Preferential Solvation of a Dipolar Solute in Mixed Binary Solvent. A Study by UV-Visible Spectroscopy

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CERTIFICATE

This is to certify that the dissertation entitled "**Preferential Solvation of a Dipolar Solute in Mixed Binary Solvent. A Study by UV-Visible Spectroscopy**" being submitted by **Saroj Kumar Mahanta** to the Department Of Chemistry, National Instuitute Of Technology, Rourkela-769008, for the award of the degree of Master Of Science in Chemistry, is a record of bonafide research carried out by him under my supervision and guidance. The dissertation report has reached the standard fulfilling the requirements of the regulations relating to the nature of the degree.

I further certify that to the best of my knowledge Mr. Mahanta bears a good moral character.

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Preferential Solvation of a Dipolar Solute in Mixed Binary Solvent. A Study by UV-Visible Spectroscopy

1. Introduction

1.1 Solute-Solvent Interactions

Solutions are homogeneous liquid phases consisting of solute and solvent in variable ratios. In solution, the solute is dispersed uniformly throughout the solvent. Normally, the component which is in excess is called the solvent and the minor component(s) is the solute. Solvent may be a pure liquid or it may be a mixture of two or more liquids.

Solute/solvent mixtures A + B, that obey Raoult's law over the entire composition range from pure A to pure B are called ideal solutions. According to Raoult, the ratio of the partial pressure of component $A(p_A)$ to its vapour pressure as a pure liquid (p^*_A) is equal to the mole fraction of $A(X_A)$ in the liquid mixture, i.e. $p_A / p^*_A = X_A$. Many mixtures obey Raoult's law very well, particularly when the components have a similar molecular structure (e.g. benzene and toluene).

The intermolecular interaction between the solvent and the solute molecules determines the mutual solubility of the components in a mixture rather than the rule ''like dissolves like''. A compound A dissolves in a solvent B only when the intermolecular forces of attraction K_{AA} and K_{BB} for the pure compounds can be overcome by the forces K_{AB} in solution. The sum of the interaction forces between the molecules of solvent and solute can be related to the polarity of A and B. A qualitative prediction of solubility with respect to polarity is tabulated in table 1.

Table 1. Solubility and polarity

Solute A	Solvent B	Interaction			Solubility of A in B
		A----A	B----B	A----B	
Nonpolar	nonpolar	weak	weak	weak	Highly soluble
Nonpolar	polar	weak	strong	weak	Sparingly soluble
Polar	nonpolar	strong	weak	weak	Sparingly soluble
Polar	polar	strong	strong	strong	Highly soluble

Intermolecular forces also called van der Waals forces are usually classified into two distinct categories. The first category comprises non-specific interactions such as induction and dispersion forces. The second group consists of specific interactions such as hydrogen-bonding forces, and charge-transfer or electron-pair donor–acceptor forces. On the basis of the types of forces that may be dominant in solute-solvent interaction, solvents may be divided into three families.

A. Protic solvents:

Solvents containing proton-donor groups are designated as protic solvents or HBD solvents. Solvents containing proton-acceptor groups are called HBA solvents. The relative permittivity (dielectric constant) of these type of solvents is large (usually >> 15). The abbreviations HBD (hydrogen-bond donor) and HBA (hydrogen-bond acceptor) refer to donation and acceptance of the proton, and not to the electron pair involved in hydrogen bonding. Typical protic or HBD solvents are water, ammonia, alcohols, carboxylic acids and primary amides. Typical HBA solvents are amines, ethers, ketones, and sulfoxides. Solvents acting both as HBD and as HBA simultaneously are termed as amphiprotic solvents e.g. water, alcohols, amides. During solute-solvent interaction, the solute acts as a HBA-base and the solvent as a HBD-acid in type-A hydrogen bonding, and; in type-B hydrogen bonding, the roles are reversed. Hydrogen bonding is responsible for the strong, temperature-dependent self- and hetero-association of amphiprotic solvents (e.g. water, alcohols, amides). The molecular structure of binary HBD/HBA solvent mixtures is largely determined by intermolecular hydrogen bonding between the two components, which usually leads to pronounced deviations from ideal solution behaviour. Hydrogen bonding plays a particularly important role in the interactions between anions and HBD solvents. Hence, HBD solvents are good anion solvators.

