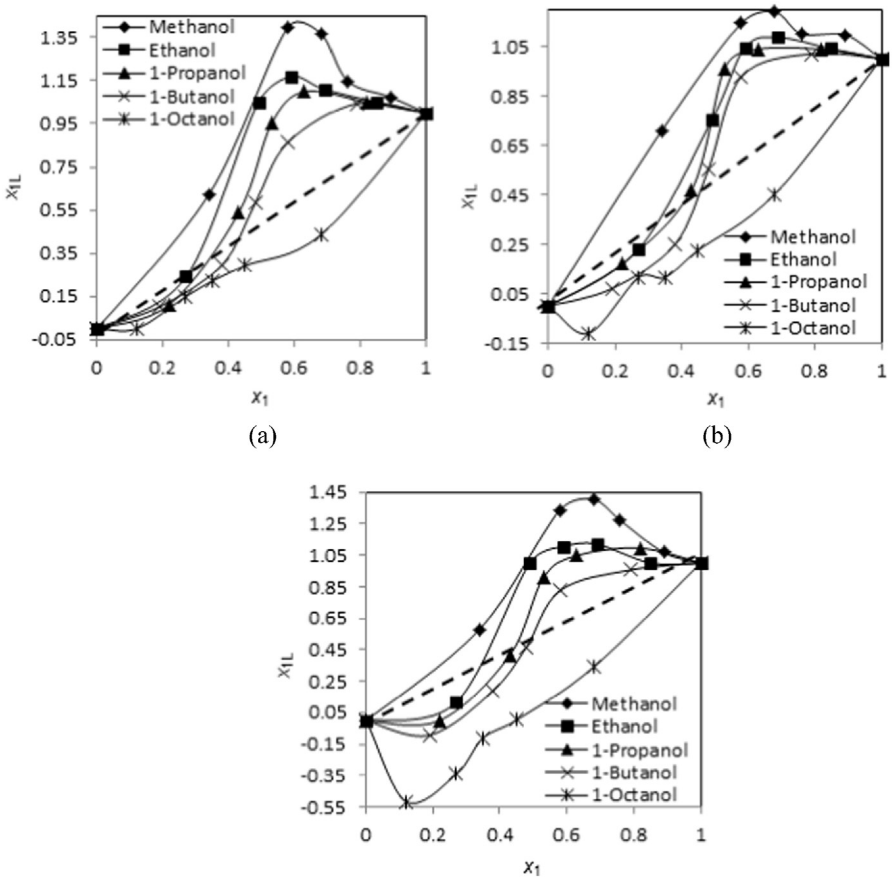


(a) (b)

Fig. 6. Plot of local mole fraction (x_{1L}) vs. mole fraction (x_1) of acetone in acetone–hexane binary mixture (a) and DCM in DCM–hexane binary mixture for the solvation of dyes **C1**, **C4** and **C16**.

ideal line followed by a cross over towards the positive side in each case (Fig. 4). The negative deviation from the ideal line with the increase in the alcohol mole-fraction represents the preferential solvation by hexane and the positive deviation represents the PS by alcohols. The **C1** dye in all the alcohols shows an initial negative deviation which crosses over to the positive region at a mole-fraction range of 0.53–0.7 (Fig. 4a). Hence, initially the dye is preferentially solvated by hexane followed by preferential solvation by alcohols due to the possible interaction between the polar hydroxy groups of the alcohols and the cationic chromophore of the dye. 2-Propanol–hexane mixture behaves most ideally after the crossover to positive region at a mole fraction of 0.7 compared to the mixture of any other alcohol and hexane. The alcohol–hexane interaction is due to the bulky alkyl groups of the alcohol and nonpolar hexane, which provides a similar environment as that of pure hexane.

When the dye contains a C4 or C16 hydrocarbon chain, an apolar character is introduced to the solvation phenomenon. In case of the **C4** dye, a crossing over from negative to positive region with respect to the ideal line is observed at a mole-fraction range of 0.50–0.67 (Fig. 4b), in case of the **C16** dye, a positive deviation is observed throughout in case of ethanol whereas for other alcohols the crossover



(a) (b)

(c)

Fig. 7. Plot of local mole fraction (x_{1L}) vs. mole fraction (x_1) of alcohols in alcohol–dioxane binary mixture in the solvation of dyes **C1** (a), **C4** (b) and **C16** (c).

