

Solvatochromic and Preferential Solvation Studies on Schiff Base 1,4-Bis(((2-Methylthio)Phenylimino)Methyl) Benzene in Binary Liquid Mixtures

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Abstract The solvatochromic behavior of the 1,4-bis(((2-methylthio) phenylimino)methyl) benzene [BMTMPMB] in single solvents and binary mixtures were investigated. Fluorescence spectra show the dual emission due to twisted intramolecular charge transfer (TICT) state. The preferential solvation parameters: local mole fraction, X_2^L , solvation index δ_{s2} , exchange constant K_{12} were calculated for the binary mixtures, ACN+MEOH, DMSO+CCl₄ and CCl₄+1,2 DCE. The dipole moment ratios between ground and excited states were deduced using the solvatochromic shifts of absorption and fluorescence spectra as a function of dielectric constant (ϵ), refractive index (n) and it was found to be 1.25.

Keywords N-(2-methylthiophenyl)-2-hydroxy-1-naphthalidimine · Schiff base · Solvatochromism · Preferential solvation · Binary liquid mixtures · Absorption and fluorescence spectroscopy

Introduction

Schiff bases are important ligands in coordination chemistry due to their ease of preparation and their ability to be readily modified both electronically and sterically. Neutral Schiff bases are used to prepare complexes with wide range of properties.

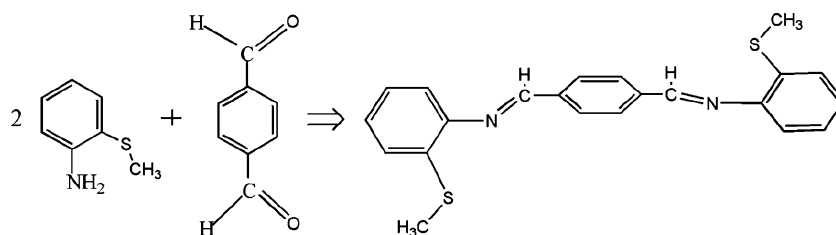
Ligands with soft and hard donor sites are very useful in catalysis [7]. Molecules possessing O, N and S donor sites are important in the development of coordination chemistry as well as in the biochemistry of a number of metal ions particularly the transition metals [15]. There has been continuous interest in the chemistry of the metal complexes of Schiff bases containing N and S donor atoms because of their structural features and biological activities [4, 9]. Schiff bases were investigated because of their immense significance in the fundamental, biological and applied sciences [20].

Solvents play an important role in physical and chemical processes. Solvent effects are related to the nature and the extent of the solute-solvent interactions developed in the solvation shell of the solutes [13]. Organic mixed solvents are widely used as the mobile phase in liquid chromatography, capillary electrophoreses and as a reaction medium. Solvent mixtures have improved physical properties such as solvation power, density, viscosity and refractive index compared with their neat solvents [17]. Electronic spectroscopic parameters have been extensively utilized for obtaining information on solvation in pure and binary mixtures [12, 16]. Solvatochromism is used to describe the pounced change in position sometimes in intensity of an absorption band, accompanying a change in the polarity of the medium. The use of solvatochromic indicators is a suitable and easy method for studying solute-solvent interactions. The transition energy of the indicator depends on the solvation sphere composition and the solvent properties [14]. The preferential solvation phenomenon that is the selective enrichment of the certain solvent component in the solvation shell of a given solute is of paramount importance in the interpretation of many physiochemical parameters measured in the mixtures [6]. Hydrogen bonding plays an important role in the study of preferential solvation and has been widely investigated because it is

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Scheme 1 Synthesis of BMTPMB



present in large variety of chemical, biochemical and pharmacological events [3].

In the present study we have used optical absorption and fluorescence emission techniques to investigate 1,4-bis(((2-methylthio)phenylimino)methyl) benzene (BMTPMB) in single solvents and binary liquid mixtures. This paper describes an analysis of the solvatochromic behavior of BMTPMB. In order to expedite the binary mixtures comprising of non polar and polar solvents, we have chosen preferential solvation model.

Experimental

Synthesis of Schiff Base 1,4-Bis(((2-Methylthio)Phenylimino)Methyl) Benzene[BMTPMB]

An alcoholic solution containing terephthalaldehyde (1.34 g, 10 mM) and 2-(methylthio)aniline (2.78 g, 20 mM) taken in the 1:2 molar ratio was magnetically stirred for about 6 hours and the contents were kept over-night. The pure yellow coloured fine crystals were filtered, washed with alcohol and dried. After dried it is used for the analysis. (Scheme 1).

