

Preferential Solvation Studies of 1, 5 Diamino Anthraquinone in Binary Liquid Mixtures

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Abstract The absorption and fluorescence spectra of 1,5-diaminoanthraquinone(1,5-DAAQ) have been investigated in organic solvents-Benzene(BZ), Ethanol (ETOH), Acetonitrile (AN), Dimethylformamide (DMF) and Dimethyl sulfoxide (DMSO). There is an intra molecular hydrogen bond formed between quinoid oxygen and the substituents NH_2 [C = O...H-N]. The interaction of the hydrogen atom of - NH_2 leads to red shift in both absorption and fluorescence spectra. The dipole moment ratio of 1,5 DAAQ in ground and excited states was calculated from stokes shift obtained from optical absorption and fluorescence spectra. Photo physical properties of 1,5-DAAQ dye was studied using this absorption and fluorescence spectroscopy techniques in binary liquid mixtures(AN + DMF, AN + DMSO, AN + ETOH and BZ + ETOH).

Keywords 1, 5-diaminoanthraquinone · Preferential solvation · Photo physical properties · Absorption and fluorescence spectroscopy · Solute solvent interaction

Introduction

Anthraquinone derivatives are important class of a system that absorb in the visible region. They are used in

principally in photographic dye chemicals, in paper industries as a catalyst, in textile industry for colouring textile materials and in medicine as an antioxidant. The biological effects of these drugs are due to the interaction of the chromophore group with DNA [1]. Diamino anthraquinones find applications in the field of biochemistry and electrochemistry. They are used in the synthesis of electroactive dendrimers and preparation of solid state redox super capacitors [2]. Mixed solvents are common in practical chemistry, ranging from their use for chromatographic separations in organic synthesis to study the reaction kinetics and to hydrometallurgical application. In some cases liquid mixtures are the default medium obtained from nature as crude oil, while in other cases they are used by design to improve physical characteristics such as density, viscosity etc. Also solvent mixtures may be selective for their chemical characteristics to improve solubility or to affect the rate of formation and yield of desirable products [3]. In general the optical properties of the anthraquinone derivatives depend on (i) the nature of the position of the substituents (ii) the ability to form hydrogen Bonds (iii) the occurrence of intermolecular interactions [4].

Solvation is the process of covering a solute particle by an overcoat of solvent molecules, the solvation shell, in which each molecule of the solvent is held in the vicinity of the solute molecule by non covalent bonds. Studying the solvation process is very important for understanding the mechanism by which solvents affect chemical reactions [5]. Solvatochromic effects have been used extensively to investigate the nature of the transition, the site of solvent interaction, the change in geometry, as probes of biological systems [6]. Solvation of solute and its source in terms of solute-solvent and solvent-solvent interaction are important areas in physical chemistry. Solvent-solvent interaction also plays a significant role in the overall solvation process.

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Mixed binary solvents provide systems where it is possible to vary the solvent-solvent interaction as such, study in these media is likely to throw light on the role of such interaction on the solvation process [7]. The dipole moment of an electronically excited state of a molecule is an important property that provides information of the electronic and geometrical structure of the molecule in the short lived state. Among the existing methods associated with electronic excitation of a molecule the most popular ones are based on a linear correlation between the wave numbers of the absorption and fluorescence maximum and a solvent polarity function which usually involves both dielectric constant (ϵ) and the refractive index (n) of the medium [8].

Our group has made optical absorption, fluorescence emission and SERS measurements of 1,5-diaminoanthraquinone (1,5-DAAQ) to elucidate the behavior of the molecule in different environments [9]. An extension of the above analysis the behavior of 1, 5-diaminoanthraquinone in binary mixtures is probed by using optical absorption and fluorescence spectroscopy methods.

Experimental

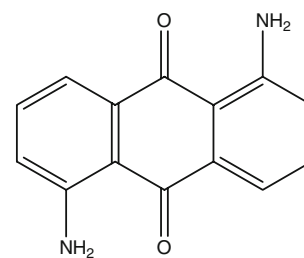
1,5-diaminoanthraquinone provided by Chemical Physics Group, TIFR, Mumbai was used without further purification. For studying the solvent effect benzene, ethanol, dimethyl sulfoxide, dimethyl formamide and acetonitrile from Merck Chemical laboratory with 99.9% purity were used without further purification. The concentration of 1,5-DAAQ in these solvents was 0.01 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 Ultrasonicator for 5 min in order to make a homogeneous mixture. All the mass measurements were carried out by using a electrical balance (Adair Dutt 180) with accurate to four decimal places. Optical absorption spectra were recorded by a Shimadzu UV-2450 spectrometer. Fluorescence measurements made by Carry Varian Spectrofluorimeter. All the experiments were performed at room temperature.