Table 2
Absorption maxima of **C1** in different alcohol–dioxane binary mixtures and disorder.

Dioxane (vol.%)	Absorption maxima (nm)					Disorder
	MeOH	EtOH	1-PrOH	1-BuOH	1-OcOH	
0	463	467	469	471	464	0
20	464	468	470	472	456	0.317
40	465	469	471	468	454	0.595
50	468	470	468	462	453	0.966
60	468.4	468	460	456	452	0.936
80	458	454	452	452	450	0.829
100	450	450	450	450	450	0

is observed at a mole-fraction range of 0.48–0.60 (Fig. 4c). Just like the **C1** dye, 2-propanol–hexane mixture behaves most ideally for **C4** dye whereas the 1-butanol–hexane mixture behaves most ideally for **C16** dye after the crossover to positive region at mole fractions of 0.67 and 0.60 respectively compared to the mixture of any other alcohol and hexane. Hence, going from **C1** dye to **C16** dye, the PS by hexane decreases and becomes minimum for **C16** dye, which may be due to the increase in the length of hydrophobic cleft and decrease in the influence of hexane on the chromophoric region making way for alcohol interaction at that region (Scheme 1). Both types of solvents such as non-polar hexane and polar alcohols contribute to the solvatochromism since solvation is due to both polar and non-polar interactions.

In case of the γ-isomers of the styrylpyridinium dyes with C1, C6 and C16 hydrophobic clefts, the plots for some of the alcohols such as ethanol, 1-propanol, and 1-butanol in the presence of **C1** exhibit a positive deviation throughout, indicating PS by these alcohols; in presence of the **C6** dye, addition of ethanol and 1-propanol led to an immediate expulsion of hexane from the solvent cage and the alcohols solvate the dye preferentially throughout the solvent composition, and similar is the observation for **C16**, where the polar interaction is found to be more prominent [35]. With increasing mole fraction of alcohol, it is observed that **C16** is extensively solvated by the alcohol at a lower mole fraction than in the case of **C6**, which in turn is lower than that in the case of **C1**, a similar observation found in case of the α-isomers.