For studying the solvent effect, Carbon tetrachloride (CCl_4), 1,2 Dichloroethene(1,2 DCE), Acetonitrile (ACN), Methanol (MEOH) and Dimethyl sulfoxide (DMSO) from Merck Chemical laboratory with 99.9% purity were used without further purification. The concentration of BMTPMB in these solvents was 0.04 mM for all these optical and fluorescence studies. Binary mixtures were prepared by mixing in the volume ratio of 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1. The prepared solution was kept in a

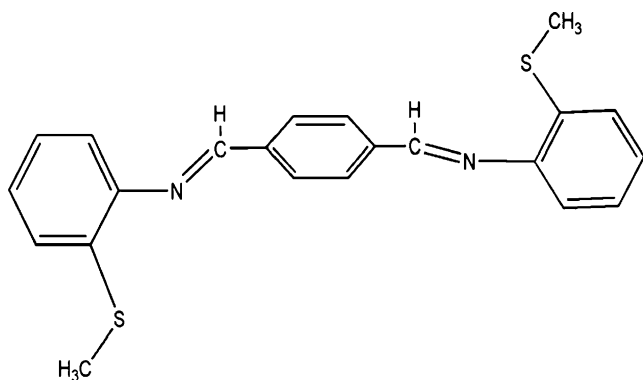


Fig. 1 Molecular structure of Schiff base BMTPMB

Ultrasonicator for 5 min in order to make a homogeneous mixture. Optical absorption spectra were recorded by Shimadzu UV-2450 spectrometer. Fluorescence measurements were made by RF 5301 PC Spectrofluorophotometer. All the experiments were performed at room temperature.

Result and discussion

Absorption and fluorescence spectral studies of BMTPMB

The solvent effect on the absorption spectra of BMTPMB is investigated in three types of solvents. They are non polar solvent CCl_4 , polar protic solvent MEOH, dipolar aprotic solvents DMSO, ACN and 1,2 DCE. Molecular structure of BMTPMB is shown in Fig. 1. The absorption spectra of BMTPMB are presented in Fig. 2. The spectra show a broad band in the visible region 380–400 nm. This broad band is due to π - π^* transition. The bands in the UV region are due to n - π^* transition. BMTPMB has an absorption maximum at 380 nm in MEOH, 385 nm in ACN, 388 nm in 1,2 DCE, 392 nm in DMSO and 389 nm in CCl_4 . Figure 2 shows that the absorption maximum of BMTPMB at 389 nm in CCl_4 exhibits a blue shift in polar aprotic solvents like 1,2 DCE, ACN and polar protic solvent MEOH except in polar aprotic solvent like DMSO. In the

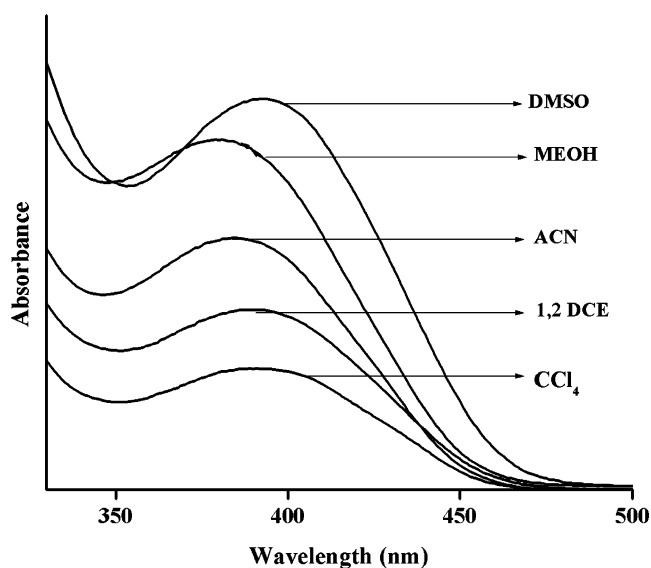
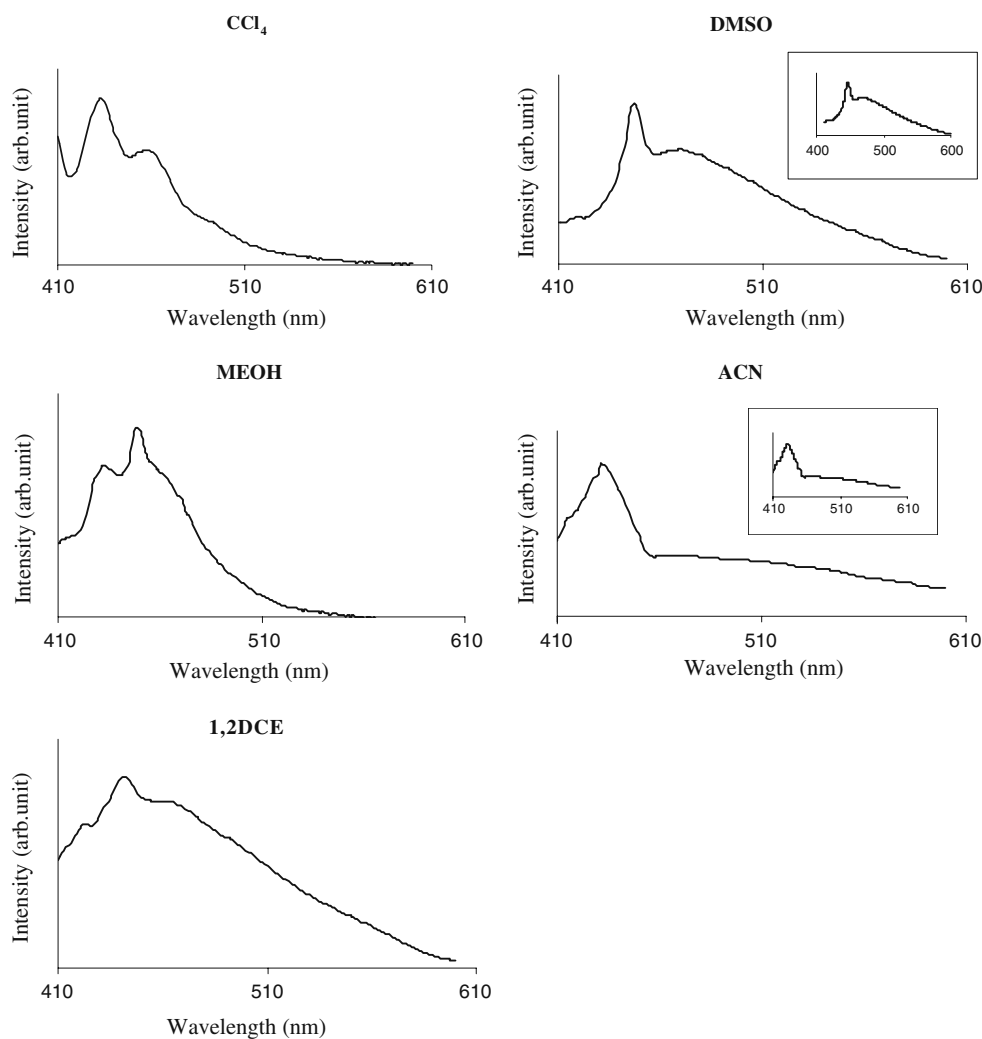