Result and discussion

Single solvent effects

The molecular structure of 1, 5 DAAQ is presented in Fig. 1. 1, 5 DAAQ shows an absorption band in the visible region 400–500 nm in various solvents (Fig. 2). This is associated with π - π^* transition. The absorption of 1, 5 DAAQ is at 472 nm in BZ, 479 nm in AN, 488 nm in DMF, 494 nm in DMSO and 489 nm in ETOH. The peaks

Fig. 1 Molecular structure of 1,5 DAAQ



are red shifted in all the above mentioned solvents with respect to a non polar solvent (benzene). It is weakly structured in non polar (benzene) and polar aprotic (DMF, DMSO, AN) solvents. This weak progression has disappeared in polar protic solvent (ethanol). This may due to the formation of intermolecular hydrogen bond between OH of ethanol and quinoid oxygen. All observed red shift is due to the changing of solute environment from non polar to polar. The polarity of the solvent has a significant influence on the position as well as the intensity of absorption.

Generally the absorption spectrum of anthraquinone derivatives gives five characteristic π - π^* bands, four in the UV region and a broad band in the visible region. The appearance of this broad π - π^* arises due to the intramolecular charge transfer between the electron releasing substituted and the carbonyl group [9]. 1, 5 DAAQ, a bifunctional molecule, contains both hydrogen bond acceptor (C = O) and hydrogen bond donar (NH₂). The absorption bands of substituted anthraquinone when compared with the unsubstituted anthraquinone, directly shift to shorter or longer wavelengths according to the substituting group. When electron donating group is substituted group in anthraquinone, there will be absorption longer than 350 nm [10]. In the present case the band observed in the visible region is due to the intramolecular charge transfer between the amino group (NH₂) and the carbonyl group (C = O) in the anthraquinone ring. Also it has the ability to form intermolecular hydrogen bond with polar protic and

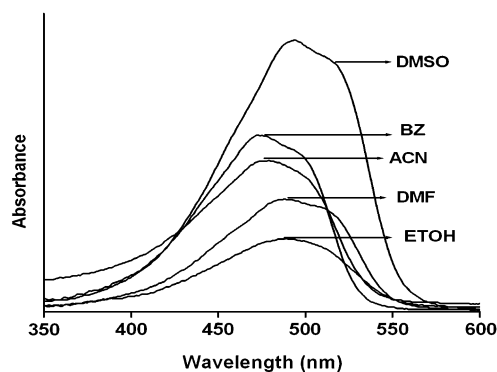


Fig. 2 Absorption spectra of 1, 5-DAAQ in single solvents

aprotic solvents (ETOH, DMF). In the case of polar protic solvent (ethanol) the hydrogen bond is formed between the OH of the ethanol and oxygen of the anthraquinone ring. In this case both inter and intra molecular hydrogen bond play an important role. Because of the intramolecular charge transfer character of the 1,5 DAAQ the charge is displaced from the NH₂ group to the anthraquinone ring. In the case of DMF the bond is formed between oxygen of the DMF and NH of the anthraquinone. This inter-intra molecular hydrogen bond is responsible for the observed red shift in ethanol and DMF.

1-aminoanthraquinone shows a large red shift in polar solvents in compared with 1, 5 DAAQ. This may be due to the intramolecular charge transfer nature which is more effective in single amino substituted anthraquinone than for doubly substituted anthraquinone. The interesting feature is that HOMO will have the symmetric contributions from both substitutions in doubly substituted anthraquinone. This will lead to a situation on quenching of charge transfer nature on having two amino groups opposite to anthraquinone core. Hence on increasing the number of substituents the intra molecular charge transfer character decreases [9].

The fluorescence spectra of 1, 5 DAAQ in different solvents are shown in Fig. 3. These spectra present a broad band at 541.9 nm in BZ, 565 nm in AN, 572.9 nm in DMF, 580 nm in DMSO and 573.9 nm in ETOH. This shows a red shift with respect to nonpolar solvent as in the case of absorption spectra. It is also weakly structured in nonpolar and polar aprotic solvents as in the case of absorption spectra. The anthraquinone nucleus offers a near ideal case for studying ESIPT. 1-hydroxyanthraquinone and 1-aminoanthraquinones are known to form intra molecular hydrogen bond with the quinone oxygen, forming six membered ring. Dual emission has been observed for 1-hydroxyanthraquinone, 1-5 dihydroxy anthraquinone and 1, 8 dihydroxy anthraquinone. Generally in aminoanthraquinones, the strength of the intermolecular hydrogen