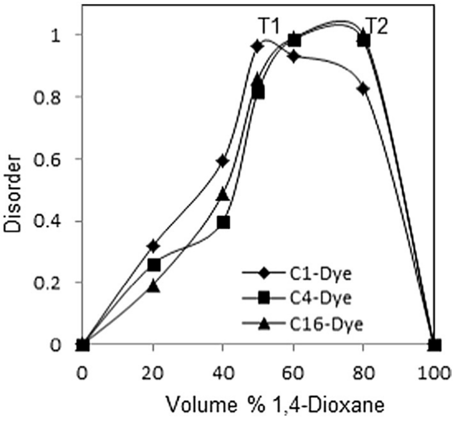
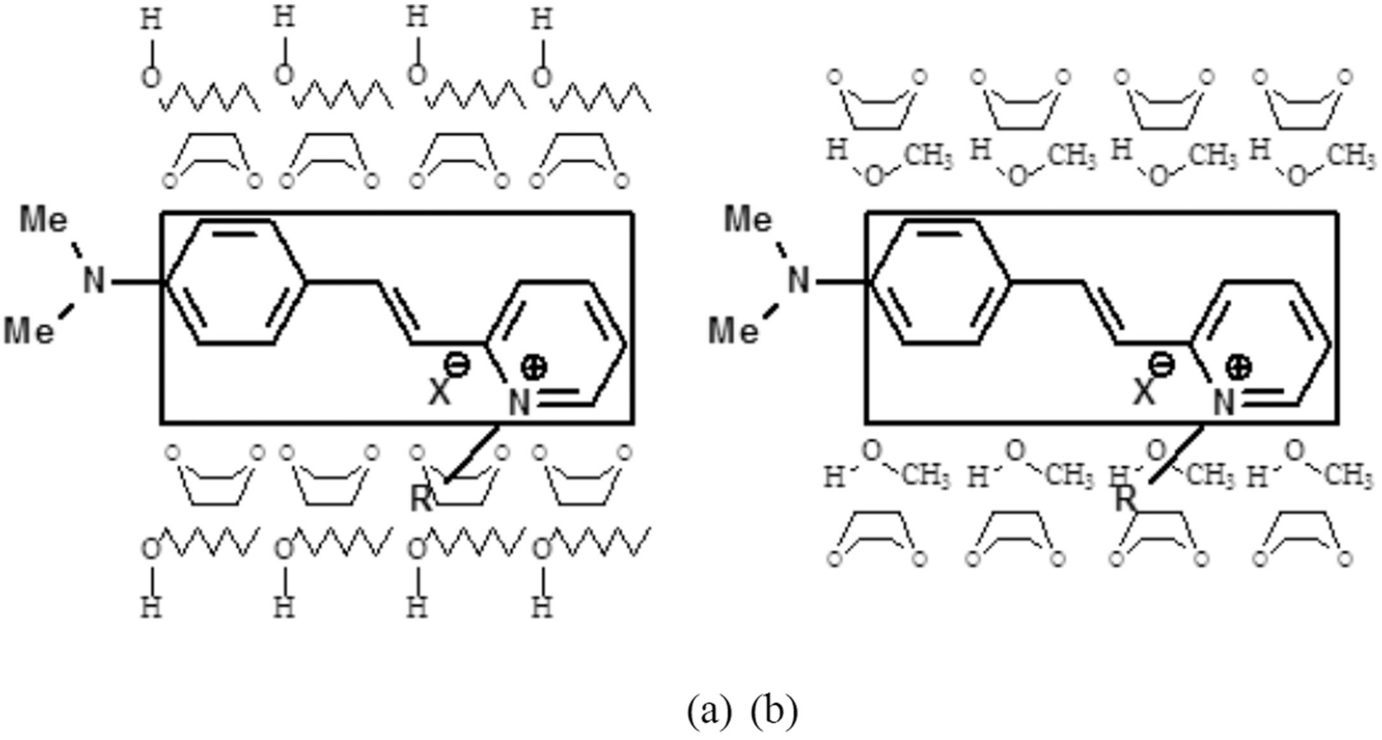


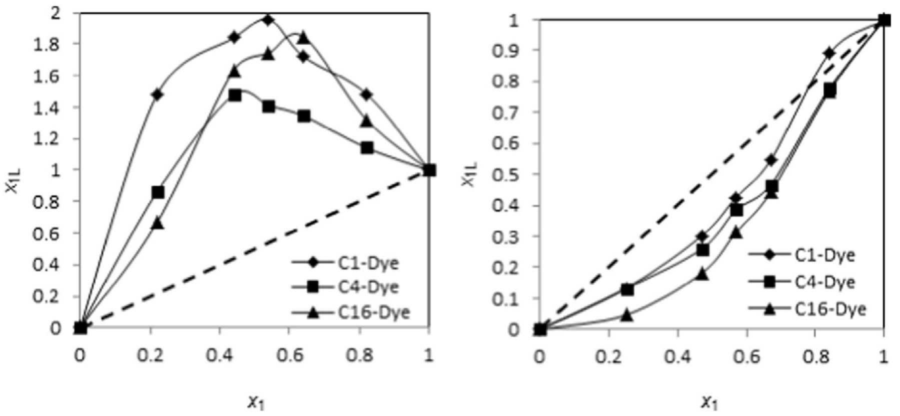
Fig. 8. Plots of local mole fraction (x_{1L}) vs. mole fraction (x_1) of alcohols in alcohol–dioxane binary mixture in the solvation of dyes **C1**, **C4** and **C16**.