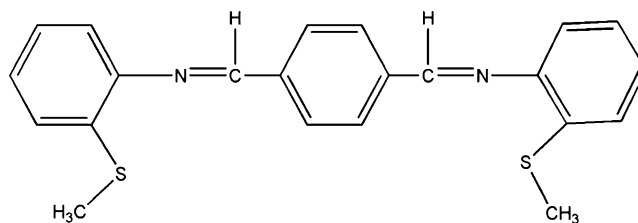
Fig. 2 Absorption spectra of BMTPMB in single solvents

Fig. 3 Fluorescence spectra of BMTPMB in single solvents

molecular structure of the title compound the outer benzene rings are twisted away from the central benzene rings due to steric repulsion between the hydrogen atom attached to the cyano group and the CH group of the outer benzene rings [7]. The observed changes in the electronic spectrum of Schiff bases are attributed to coordination of imine nitrogen(C=N) atom to metal ions with an additive effect due to deprotonated phenolic groups upon chelation [1, 10]. Smaller shifts in absorption maximum are due to the change in the dielectric environment of the probe molecule, and the larger shifts indicate that there may be specific solute-solvent interactions between the probe molecule and the solvents.

Figure 3 shows the fluorescence spectra of BMTPMB in CCl_4 , 1,2 DCE, ACN, DMSO and MEOH. The fluorescence emission of BMTPMB shows two peaks in the region 410–610 nm in all the above mentioned solvents except in ACN. CCl_4 has a short wavelength peak around 433 nm and a long wavelength peak at 457 nm. In the case of MEOH short wavelength peak is around 438 nm and a long wavelength peak appears at 449 nm. In the case of 1,2 DCE

short wavelength peak is around 443 nm and a long wavelength peak is observed around 465 nm. In the case of 1,2 DCE and DMSO short wavelength peaks are more prominent than the long wavelength peaks. In ACN the bands are not well resolved and appeared as one. These spectra show the short wavelength peaks are red shifted with respect to CCl_4 in all the solvents except ACN. The long wavelength peaks are red shifted with respect to CCl_4 in all the solvents except MEOH. The observed red shifts in short and long wavelength peak indicate that BMTPMB is more stabilized in the excited state than the ground state. The observed changes in the absorption and emission spectra