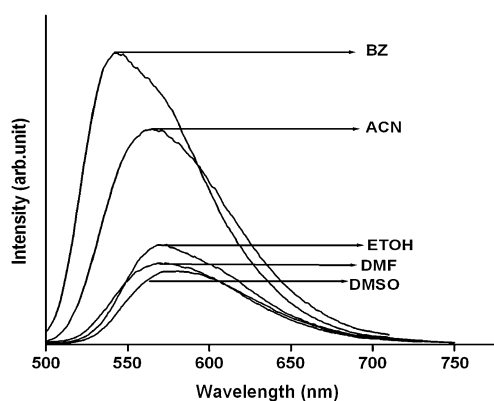


Fig. 3 Fluorescence spectra of 1, 5-DAAQ in single solvents

bond is increased in the excited state by the intramolecular charge transfer nature of the excited state. 1-aminoanthraquinone shows only one fluorescent feature, which has been assigned to the S₁-S₀ emission [11]. 1, 5 DAAQ does not under go an ESIPT reaction. The absence of ESIPT in 1,5 DAAQ may be due to the fact that NH protons have only weakly hydrogen bond donating character as compared to OH protons [12]. Dual fluorescence can result from a number of events. The most likely process giving rise to this phenomenon is the excited states capable of either undergoing proton transfer reactions or evolving into twisted internal charge transfer states [11]. There is no dual fluorescence in the present case; this is due to absence of the excited state intramolecular proton transfer [9].

Solvatochromic shifts in single solvents

The molar transition energy (E_T), of the 1, 5 DAAQ, was determined by using the following equation

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

Figure 4 shows the plot between E_T and $F(D) = \frac{2(\epsilon+1)}{(2\epsilon+1)}$ in the ground and excited state. λ_{max} is the wavelength of absorption and fluorescence maximum of 1, 5 DAAQ. This plot shows the nonlinearity of the transition energy with the dielectric constant. This behavior is due to specific solute-solvent interaction. When we increase the solvent polarity transition energy decreases with respect to non polar solvent BZ indicating the existence of solvatochromism.

Estimation of dipole moment ratio

In order to estimate the ground and excited state dipole moments of the molecules, solvent polarity $f(\epsilon, n)$ and $f(\epsilon, n) + g(n)$ parameters are determined and presented in Table 1. Spectral shifts of $\bar{\nu}_a - \bar{\nu}_f$ and $\bar{\nu}_a + \bar{\nu}_f$ in cm⁻¹ of all the five solvents versus the solvent polarity function $f(\epsilon, n)$ and $f(\epsilon, n) + g(n)$ were shown in Figs. 5 and 6. The dipole moment ratio of ground and excited states are determined based on the following equations

$$\bar{\nu}_a - \bar{\nu}_f = m_1 f(\epsilon, n) + \text{constant} \quad (2)$$

$$\bar{\nu}_a + \bar{\nu}_f = -m_2 [f(\epsilon, n) + g(n)] + \text{constant} \quad (3)$$

Where

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

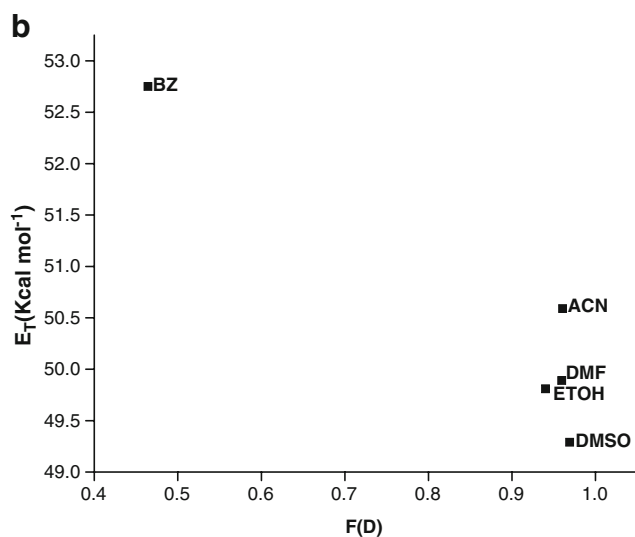
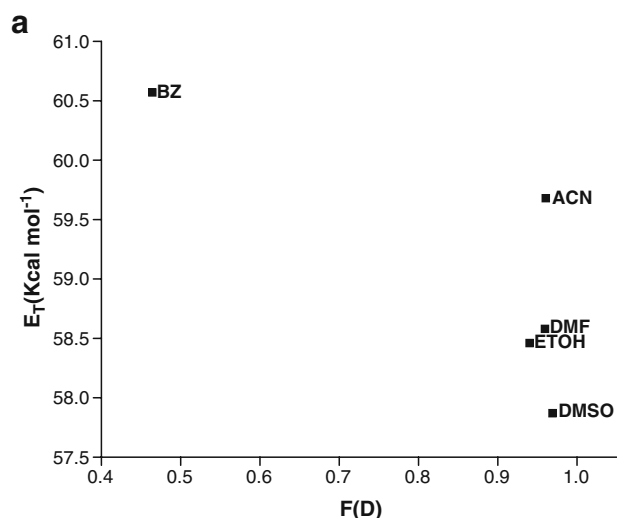