B. Dipolar aprotic solvents:

Dipolar aprotic solvents have polar groups, so their relative permittivity is moderately large (≥15) however they have no protons to be involved in hydrogen bonding. Neverthless, their lone pairs can act as hydrogen bond acceptors in any hydrogen bond formation between solvent and solute and they can take part in donor-acceptor (charge transfer) complex formation. Owing to the electrostatic dipole-dipole attraction, these solvents have a remarkably ordered structure. In this class we find ketones, esters, dialkylamides, nitriles and sulfoxides.

C. Apolar aprotic solvents:

 Apolar aprotic solvents show small relative permitivities (<15). They are unable to form hydrogen bonds or be involved in be involved in donor-acceptor (charge transfer) complex formation. There exists only weak dispersion forces between the individual solvent molecules. For this reason the liquid show very little order, if any. In this class we find ethers, halogenated hydrocarbons and hydrocarbons.

1.2 Solvation

The term solvation refers to the surrounding of each dissolved molecule or ion by a shell of more or less tightly bound solvent molecules. This solvent shell is the result of intermolecular forces between solute and solvent. During the dissolution process, when a relatively small amount of solute dissolves in relatively large amount of solvent to form a homogeneous phase, a variety of intermolecular forces play a role such as solvent-solvent interaction, solute-solvent interaction and solute-solute interaction. The forces holding together the solute molecules gradually disappear during the dissolving process and to same extend an analogous process takes place in a portion of the solvent. These disappearing intermolecular forces are to be replaced by the new intermolecular forces that will be operative between solute and solvent molecules. The solute molecules will disturb the structure of the solvent when they enter into solution, and they create some more or less ordered solvation shell around themselves.

For the dissolving process to be spontaneous, the lowering of the free energy resulting from the solvation must over-power the free energy increase due to the annihilation of the interactions that existed between the solute molecules and between the solvent molecules. A solvation shell is formed from the solvent molecules around the solute molecules, which is sometimes referred as "cybotactic" region. The degree of orientation of the solvent molecule is reduced as the distance away from the solute molecule increases. On the basis one may divide the cybotactic region into two parts. In the first part i.e. the primary solvation shell the orientation of the solvent molecules is stronger. In the second part the solvent molecules are farther away from the solute molecule and therefore the degree of their orientation is smaller. The rearrangement associated with solvation is quite dramatic and even the macroscopic properties of the solvent will change for example the density of the liquid often increases.

1.3 Preferential Solvation

The description of solvation of ions and molecules in solvent mixtures is even more complicated. Besides the interaction between solvent and solute, the interaction between unlike solvent molecules plays an important supplementary role. This leads to large deviations from the ideal behaviour expected from Raoult's law of vapour pressure depression of binary mixtures.

From investigations of the solvation of ions and dipolar molecules in binary solvent mixtures it has been found that the ratio of the solvent components in the solvent shell can be different from that in the bulk solution. As expected, the solute is surrounded preferably by the component of the mixture which leads to the more negative Gibbs energy of solvation, ΔG^0_{solv}. The observation that the solvent shell has a composition other than the macroscopic ratio is termed selective or preferential solvation.[1] These terms are generally used to describe the molecular-microscopic local solute-induced inhomogeneity in a multicomponent solvent mixture. They include both (i) nonspecific solute/solvent association caused by dielectric enrichment in the solvent shell of solute ions or dipolar solute molecules, and (ii) specific solute/solvent association such as hydrogen-bonding or EPD(electron pair donor) /EPA (electron pair acceptor) interactions.