**Fig. 4** Molecular structure of BMTPMB in the excited state

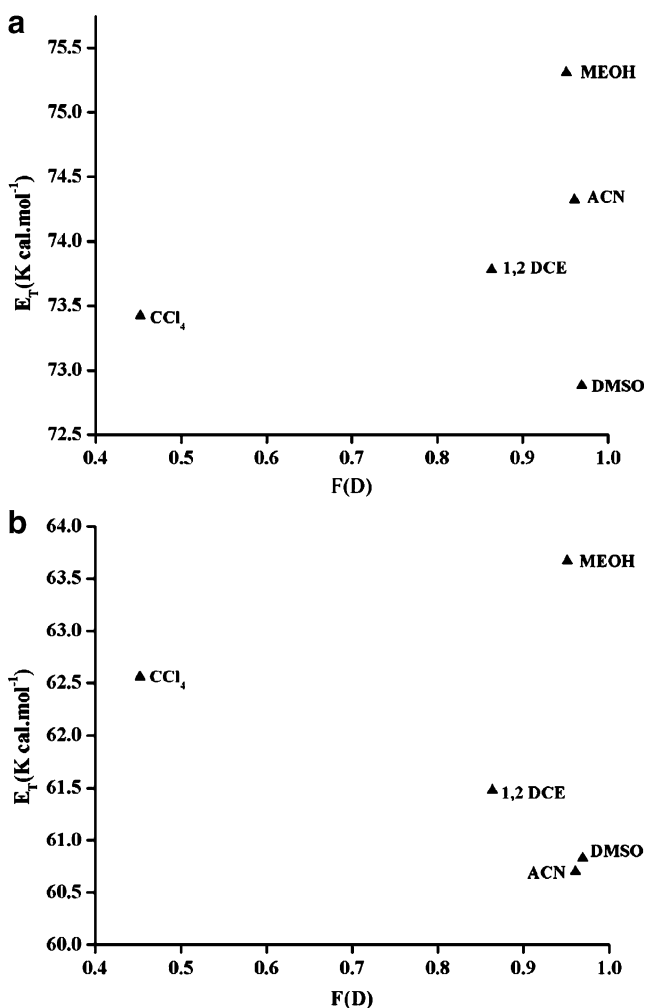


Fig. 5 a Plot of E_T vs. $F(D)$ for BMTPMB a Absorption. b Plot of E_T vs. $F(D)$ for BMTPMB b Fluorescence

suggests the possibility of the intermolecular interactions between the solute and the solvent molecules. The absence of mirror image relationship usually indicates the different geometric arrangements of nuclei in the excited state as compared to the ground state [24]. In the present case the absence of mirror image relationship of fluorescence spectra confirms the different geometry of the excited state of the probe molecule. BMTPMB shows a dual emission character. Dual fluorescence can result due to excited state intramolec-

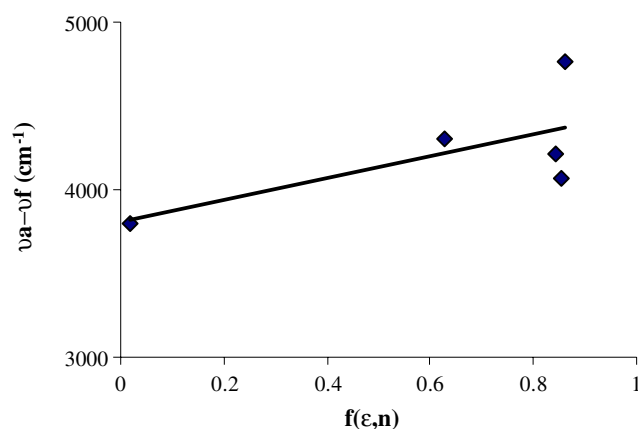


Fig. 6 Plot of $(\nu_a - \nu_f)$ vs. the solvent polarity function $f(\epsilon, n)$

ular proton transfer (ESIPT) or twisted intramolecular charge transfer (TICT) state [23]. In the present case there is no possibility that a probe molecule can undergo ESIPT. Therefore the observed dual fluorescence may be due to TICT character of the probe molecule. Intra molecular charge transfer and internal rotation can also occur in the non polar and highly symmetric molecules. In the dual fluorescence spectrum, the shorter wavelength peak arises due to emission from the locally excited (LE) and the longer wavelength peak arises due to emission from the TICT state. In the present case, longer wavelength peak undergoes red shift with increasing solvent polarity indicating the highly dipolar character (TICT state) [2]. There is a possibility that the charge transfer can take place from the nitrogen of imine group to the Pi electron system of the benzene. In the crystallographic structure, the outer benzene rings are twisted away from the co planarity with the central benzene ring [7]. The configuration of the probe molecule may change on excitation. In the excited state, the outer benzene rings are twisted such that it comes to co planarity with the central benzene ring. In this situation all the three benzene rings in the probe molecule come to the same plane (Fig. 4). The absence of mirror image relationship also confirms the different geometry of the fluorophore in the excited state. Formation of TICT states usually increases the magnitude of the dipole moment of the molecule [21]. In the present case the dipole moment ratio between the ground and excited states is greater than one. This indicates that the

Table 1 Photo physical parameters of BMTPMB obtained from optical absorption and fluorescence measurements