Fig. 4 Plot of E_T vs. $F(D)$ for 1, 5-DAAQ. **a** Absorption **b** Fluorescence

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

Table 1 Photo physical parameters of 1,5 DAAQ obtained from optical absorption and fluorescence measurements

Solvents	F(D)	$E_T(\text{kcal mol}^{-1})$		$f(\epsilon, n)$	$f(\epsilon, n) + g(n)$	$\bar{\nu}_a - \bar{\nu}_f (\text{cm}^{-1})$	$\bar{\nu}_a + \bar{\nu}_f (\text{cm}^{-1})$
		a	b				
BZ	0.4642	60.57	52.75	0.02	0.24	2734.22	39638.66
ACN	0.9605	59.68	50.59	0.86	1.33	3146.33	38573.72
DMF	0.9596	58.58	49.89	0.84	1.42	3009.29	37944.72
DMSO	0.969	57.87	49.21	0.84	1.48	3001.54	37484.28
ETOH	0.9402	58.46	49.81	0.81	1.30	3027.38	37872.40

a: absorption
b: Fluorescence

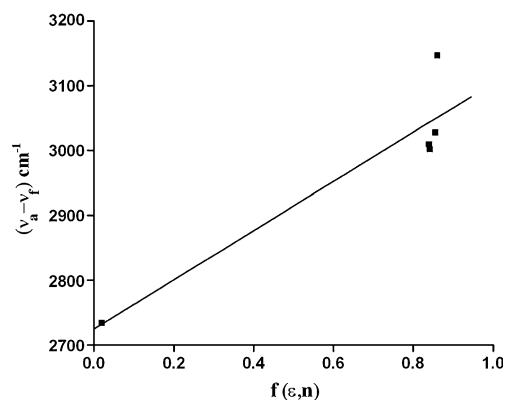


Fig. 5 Plot of $(\bar{\nu}_a - \bar{\nu}_f)$ vs. the solvent polarity function $f(\epsilon, n)$

And

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

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

Here $f(\epsilon, n)$ and $f(\epsilon, n) + g(n)$ is the solvent polarity parameter. μ_e and μ_g are the ground and excited dipole moment, c is the velocity of light, and 'a' is the Onsager cavity radius. The slope m_1 and m_2 obtained from the Figs. 5 and 6. i.e. m_1 is from the plot between $f(\epsilon, n)$ and $\bar{\nu}_a - \bar{\nu}_f (\text{cm}^{-1})$ and m_2 is between $f(\epsilon, n) + g(n)$ and $\bar{\nu}_a + \bar{\nu}_f (\text{cm}^{-1})$. From the slope values the ratio of ground and excited state dipole moments of 1, 5 DAAQ was calculated by using the equation

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

DAAQ is a symmetrical molecule. So the dipole moment of this molecule is zero or at least very small [12]. The ratio of the dipole moment in ground and excited state for the present case was found to be 1.67.

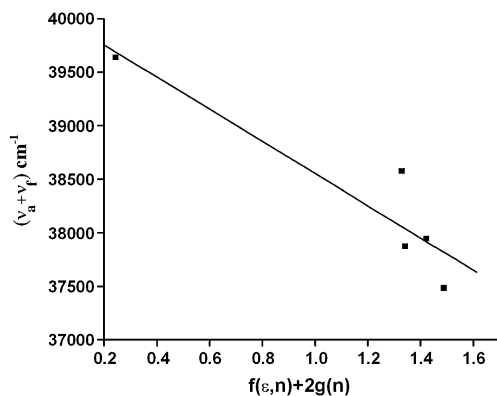


Fig. 6 Plot of $(\bar{\nu}_a + \bar{\nu}_f)$ vs. the solvent polarity function $f(\epsilon, n) + 2g(n)$

Solvatochromic studies in binary liquid mixtures

The preferential solvation method was used to study about the solvent effects in binary mixtures. Preferential solvation arises whenever the bulk mole fraction composition is different from the solvation micro sphere [13]. 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 cybotatic region of the dye.

The local mole fraction (X_2^L) and (X_1^L) were calculated by using the formula

$$X_2^L = \frac{\bar{\nu}_{12} - \bar{\nu}_1}{\bar{\nu}_2 - \bar{\nu}_1} = 1 - X_1^L \tag{9}$$

where $\bar{\nu}_1$, $\bar{\nu}_2$ are the absorption and emission maximum expressed in wave numbers of solvent 1 and solvent 2. $\bar{\nu}_{12}$ 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 [10].