One thing is clear from the comparison of the solvation of γ- and α-isomers is that both the dyes substantially behave similarly towards the solvent mixture of alcohol–hexane; however, the position of the N-alkyl chain plays the most important role due to the difference in its closeness to the charged chromophore. In the former, the N-alkyl group being present at a para position is far apart from the chromophore moiety, which in the later is at a closer approximation due to ortho positioning. As a consequence, the apolar–apolar interaction is much separated from polar–polar interaction in the former, whereas these interactions overlap with each other in the later along with the dominance of the apolar–apolar interactions over the polar–polar interactions. Hence, preferential solvation of hexane dominates from the beginning, which of course changes to preferential solvation by the alcohols at higher alcohol mole fractions in case of the α-isomers, which is a reverse situation with respect to the case of the γ-isomers.

Considering the alcohols as the parent solvent (S1) and hexane as the cosolvent (S2), the disorder or chaos introduced by hexane has been calculated in the alcohol–hexane binary mixtures with the



Scheme 3. Schematic representation of preferential solvation of α-styrylpyridinium dyes in 1-octanol–dioxane (a) and methanol–dioxane (b) binary mixtures.



(a) (b)

Fig. 9. Plot of local mole fraction (x_{1L}) vs. mole fraction (x_1) of acetone in acetone–dioxane binary mixture (a) and DCM in DCM–dioxane binary mixture for the solvation of dyes **C1**, **C4** and **C16**.

increase in the volume percentage of hexane. The disorder has been calculated from $1 - R^2$, where R^2 is the correlation coefficient for the plot of various absorption maxima of the alcohols at various volume percentages of hexane. Had there been no effect of hexane on the solvent cage generated from the alcohol–hexane binary solvent mixture, plots would have been perfectly linear at all volume percentages of hexane with $R^2 = 1.00$, and in that case the disorder $(1 - R^2)$ would have been nil. On the contrary, variable disorder is observed with the variation of volume percentages of hexane in the binary alcohol–hexane mixture (Table 1) indicating an influence of hexane on the solvent cage.

The plots of disorder versus the volume % of hexane for the dyes **C1**, **C4** and **C16** possess two peaks for each dye (Fig. 5). The first peak for **C4** and **C16** appears at a lower volume percentage of hexane, whereas that of **C1** appears at a slightly higher value. The second peak for all the dyes appears at the same volume percentage of hexane.

Appearance of two peaks represents the presence of two transitions (T1, T2) during the solvation of the dyes by the binary solvent mixtures of alcohol–hexane (Scheme 2).

Appearance of the peak T1 for **C1** at a higher mole fraction of hexane with respect to that for **C4** and **C16** may be due to lower hydrophobicity of C1 chain in comparison to the C4 and C16 chains.

Binary solvent mixtures containing acetone or DCM as the principal solvents (S1) and hexane as the cosolvent (S2) have been probed by the α-styrylpyridinium dyes to understand the electronic impacts of these mixtures on the structure of the dyes. When the binary mixture containing acetone–hexane is used, the **C1** and **C4** dyes show an initial PS by hexane up to acetone mole fractions of 0.45 and 0.58 respectively followed by PS by acetone; the **C16** dye maintaining perfect ideality up to acetone mole fraction of 0.3 followed by PS by acetone (Fig. 6a). Besides, the **C4** dye is more preferentially solvated by hexane whereas the **C1** dye is more preferentially solvated by acetone. Such an observation is in conformity with the fact that the chain-length of the dyes plays an important role towards the preferential solvation by more non-polar or more polar solvents present in the mixture. In DCM–hexane binary mixture, however, the **C1** and **C4** dyes show PS by hexane from the beginning to the end with higher preferential solvation of the **C4** dye by hexane; the **C16** dye maintaining perfect ideality up to DCM mole fraction of 0.3 followed by PS by hexane (Fig. 6b). In other words, all the dyes are preferentially solvated by hexane, none by DCM. This shows that the DCM–hexane binary mixture is dominated by the non-polarity of hexane over the dipolarity of DCM at all proportions.

3.2.2. Preferential solvation in alcohols–dioxane, acetone–dioxane and DCM–dioxane binary mixtures

In the binary mixture containing alcohol–dioxane, the trend in preferential solvation by alcohols is different from that observed in alcohol–hexane binary mixture (Fig. 7). In methanol–dioxane and 1-octanol–dioxane binary mixtures, the dyes are preferentially solvated by methanol and dioxane respectively throughout the solvent composition without being solvated by the other components in the respective cases. For each dye, the extent of solvation by the alcohols goes on decreasing with the increase in the chain length of the alcohols such that when the chain length of alcohol becomes C8 in 1-octanol, the dyes are preferentially solvated by dioxane only throughout the solvent composition. Besides, the extent of solvation of the dyes in 1-octanol goes on increasing in the order **C1** < **C4** < **C16**.