Solvents	F(D)	$E_T(\text{kcal mol}^{-1})$		$f(\epsilon, n)$	$f(\epsilon, n) + g(n)$	$\nu_a - \nu_f (\text{cm}^{-1})$	$\nu_a + \nu_f (\text{cm}^{-1})$
		a	b				
CCl ₄	0.452	73.42	62.56	0.02	0.65	3,798	47,562
DMSO	0.969	72.88	60.83	0.84	1.48	4,214	46,767
1,2DCE	0.863	73.78	61.48	0.62	1.22	4,301	47,311
ACN	0.960	74.32	60.70	0.86	1.33	4,762	47,225
MEOH	0.950	75.31	63.49	0.85	1.301	4,071	48,615

a absorption, b Fluorescence

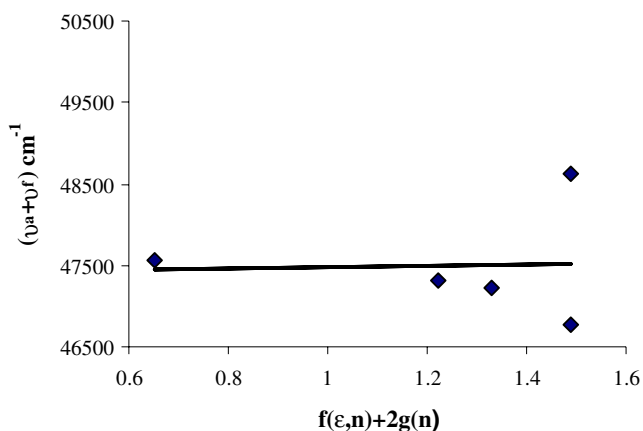


Fig. 7 Plot of (ν_a+ν_f) vs. the solvent polarity function f(ε, n) +2g(n)

excited state dipole moment is greater than the ground state, which confirms the existence of TICT state in the probe molecule.

Solvatochromism

When the solute is dissolved in a solvent, the solvent exerts a definite influence on the solute. This influence depends on the nature of the solvent. This influence reflects changes in the absorption and fluorescence spectrum [18].

The molar transition energies (E_T) for BMT₂PMB are calculated by using the Eq. 1

$$E_T(\text{Kcal mol}^{-1}) = \frac{28591}{\lambda_{\text{max}}(nm)} \tag{1}$$

In the case of dual emission the long wavelength maximum can be taken for calculating E_T values. E_T values of the absorption and emission is plotted (Fig. 5a and b) against the solvent dielectric polarity F(D) = $\frac{2(\epsilon+1)}{(2\epsilon+1)}$ in the ground and excited states and the values are shown in Table 1. Figure 5a and b shows the non linearity of E_T values on increasing the solvent polarity. This non linearity indicates the existence of solvatochromism. The non linear behavior may be due to solute-solvent interactions. Here MEOH shows high E_T values (both in ground and excited states) than the non polar solvent CCl₄. MEOH has the ability to form dimer through self association which has a non polar nature. This may be the reason for the observed high E_T values.

Estimation of dipole moment ratio

In order to calculate the dipole moment ratio, the absorption and emission maxima wavenumbers have been calculated by using the absorption and fluorescence wavelength maxima [22]. The magnitude of the Stokes shift indicates that the excited state geometry is different from that of

ground state. Solvent polarity f(ε, n) and f(ε, n)+g(n) parameters are determined and presented in Table 1. Spectral shifts of ν_a-ν_f and ν_a+ν_f in cm⁻¹ of all the five solvents versus the solvent polarity function f(ε, n) and f(ε,n)+g(n) are shown in Figs. 6 and 7. The dipole moment ratio of ground and excited states are determined based on the following equations

$$\nu_a - \nu_f = m_1 f(\epsilon, n) + \text{constant} \tag{2}$$

$$\nu_a - \nu_f = -m_2 [f(\epsilon, n) + g(n)] + \text{constant} \tag{3}$$

Where

$$f(\epsilon, n) = \left(\frac{\epsilon + 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right) \left(\frac{2n^2 + 1}{n^2 + 2} \right) \tag{4}$$

$$g(n) = \frac{3}{2} \left(\frac{n^4 - 1}{(n^2 + 2)^2} \right) \tag{5}$$

and

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \tag{6}$$

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \tag{7}$$

Here f(ε, n) and f(ε,n)+g(n) is the solvent polarity parameter. μ_e and μ_g are the ground and excited dipole