Preferential solvation studies in binary liquid mixtures

1 AN + DMF

Figure 7 shows the plot of $\bar{\nu}_{12}$ versus the bulk mole fraction of DMF(X_2). The Fig. (7a) presents the behaviour of $\bar{\nu}_{12}$ for absorption with respect to DMF concentration. The $\bar{\nu}_{12}$ value decreases as the DMF concentration increases. At higher concentrations DMF may form a dimer through self association. In that environment DMF becomes a non polar entity with negligible dipole moment. The observations of Table 2 show that the local mole fraction of DMF is greater than the bulk mole fraction, then the δ_{s2} value is positive and $K_{12} < 1$. This indicates that the solute molecule is preferentially solvated by solvent 1 (AN) rather than solvent 2 (DMF). This could be due to the cluster formation of solvent 2 (DMF) and more monomeric species of AN (polar environment). In the excited state the solute molecule is preferentially solvated by solvent 1 (AN) upto

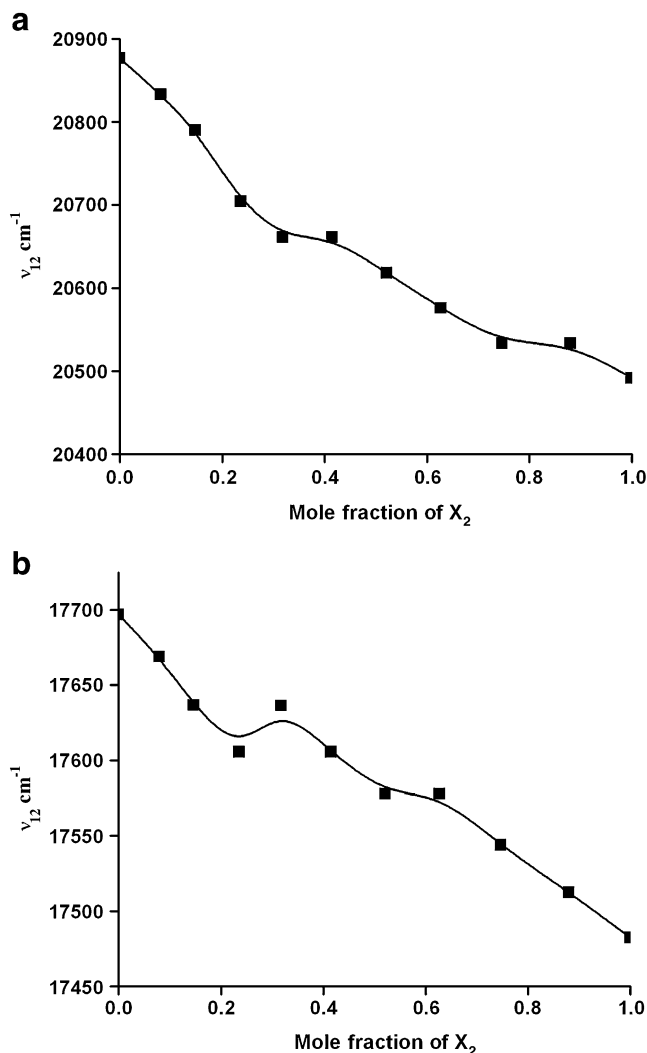


Fig. 7 Plot of ν_{12} vs. mole fraction of DMF(X_2) in AN + DMF mixture for 1,5-DAAQ **a** absorption **b** emission