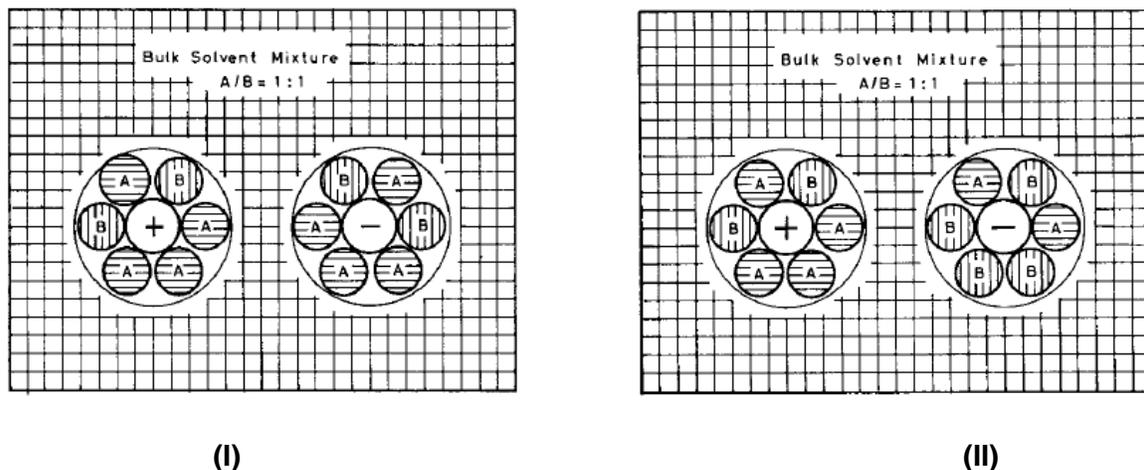(I)   (II)

Figure 1: Schematic model for the selective solvation of ions by one component of a binary 1:1 mixture of the solvents A and B (I) Homoselective solvation: both ions are preferentially solvated by the same solvent A. (II) heteroselective solvation: the cation is preferentially solvated by A and the anion by B.

When in a mixture of two solvents, both ions of a binary salt are solvated preferably by the same solvent, the term applied is homoselective solvation. Similarly, the preferred solvation of the cation by one, and the anion by the other solvent, is termed heteroselective solvation (Figure 1).

Different methods for the study of preferential solvation have been developed e.g. conductance and Hittorf transference measurements, NMR measurements (especially the effect of solvent composition on the chemical shift of a nucleus in the solute), and optical spectra measurements like IR absorption shifts or UV/Vis absorption shifts of solvatochromic dyes in binary solvent mixtures.
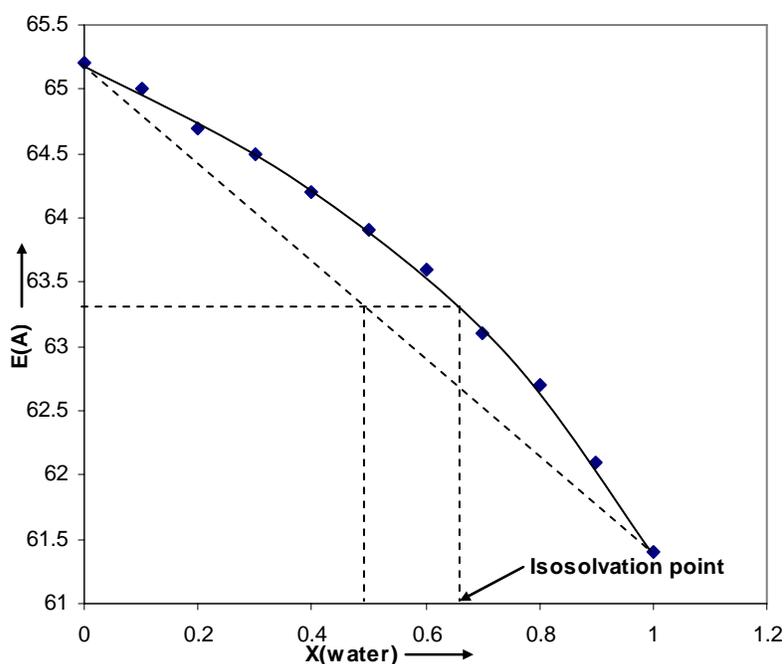

Figure 2: Plots of E(A), the energy of maximum absorption of the ketocyanine dye as a function of solvent composition in mixed binary solvent Water+methanol[2]. Straight line: ideal case without preferential solvation, primary solvation shell of the same composition as the bulk solvent mixture. Curved line: real case with preferential solvation of the dye by methanol and isosolvation point at X (water) = 0.66 or X(methanol) = 0.34, that is, the mole fraction of the bulk solvent for which the solvated dye absorption energy is the average of the energies obtained in the pure solvents

A convenient measure of the degree of selective solvation is the bulk solvent composition at which both solvents of a binary mixture participate equally in the contact solvation shell. This is the solvent composition at which the energy maximum lie midway between the values for the two pure solvents. This composition has been called the equisolvation or iso-solvation point (usually expressed in mole fractions of one solvent). This point describes the bulk solvent composition at which both solvents participate equally in the solvation shell (Figure 2).