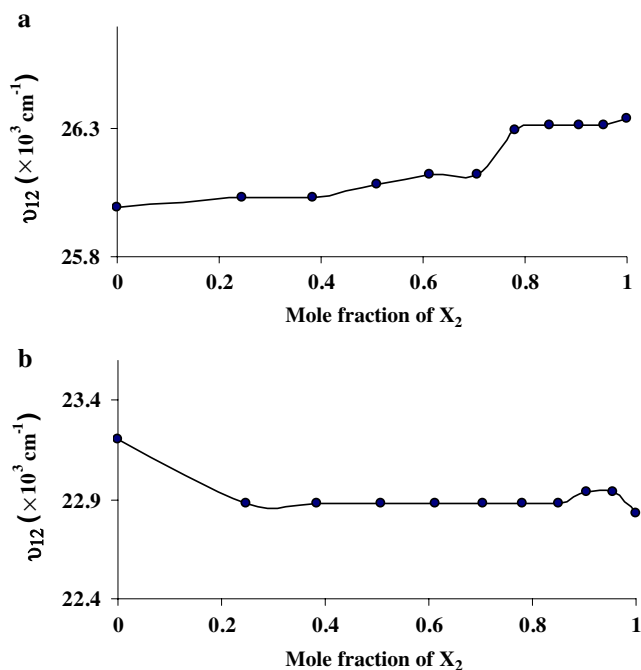


Fig. 8 Plot of ν₁₂ vs. Mole fraction of X₂(MEOH) in the binary mixture of ACN+MEOH **a** Absorption, **b** fluorescence

Table 2 Preferential solvation data of BMTPMB in binary mixtures

	ACN+MEOH (X_2)		X_2^L		δs_2		K_{12}	
	a	b	a	b	a	b	a	b
0								
0.24	0.11	0.85	-0.130	0.612	2.039	0.043		
0.38	0.11	0.85	-0.267	0.475	3.416	0.073		
0.50	0.25	0.85	-0.256	0.350	1.973	0.109		
0.61	0.36	0.85	-0.244	0.245	1.535	0.147		
0.70	0.36	0.85	-0.336	0.153	2.066	0.198		
0.78	0.86	0.85	0.080	0.079	0.263	0.267		
0.84	0.92	0.85	0.071	-0.009	0.197	0.374		
0.90	0.92	0.71	0.014	-0.188	0.309	1.410		
0.95	0.92	0.71	-0.036	-0.238	0.688	3.134		
1								
DMSO+CCl ₄								
(X_2)								
0	0	0.30	-0.086	0.215	0	0.238		
0.04	0.11	0.60	-0.045	0.448	1.778	0.148		
0.09	0.11	0.68	-0.140	0.431	3.460	0.204		
0.15	0.11	0.53	-0.234	0.259	5.877	0.489		
0.22	0.11	0.60	-0.328	0.088	9.449	1.079		
0.29	0.38	0.68	-0.159	0.066	1.446	1.273		
0.39	0.84	0.68	0.193	0.034	0.576	1.440		
0.49	0.76	0.84	0.029	0.103	1.787	1.107		
0.62	0.61	0.84	-0.269	-0.041	9.198	2.735		
0.75								
1								
CCl ₄ +1,2DCE(X_2)								
0	-0.88	0.50	-0.015	0.383	-0.290	0.134		
0.12	0.10	0.62	-0.157	0.366	3.033	0.209		
0.26	0.10	0.50	-0.244	0.155	4.574	0.265		
0.34	0.10	0.62	-0.349	0.175	7.149	0.493		
0.45	0.10	0.62	-0.453	0.070	10.756	1.103		
0.55	0.10	0.62	-0.549	-0.025	15.987	1.726		
0.65	0.10	0.62	-0.641	-0.117	25.005	1.719		
0.74	0.78	0.75	-0.051	-0.086	1.406	1.719		
0.83	0.78	0.87	0.134	-0.046	2.879	1.509		
0.92								
1								

a absorption, *b* Fluorescence

moments, *c* is the velocity of light, and ‘*a*’ is the Onsager cavity radius. The slope m_1 and m_2 are obtained from the Figs. 6 and 7. i.e. m_1 is from the plot between $f(\epsilon, n)$ and $\nu_a - \nu_f$ (cm^{-1}) and m_2 is between $f(\epsilon, n) + g(n)$ and $\nu_a + \nu_f$ (cm^{-1}). The slope values are considered as constants. From the slope values the ratio of excited and ground state dipole moments of BMTPMB is calculated by using the equation

$$\frac{\mu_e}{\mu_g} = \left| \frac{m_1 + m_2}{m_2 - m_1} \right| \quad (8)$$

The dipole moment ratio is found to be 1.25.