Table 2 Preferential solvation data

	AN + DMF(X ₂)	X ₂ ^L		δ _{s2}		K ₁₂	
		a	b	a	b	a	b
0							
0.08	0.11	0.11	0.032	0.032	0.684	0.684	
0.14	0.22	0.24	0.078	0.096	0.591	0.535	
0.23	0.44	0.36	0.213	0.131	0.378	0.532	
0.31	0.56	0.24	0.242	-0.074	0.365	1.450	
0.41	0.56	0.36	0.145	-0.048	0.556	1.225	
0.52	0.67	0.48	0.149	-0.033	0.534	1.141	
0.62	0.78	0.48	0.153	-0.139	0.742	1.765	
0.74	0.89	0.62	0.143	-0.119	0.362	1.754	
0.87	0.94	0.75	0.065	-0.124	0.422	2.366	
1							
	AN + DMSO(X ₂)						
0							
0.07	0.34	0.62	0.261	0.546	0.165	0.051	
0.16	0.40	0.69	0.241	0.527	0.288	0.249	
0.26	0.54	0.87	0.277	0.607	0.304	0.052	
0.34	0.67	0.75	0.328	0.410	0.255	0.170	
0.43	0.67	0.81	0.234	0.378	0.378	0.175	
0.54	0.73	0.69	0.195	0.149	0.421	0.528	
0.64	0.93	0.87	0.293	0.232	0.123	0.257	
0.76	0.87	0.87	0.106	0.114	0.481	0.448	
0.88	0.80	0.92	-0.083	0.044	1.929	0.571	
1							
	AN + ETOH(X ₂)						
0							
0.15	0.10	0.33	-0.056	0.179	1.519	0.336	
0.29	0.10	0.55	-0.189	0.266	3.077	0.276	
0.40	0.10	0.55	-0.304	0.151	4.869	0.437	
0.51	0.10	0.67	-0.416	0.153	6.985	0.386	
0.61	0.30	0.55	-0.309	-0.055	2.504	0.868	
0.70	0.30	0.67	-0.402	-0.034	3.545	0.757	
0.78	0.50	0.67	-0.283	-0.116	2.156	1.074	
0.86	0.60	0.50	-0.255	-0.355	2.375	3.554	
0.93	0.60	0.88	-0.328	-0.047	5.461	1.077	
1							
	BZ + ETOH(X ₂)						
0							
0.15	0.53	0.97	0.379	0.753	0.161	0.018	
0.29	0.65	0.97	0.364	0.621	0.216	0.039	
0.40	0.65	0.97	0.248	0.563	0.360	0.021	
0.51	0.65	0.96	0.136	0.424	0.567	0.064	
0.61	0.88	0.96	0.272	0.356	0.204	0.049	
0.70	0.88	0.94	0.179	0.263	0.310	0.075	
0.78	0.71	0.96	-0.075	0.182	1.500	0.113	
0.86	0.71	0.91	-0.147	0.112	2.488	0.172	
0.93	0.77	0.91	-0.856	0.039	4.159	0.391	
1							

a: absorption

b: Fluorescence

the DMF concentration $X_2=0.23$. When we increase the DMF concentration above 0.23, the solute is solvated by solvent 2(DMF). This was confirmed by negative δ_{s2} values and preferential solvation constant K_{12} which is greater than one. This may be due to strong solvent–solvent interaction over solute–solvent interaction. Some times the \bar{v}_{12} values of binary mixtures are higher than the pure solvents. The combined action of the two solvents in the mixture is different from individual components. This is called synergistic effect. In the present case \bar{v}_{12} values are in intermediate between the \bar{v}_1 and \bar{v}_2 values, so there is no synergism is observed here.

2 AN + DMSO

The plot between wave number \bar{v}_{12} against the mole fraction of DMSO in AN + DMSO mixture in the ground and excited states is shown in Fig. 8. Table 2 shows that the

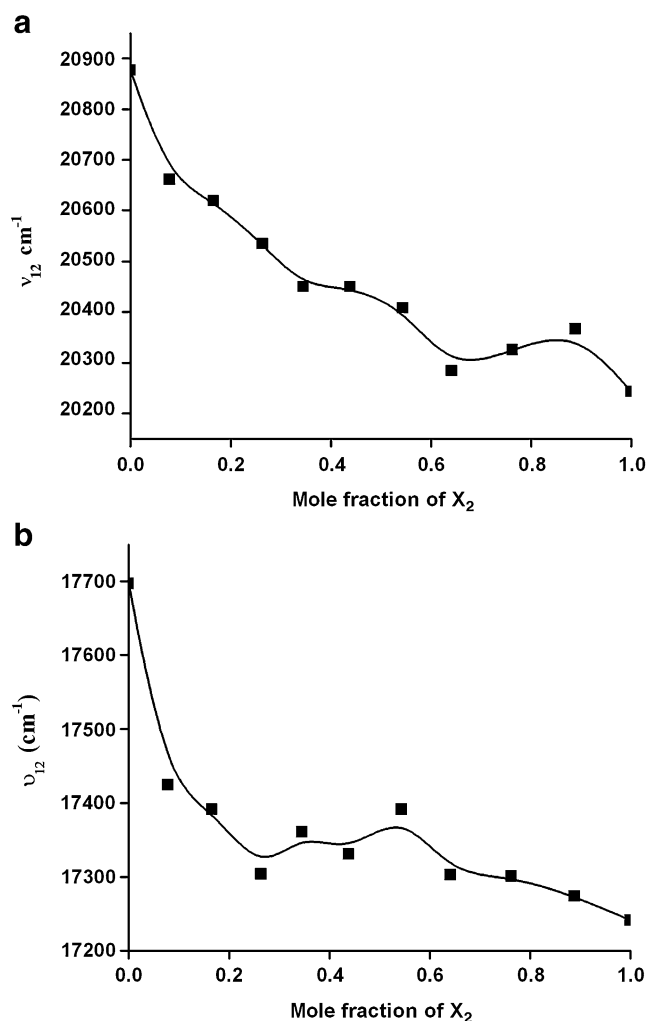


Fig. 8 Plot of ν_{12} vs. mole fraction of DMSO(X_2) in AN + DMSO mixture for 1, 5-DAAQ **a** absorption **b** emission