1.4 Solvent effects on the absorption spectra of organic compounds

When absorption spectra are measured in solvents of different polarity, it is found that the positions, intensities, and shapes of the absorption bands are usually modified by these solvents. These changes are a result of physical intermolecular solute–solvent interaction forces (such as ion-dipole, dipole-dipole, dipole-induced dipole, hydrogen bonding, etc.), which above all tend to alter the energy difference between ground and excited state of the absorbing species containing the chromophore. The medium influence on absorption spectra can be considered by comparing the spectral change observed by changing the nature of the solvent. Thus, solvent effects on absorption spectra can be used to provide information about solute-solvent interactions.

The pronounced change in position (and sometimes intensity) of a UV/Vis absorption band that accompanies a change in the polarity of the medium is generally described as solvatochromism. A hypsochromic (or blue) shift with increasing solvent polarity is usually called negative solvatochromism. The corresponding bathochromic (or red) shift is termed positive solvatochromism.[3] The solvent effect on spectra, resulting from electronic transitions, is primarily dependent on the chromophore and the nature of the transition ($\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and charge-transfer absorption).

The long-wavelength absorption band undergoes a bathochromic shift as the solvent polarity increases (positive solvatochromism), if the excited state is more dipolar than the ground state ($\mu_g < \mu_e$). If the ground state is more dipolar than the excited state ($\mu_g > \mu_e$), the opposite behaviour, a hypsochromic shift, occurs (negative solvatochromism). The extent and direction of solvatochromism depends on whether the zwitterionic mesomeric structure is more important in the ground state or in the excited state.

A qualitative interpretation of solvent shifts is possible by considering (a) the momentary transition dipole moment present during the optical absorption, (b) the difference in

permanent dipole moment between the ground and excited state of the solute, (c) the change in ground-state dipole moment of the solute induced by the solvent, and (d) the Franck–Condon principle. Thus, two limiting cases can be distinguished for intramolecular electronic transitions of dipolar solute in solution.

(1) *Dipolar solute in a nonpolar solvent:* In this case, the forces contributing to solvation are dipole-induced dipole and dispersion forces. If the solute dipole moment increases during the electronic transition, the Franck–Condon excited state is more solvated by dipole-solvent polarization, and a red shift, depending on the solvent refractive index n and the change in solute dipole moment, is expected. The Franck–Condon excited state is less solvated if the solute dipole moment decreases during the electronic transition, and a blue shift, again proportional to the two above mentioned factors, is expected.

(2) *Dipolar solute in a polar solvent:* Since the ground-state solvation results largely from dipole-dipole forces in this case, there is an oriented solvent cage around the dipolar solute molecules, resulting in a net stabilization of their ground state. If the solute dipole moment increases during the electronic transition ($\mu_g < \mu_e$) , the Franck–Condon excited state is formed in a solvent cage of already partly oriented solvent dipoles. The better stabilization of the excited state relative to the ground state with increasing solvent polarity will result in a bathochromic shift (Figure 3). Its magnitude will depend on the extent of the change in the solute dipole moment during the transition, the value of the solvent dipole moment, and the extent of interaction between the solute and solvent molecules.

If the dipole moment of the solute decreases during the electronic transition, the Franck–Condon excited state is formed in a strained solvent cage of oriented dipoles not correctly disposed for its efficient stabilization. Thus, with increasing solvent polarity, the energy of the ground state is lowered more than that of the excited state, and this produces a hypsochromic shift.