Preferential solvation studies

In order to explain the solvatochromism in solvent mixtures we have employed preferential solvation model. Non linear variation of any solute property with the mole fraction of a solvent component is usually explained in terms of preferential solvation of the solute [5]. Hence the results obtained from the experimental values can be explained by assuming the solvent composition in the vicinity of the solute differs from that of the bulk. The shift in the ν_{12} values of the solvatochromic indicator is observed in binary

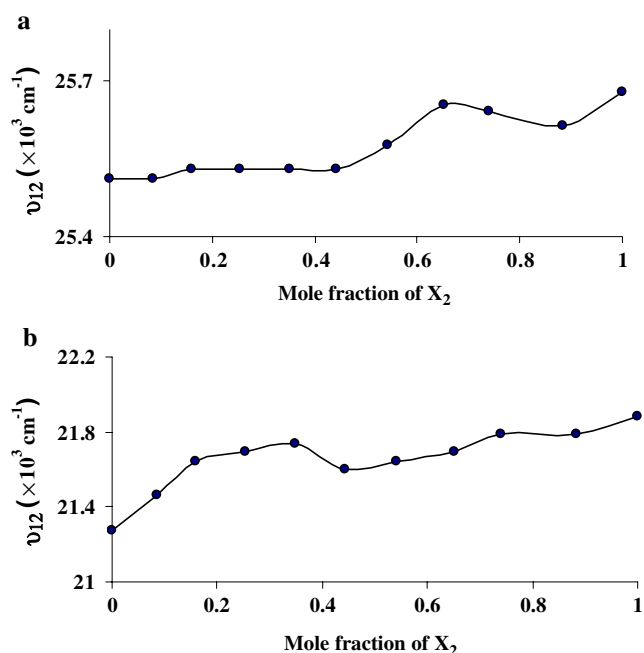


Fig. 9 Plot of ν_{12} vs. Mole fraction of $X_2(\text{CCl}_4)$ in the binary mixture of DMSO-CCl_4 **a** Absorption, **b** fluorescence

mixtures. The nonlinearity of the ν_{12} values versus mole fraction plots in binary mixture arises due to preferential solvation. To study about the preferential solvation of the solute molecule different solvation parameters are used. These parameters are local mole fraction (X_2^L) and (X_1^L), preferential solvation constant K_{12} and index of preferential solvation (δ_{s2}). Here (X_2^L) and (X_1^L) are the mole fraction of solvent 2 and solvent 1 in the cybotactic region of the dye.

The local mole fraction X_2^L and X_1^L are deduced by using the formula

$$X_2^L = \frac{\nu_{12} - \nu_1}{\nu_2 - \nu_1} = 1 - X_1^L \tag{9}$$

where ν_1 , ν_2 are the absorption and emission maximum expressed in wave numbers of solvent 1 and solvent 2. ν_{12} indicates absorption and emission maximum of binary mixtures expressed in cm^{-1} .

The preferential solvation index (δ_{s2}) provides the measure of the preferential solvation with respect to the co-solvent and is represented as the difference between X_2^L and X_2 .

$$\delta_{s2} = X_2^L - X_2 \tag{10}$$

The preferential solvation of the solute in binary mixtures can be explained by evaluating the preferential solvation constant K_{12} (exchange constant)

$$K_{12} = \frac{X_1^L/X_2^L}{X_1/X_2} \tag{11}$$

When $K_{12} < 1$ indicates a preference for solvent 1 over solvent 2, Whereas $K_{12} > 1$ indicates a preference for solvent 2 over solvent 1 [19].

Binary mixtures containing ACN+MEOH

Figure 8 shows the variation of ν_{12} versus mole fraction of MEOH. This fig indicates that ν_{12} values varies non linearly with respect to X_2 in the ground and excited states. A deviation from the linearity may be explained on the basis of preferential solvation of BMTPMB by one of the solvent component. In the ground state the ν_{12} values increase with the addition of MEOH into ACN. The preferential solvation data for BMTPMB in the binary mixtures ACN+MEOH are tabulated (Table 2) for both ground and excited states. In the ground state $K_{12} > 1$ upto the bulk mole fraction X_2 (MEOH)=0.70, when $X_2 > 0.70$ the K_{12} values are smaller than one. $K_{12} > 1$ indicates the preference of solvent 2 (MEOH) by BMTPMB and $K_{12} < 1$ indicates the preference of solvent 1 (ACN). At low concentration of MEOH, there are more monomeric MEOH molecules which are available to have an interaction with the solute. There may be an intermolecular hydrogen bond interaction between the hydroxyl group of MEOH and the imine group of BMTPMB as the imine group always has a tendency to form a hydrogen bond [8] with hydroxyl groups. At high concentration of MEOH, there will be a