local mole fraction of DMSO is greater than the bulk mole fraction. Preferential solvation arises whenever the proportion of molecules of any given solvent component within the probe solvational micro sphere is not equal to its bulk mole fraction [13]. In the present case also the solute is preferentially solvated by solvent 1(AN) due to the self association of DMSO [14]. This was confirmed by positive δ_{s2} and the solvation constant K_{12} which is smaller than one in both ground and excited states. The Fig. 8 shows that there is a decrease in \bar{v}_{12} value with increasing concentration of the DMSO. In the present case \bar{v}_{12} values are in intermediate between the \bar{v}_1 and \bar{v}_2 values, so there is no synergism observed here.

3 AN + ETOH

Figure 9 shows the plots between the wave number and the mole fraction of ETOH (X_2) of the AN + ETOH

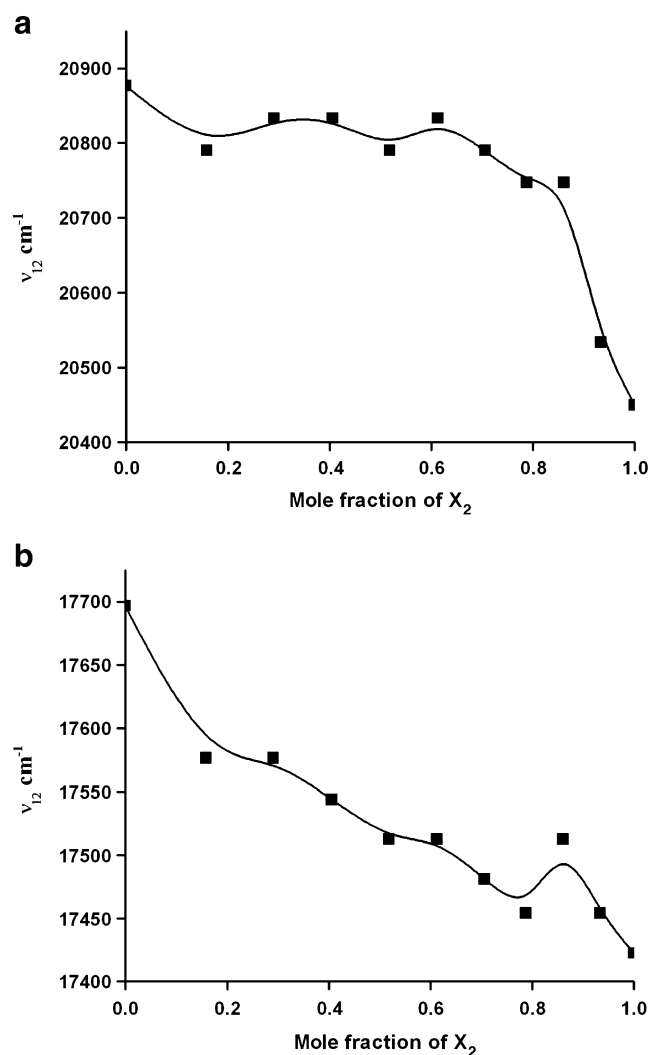


Fig. 9 Plot of ν_{12} vs. mole fraction of ETOH(X_2) in AN + ETOH mixture for 1, 5-DAAQ **a** absorption **b** emission

mixture. In the ground state the $\bar{\nu}_{12}$ value of the AN + ETOH mixture decreases as the ethanol concentration increases. Table 2 shows the preferential solvation data for this AN + ETOH mixture. The difference in the bulk mole fraction and local mole fraction shows that the solute is preferentially solvated by ethanol. This was confirmed by K_{12} values which is greater than one and negative δ_{s2} values. In the excited state, the $\bar{\nu}_{12}$ value of the AN + ETOH mixture decreases as the ethanol concentration increases. Table 2 shows the preferential solvation data for this AN + ETOH mixture. In the excited state the solute molecule is preferentially solvated by solvent 1 (AN) upto the ethanol concentration $X_2=0.51$. Here the local mole fraction of ethanol is greater than the bulk mole fraction. In this situation alcohol molecules tend to self associate strongly and they have less preference towards the solvation [15]. This was confirmed by K_{12} values which is less than one and positive δ_{s2} values. When X_2 increases above 0.51, the solute is solvated by solvent 2(ETOH). Here

the self association of ethanol is dominated by the dimerization of the acetonitrile and leaves ethanol as monomer which leads to a situation that the local mole fraction of ETOH is less than the bulk mole fraction. Hence the solute is preferentially solvated by solvent 2 (ETOH). This was confirmed by K_{12} values which is greater than one and negative δ_{s2} values. In the present case $\bar{\nu}_{12}$ values are in intermediate between the $\bar{\nu}_1$ and $\bar{\nu}_2$ values, so there is no synergism observed here.