However, in the binary mixture containing other alcohols such as ethanol, 1-propanol and 1-butanol, the dyes **C1**, **C4** and **C16** are initially preferentially solvated by dioxane, followed by preferential solvation by alcohols at a mole fraction range of 0.3–0.44, 0.32–0.45, and 0.34–0.47 respectively. The study indicates that the longer the hydrophobic cleft

Table 3
Absorption maxima of **C1**, **C4**, and **C16** in hexane, dioxane and their binary mixture.

Solvents	Absorption max of probes (nm)			Shifting of absorption max of probes (nm)		
	C1	C4	C16	C1	C4	C16
Hexane	454	453	436	–	–	–
Dioxane	450	446	446	–	–	–
Dioxane/hexane (1:1 v/v)	447	440.7	440	Hypo	Hypo	In between

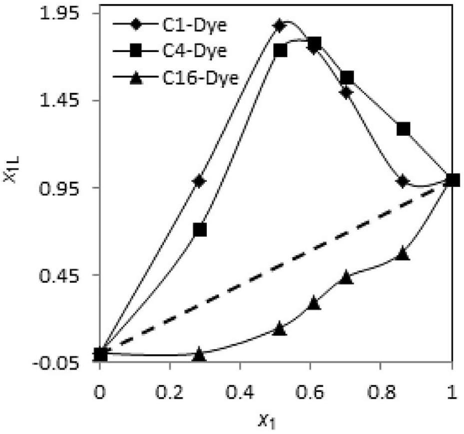


Fig. 10. Plot of local mole fraction (x_{1L}) vs. mole fraction (x_1) of dioxane in dioxane–hexane binary mixture for the solvation of dyes **C1**, **C4** and **C16**.

of the dye molecule more becomes the extent of preferential solvation by dioxane; the shorter the hydrophobic cleft more becomes the extent of preferential solvation by alcohols.

The absorption maxima at various alcohol–dioxane mixtures and the disorder at various volume percentages of dioxane for the representative **C1** dye are presented in Table 2. With the increase in the chain length of the alcohols there occurs a bathochromic shift up to an extent, followed by hypsochromism, depending on the amount of dioxane in the alcohol–dioxane binary mixture. For example, at a 40:60 dioxane:alcohol in the mixture, the bathochromism is up to 1-butanol followed by hypsochromism at 1-octanol, at 50% of each solvent, the bathochromism is up to 1-propanol followed by hypsochromism at 1-butanol and beyond, and at 60:40 dioxane:alcohol mixture and further, hypsochromism starts from methanol up to 1-octanol (Table 2).

The extent of bathochromic shift goes on decreasing with the increase in alcohol chain length as well as with the increase in the percentage of dioxane in the binary solvent mixture. Hence, with the increase in alcohol chain-length as well as with the increase in the dioxane percentage there seems to occur a better interaction of alcohol with dioxane. This also suggests the interaction between alcohol chain and dioxane to be apolar–apolar and that dioxane may be present in its boat form, rather than its chair form. Seth et al. [43] have proposed the involvement of both the chair and boat forms of dioxane molecules in the solvation of a cyanine dye. However, the boat form having higher dipole moment discharges dipole-dielectric stabilization energy during the solvation of a polar solute that overcomes the energy difference between the chair and boat forms [44], a nonideal behavior reflected also in a large nonideal quadrupolar charge distribution of dioxane itself [45]. The results can be explained through some schematic diagrams representing the solvent arrangement during the preferential solvation of the dyes by alcohols as well as dioxane in presence of the other solvent in each case (Scheme 3).