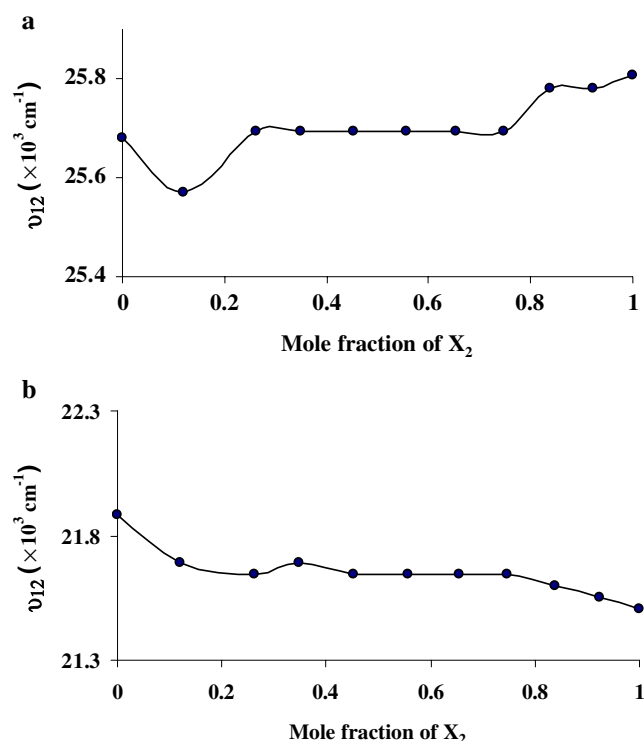


Fig. 10 Plot of ν_{12} vs Mole fraction of $X_2(1,2 \text{ DCE})$ in the binary mixture of $\text{CCl}_4-1,2 \text{ DCE}$ **a** Absorption, **b** fluorescence

formation of dimer of MEOH molecule, so there is less availability of monomeric MEOH molecule to form intermolecular hydrogen bonding with the solute. At this situation ACN molecules are in the monomeric state and therefore BMTMPMB can make an interaction with the cyano group of solvent through its methyl group. In the excited state initially ν_{12} values varies with increasing of MEOH concentration with respect to neat MEOH. In this case the solute molecule is preferentially solvated by solvent 1 (ACN) over solvent 2 (MEOH). This suggests that even though MEOH has the ability to form intermolecular hydrogen bonding with BMTMPMB, the solute prefers solvent 1 (ACN). This may be due to the steric hindrance of the probe molecule to have an association with MEOH with its imine on the excited state.

Binary mixtures containing DMSO+CCl₄

Studies of preferential solvation of BMTMPMB in binary mixtures of DMSO and CCl₄ are carried out and the preferential solvation parameters are given in Table 2. Plot of the ν_{12} versus the bulk mole fraction of the co solvent (CCl₄) is presented in Fig. 9 for both ground and excited states. This figure shows the non linear variation of the ν_{12} values with increasing the concentration of CCl₄. The non linearity of the plot indicates the existence of preferential solvation of BMTMPMB by one of the solvent component. From the solvation data the local mole fraction X_2^L is smaller than the bulk mole fraction of the solvent CCl₄ (X_2). In the ground state the K_{12} value is greater than one, indicates the solute is preferentially solvated by solvent 2 (CCl₄) rather than solvent 1 (DMSO). CCl₄ molecules become available to enter into the solvation shell because of the possibility of DMSO molecules can form dimer due to its self association nature. In the case of excited state, the ν_{12} values increase when CCl₄ is added into DMSO. Here the solute molecule is preferentially solvated by solvent 1 (DMSO) upto the concentration $X_2=0.15$. When we increase the CCl₄ concentration further the solute is solvated by solvent 2 (CCl₄). Even though it is non polar, due to its electro negativity of the chlorine atom there is a possibility of intermolecular interaction [11] with the methyl group of the solute molecule. This was confirmed by K_{12} value which is smaller than one upto $X_2=0.15$ and after that it is greater than one.

Binary mixtures containing CCl₄+1,2DCE

The wavenumbers for BMTMPMB in this mixture are plotted (Fig. 10) versus the bulk molefraction of the 1,2 DCE (X_2). This plot shows the nonlinearity behavior with respect to X_2 . The preferential solvation data for BMTMPMB for this mixture are presented in Table 2. In the ground state the

solute is preferentially solvated by solvent 2(1,2DCE) over solvent 1(CCl₄). This was confirmed by

$K_{12}>1$. This is due to the reason that the solute prefers more polar solvent to dissolve, high dielectric enrichment. That is 1,2 DCE is more polar than CCl₄. In the excited state the ν_{12} value decreases with increasing concentration of 1,2 DCE . Here the solute is solvated by solvent 1 initially. This was confirmed by $K_{12}<1$ upto $X_2=0.45$. Even though it is non polar, due to its electro negativity of the chlorine atom there is a possibility of intermolecular interaction [11] with the methyl group of the solute molecule. When $X_2>0.45$ the solute prefers solvent 2 (1,2 DCE). This may be due to the polar nature of 1,2 DCE at high concentration. Therefore the solute prefers solvent 2 (1,2 DCE).

Conclusion

Optical absorption and fluorescence spectroscopic techniques are used to study the spectral behavior of BMTMPMB in single solvents and binary mixtures. To study the spectral behavior of BMTMPMB in binary liquid mixtures we have employed preferential solvation model. The solvatochromic shifts of the absorption and fluorescence maxima are used to estimate a dipole moment ratio between ground and excited states and it is found to be 1.25. Our results has suggested that solute—solvent interactions are responsible for the observed changes in the ν_{12} values in all the binary liquid mixtures.

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