For strongly solvatochromic compounds, the observed solventinduced wavelength shifts cannot be explained only in terms of a change in the permanent dipole moment on electronic transition, ($\mu_g \neq \mu_e$). The change in ground-state dipole moment of the solute, induced by the surrounding solvent cage ($\mu_g \rightarrow \mu'_g$) must also be taken into account. The dipolar solute molecules cause an electronic polarization of the surrounding solvent molecules, creating a so-called reaction field which affects the solute's ground-state dipole moment μ_g. That is, the interaction of the dipolar solute molecules with this induced

reaction field, due to the total dipole moment (permanent and induced) of the solvent molecules, may cause an alteration of the electronic structure of the chromophore.
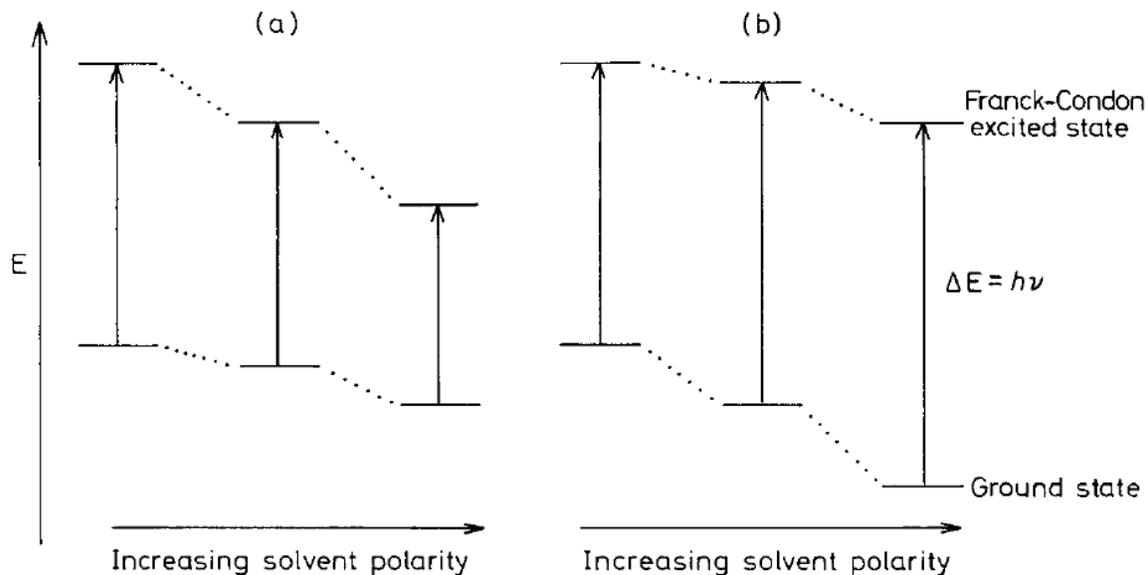

Figure 3: Schematic qualitative representation of solvent effects on the electronic transition energy of dipolar solutes in polar solvents (a) $\mu_g < \mu_e$ i.e. the dipole moment of the Franck-Condon excited state of the solute is larger than those of its ground state; (b) $\mu_g > \mu_e$

2. Experimental

The study of solute-solvent interactions is becoming increasingly important in the investigation of (1) the absorption of drugs and nutrients in biological systems,[4-5] 2) molecular recognition,[6-10] (3) the behavior of pollutants in the natural environment,[11,12] and (4) the analysis and optimization of analytical separations. [13-14] Weak intermolecular forces such as induction, dispersion, and hydrogen bonding play an important role in solute-solvent interactions and partitioning of the solute between two phases. Solute may induce a change in the composition of the solvents in the immediate neighborhood, the solvation sphere, compared with that in the bulk. The phenomenon is known as preferential solvation.[1] Polarity-sensitive indicators are used to probe solute-solvent interactions and provide a valuable approach to characterizing these processes and also the binding environments in micelles,[15] in lipid bilayers[16] and in reversed-phase chromatographic stationary phases.[17] These probes were generally aromatic molecules, mostly of the A-C_6H_4-D type (structures Ia and Ib), where A and D respectively stand for electron-acceptor (such as NO_2) and electron-donor (such as NMe_2) groups.