The plots of disorder for the **C1**, **C4** and **C16** dyes versus volume percentage of dioxane show two transitions T1 and T2 (Fig. 8). The first transition for **C1** dye occurs at a lower volume percentage of dioxane than **C4** and **C16** dyes, whereas the second transition for all the dyes occurs at the same volume percentage of dioxane. However, in contrast to the case of alcohol–hexane binary mixture, where the disorder in the first transition T1 is higher than that in the second transition T2, alcohol–dioxane binary mixture possesses higher second transition T2 than the first transition T1. This difference indicates better penetration of alcohols into the dioxane solvent cage compared to hexane solvent cage, which are present around the dye molecules during the solvation of alcohol–dioxane and alcohol–hexane binary mixtures respectively. The solvation pattern of the dyes can be explained through the solvation model proposed in Scheme 2.

When the dyes **C1**, **C4** and **C16** are solvated in the binary mixture containing acetone and dioxane, they are found to be solvated exclusively by acetone at all mole fractions of acetone; the preferential solvation by dioxane component being nil (Fig. 9a). On the other hand, the dyes in the binary mixture containing DCM and dioxane are found to be exclusively solvated by dioxane, except the dye **C1**, which is preferentially solvated by DCM at a DCM mole fraction of 0.75 (Fig. 9b).

The results are in conformity with the fact that polar chromophoric center of the dyes prefers to be solvated with more polar acetone in presence of less polar dioxane in the acetone–dioxane mixture, and prefers to be solvated by more polar dioxane in presence of less polar DCM in the DCM–dioxane mixture. In these binary mixtures, the preferential solvation is due mainly to polar–polar interaction, rather than apolar–apolar interactions of the dye probes and the solvents.

3.2.3. Preferential solvation in dioxane–hexane binary mixtures

In 1:1 v/v dioxane–hexane binary mixture, a blue shift of 6.3 nm is observed due to a change in alkyl group from C1 to C4 followed by a further blue shift of 0.7 nm for a change in the alkyl group from C4 to C16 (Table 3). Further, the absorption maxima of the dyes suffer hypsochromism in the dioxane–hexane binary mixture with respect to the neat solvents except the **C16** dye, where the absorption maximum is in between those of the neat solvents. This phenomenon is attributed to the solvent–solvent interaction which affects the electronic spectra of the dye probes. However, the blue shift observed in the 1:1 dioxane–hexane mixture due to the change in alkyl chain of the probes is due to solute–solvent interactions.

An interesting observation is noted when the x_1 values are plotted against x_{1L} for the dyes in the dioxane–hexane binary solvent mixture with the variation in the mole fraction of dioxane. The dyes **C1** and **C4** are found to be preferentially solvated by dioxane and the dye **C16** is preferentially solvated by hexane at all proportions of the binary mixture (Fig. 10).

Since dioxane is a dipolar aprotic and hexane is a perfectly nonpolar solvent, the results show the dominance of polar–polar interactions among the polar chromophore of **C1** and **C4** dye molecules and the polar dioxane molecules and the dominance of apolar–apolar interactions among the apolar hydrophobic cleft of the **C16** dye molecules and the apolar hexane molecules. In other words, in case of the dyes **C1** and **C4**, the polarity of chromophores guides their solvation pattern whereas, in case of the dye **C16**, the apolarity of hydrophobic cleft is more responsible for its solvation pattern. However, depending upon the polarity of the solvents present in the binary mixture, the hydrophobic clefts of the **C1** and **C4** dyes and the chromophores of the **C16** dye are also responsible, albeit to a smaller extent, for the solvation of the dyes.

4. Conclusion

In conclusion, the presence of N-alkyl chain at the ortho position with respect to the charged chromophoric unit markedly influences the solvation and the solvatochromic shifts of the α-N,N-dimethylaminostyryl-N-alkyl pyridinium dyes. The solvation of the charged chromophoric unit by polar solvents is highly dominated by the solvation of the hydrophobic clefts by non-polar solvents. In most cases, the purity of the individual solvents S_1 and S_2 is lost and the dye gets solvated by the solvent complexes (S_{12}). A remarkable ortho effect is observed in case of the α-isomers of the dyes, which was absent in their γ-isomers. Enrichment of both polar and apolar environments for the dyes could be achieved through the tuning of the binary mixtures.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.molliq.2015.01.046.

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