4 BZ + ETOH

Figure 10 shows the plot of wave number and the mole fraction of ETOH. In the ground state the $\bar{\nu}_{12}$ value of the BZ + ETOH mixture decreases as the concentration of ETOH increases. Table 2 shows that the local mole fraction of ETOH is greater than the bulk mole fraction upto $X_2=0.70$. In these cases the solute is preferentially solvated by benzene. Since alcohol molecules tend to self associate strongly at its higher local concentration, they have less preference towards the solvation. This was confirmed by K_{12} values which is less than 1 and positive δ_{s2} values. When X_2 increases above 0.70, the solute is solvated by solvent 2(ETOH). In these cases the local mole fraction of ETOH is less than the bulk mole fraction. Hence the formation of self associated ethanol is less and behaves as monomer (i.e highly polar than benzene). Hence the solute is preferably solvated by ethanol. This was confirmed by K_{12} values which is greater than 1 and negative δ_{s2} values. In the excited state, the solute is preferably solvated by solvent 1(BZ) due to the self association of ethanol (the local molefraction is higher than the bulk mole fraction). Which is confirmed by positive δ_{s2} values and K_{12} value which is smaller than one. In the present case $\bar{\nu}_{12}$ values are in intermediate between the $\bar{\nu}_1$ and $\bar{\nu}_2$ values, so there is no synergism observed here.

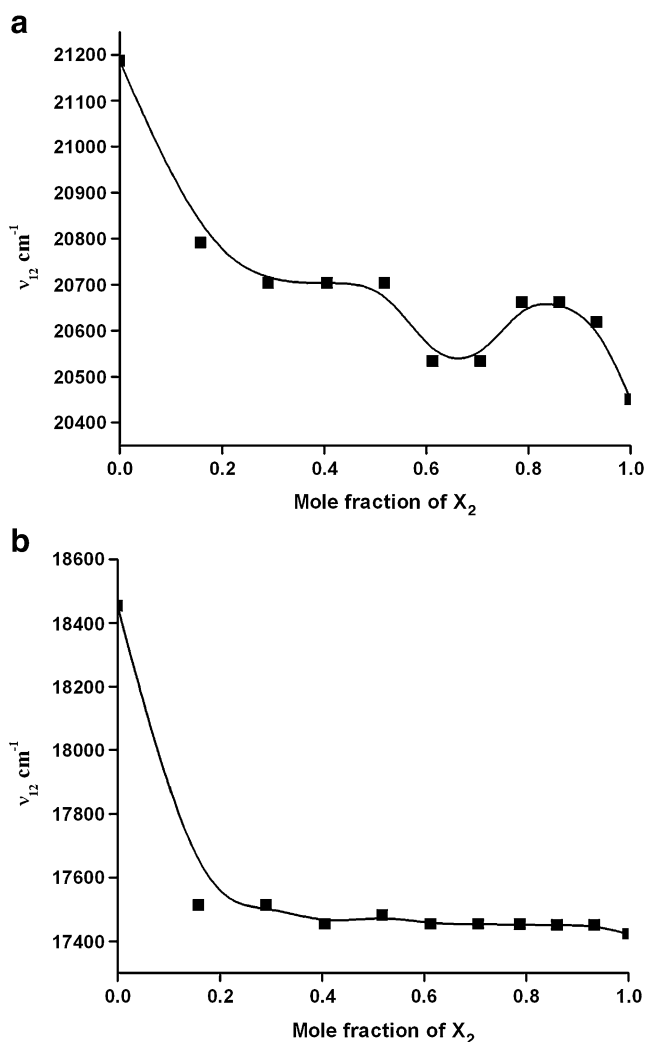


Fig. 10 Plot of ν_{12} vs. mole fraction of ETOH(X_2) in BZ + ETOH mixture for 1, 5-DAAQ **a** absorption **b** emission

Conclusion

In this work the spectral behaviour of 1,5 DAAQ in single solvents and photo physical properties of in binary mixtures were studied by using optical absorption and fluorescence spectroscopy techniques. The dipole moment ratio in excited and ground states was calculated by using solvatochromic method and it was found to be greater than one. The preferential solvation parameter local mole fraction (X_2^L), solvation index (δ_{s2}) and preferential solvation constant K_{12} were determined in all the binary mixtures which were taken for the present investigation. The data were made use of in explaining the solute-solvent and solvent-solvent interactions. In the present analysis all the binary mixtures do not show the synergistic effect.

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