1a   **1b**
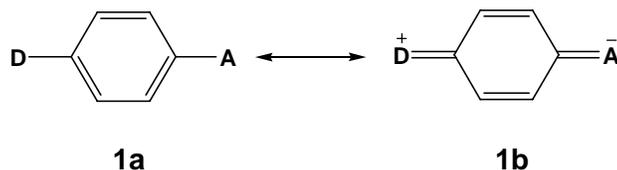
In the case of binary solvation, it has been indicated that besides solute-solvent interaction solvation characteristics depend also on solvent-solvent interaction i.e. solvent nonideality. In the event of ideal solvation, an observed property (P) of an indicator solute is given by the average of the property of the component solvents weighted by the mole fraction of the solvents.[18] Thus,

$$P = \Sigma x_i P_i \tag{1}$$

where x_i denotes the mole fraction of ith solvent. Any deviation from eq 1 would indicate the existence of solute-solvent and solvent-solvent interactions. Electronic spectroscopy provides a suitable method for studying solvation. It has been observed that maximum energy of electronic transition of various solutes depends to a great extent on the local environment around the solute.

In this project work we have studied the solvation of p-nitroaniline (PNA) as a solvatochromic indicator, in different binary solvent mixtures. The longest wavelength absorption band of PNA originates because of an intramolecular charge transfer (ICT) from the N atom of the amino group to the O atom of the nitro group.[19] Absorption band show significant solvent sensitivity. The objective of the present work is to study the role of solute-solvent and solvent-solvent interactions on the solvation characteristics of PNA in mixed binary solvents by monitoring the absorption band of the solute as a function of solvent composition. Three representative solvent mixtures, namely, Ethanol+ Dichloromethane (DCM), Ethanol + Hexane amd Butanol+ Dioxane have been included in the present study. It is known that the maximum transition energy for these compounds depends on the solvent polarity, solvent acidity (HBD ability) and solvent basicity (HBA ability) of the media. We have chosen solvent mixtures where the cosolvents differ with respect to basicity and/or polarity. Thus ethanol+ dichlromethane, ethanol+hexane and butanol+ dioxane binary mixtures have been used to study PS characteristics of the solvent mixture. These solvent mixture will give the idea about interaction of the dipolar solute in (i) polar protic and nonpolar solvent mixture

  (ii) polar protic and dipolar aprotic solvent mixture

  and (iii) hydrogen bond donor and hydrogen bond acceptor solvent mixture

The p-nitroaniline was purified by crystallizing from hot water, resulted shining light-yellow crystals. All the solvents used were dried over calcium chloride and distilled before use. Mixed solvents were prepared by carefully mixing the components by volume. Spectral measurements were taken UV-VIS spectrophotometer. The position of the band maximum (λ_{max}) was determined from optical density data. All the Band maximum in a particular solvent mixture was measured in a number of replicate measurements. The precision of the replicate measurements was ±1 nm. Concentrations of the solute in the solutions were in the range 10^{-4} to 10^{-3} M. The energy of maximum absorption (E) was calculated from the wavelength maximum ((λ_{max}) according to the following formula:

$$E \text{ (kcal/mol)} = 28590/\lambda \text{ (nm)}$$

3. Results and Discussion

Solvatochromism of the intramolecular charge transfer (ICT) band of PNA is continuous, reversible, and independent on the concentration of the solute in the range studied. The bandwidth and shape practically remain unchanged and no isosbestic point is observed in the spectrum. All of these facts indicate that the shift of band maximum is not caused by change of equilibria between different chemical species in solution.

Values of maximum energy absorption in a binary solvent mixture, E(12), at various solvent compositions for PNA have been listed in Tables 2, 3 and 4. For ideal solvation behavior, the value of a solvent-sensitive property of a solute in a mixed solvent is supposed to be given by the mole fraction average of the property in pure component solvents. Thus, the value of maximum energy of absorption in a binary mixture in an ideal case will be given by the following equation:

$$E (12id) = x_1E_1 + x_2E_2$$

E_i and x_i in the above equation represent respectively the maximum energy of absorption and mole fraction of ith solvent. Thus, for ideal solvation in a binary solvent mixture, a plot of the observed E(12) values will be linear in mole fraction over the entire range. Figure 4, 5 and 6 show the plots of E(12) as a function of mole fraction of a component solvent along with the ideal lines. It appears that the experimental data points deviate significantly from the ideal line.

The deviation Δ, from the experimental value ($\Delta = E(12)-E(12id)$) have also been listed in the tables 2, 3 and 4. A significant deviation of E(12) from the ideal value has been observed in all cases. A negative deviation is observed for ethanol+dichloromethane and ethanol+hexane mixture. However for butanol + dioxane mixture a negative deviation is observed up to for certain composition and after that the deviation is positive.

Table 2: Wavelength(nm) and energy of maximum absorption(kcal/mole) of PNA and other related parameters as a function of solvent composition in Ethanol+Dichloromethane (DCM) binary solvent mixture

| Ethanol%	DCM%	X_1	X_2	λ	E(12)	E(12id)	Δ	EtOH (l) %	X_1^L	$\delta_1 = X_1^L - X_1$
100	0	1.00	0.00	373	76.65	76.65	0.00	100	1.00	0.00
90	10	0.91	0.09	373	76.65	77.13	-0.48	100	1.00	0.09
80	20	0.82	0.18	373	76.65	77.61	-0.96	100	1.00	0.18
70	30	0.72	0.28	371	77.06	78.11	-1.05	92	0.92	0.20
60	40	0.63	0.37	370	77.27	78.62	-1.35	88	0.88	0.26
50	50	0.53	0.47	370	77.27	79.14	-1.87	88	0.88	0.35
40	60	0.43	0.57	366	78.11	79.67	-1.55	72	0.72	0.29
30	70	0.32	0.68	365	78.33	80.21	-1.88	68	0.68	0.36
20	80	0.22	0.78	363	78.76	80.77	-2.01	60	0.60	0.38
10	90	0.11	0.89	357	80.08	81.34	-1.25	35	0.35	0.24
0	100	0.00	1.00	349	81.92	81.92	0.00	0	0.00	0.00
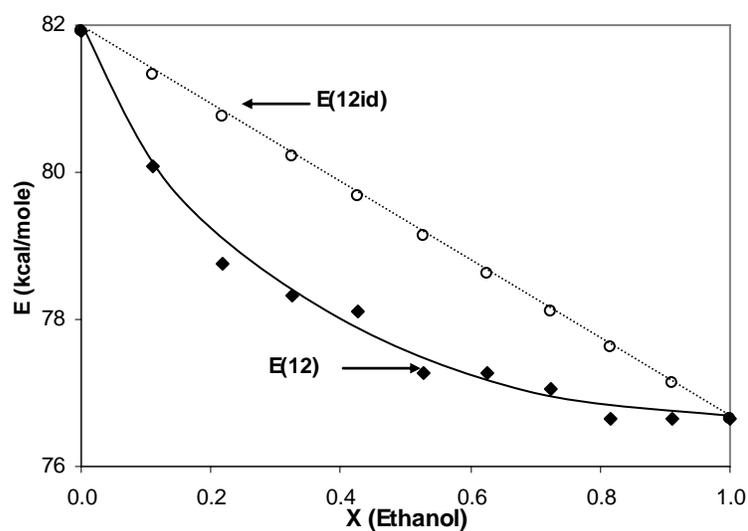
Figure 4: Plot of E, the energy of maximum absorption of the PNA as a function of solvent composition in ethanol+ dichloromethane binary mixture.

Table 3: Wavelength (nm) and energy of maximum absorption(kcal/mole) of PNA and other related parameters as a function of solvent composition in Ethanol+Hexane binary solvent mixture

| Ethanol%	Hexane%	X1	X2	λ	E(12)	E(12id)	Δ	EtOH (I) %	X_1^L	$\delta_1 = x_1^L - x_1$
100	0	1.00	0.00	372	76.85	76.85	0.00	100	1.00	0.00
90	10	0.95	0.05	372	76.85	77.44	-0.59	100	1.00	0.05
80	20	0.90	0.10	371	77.06	78.10	-1.04	98	0.98	0.08
70	30	0.84	0.16	369	77.48	78.86	-1.38	95	0.95	0.11
60	40	0.77	0.23	369	77.48	79.72	-2.24	95	0.95	0.18
50	50	0.69	0.31	367	77.90	80.71	-2.80	92	0.92	0.22
40	60	0.60	0.40	366	78.11	81.86	-3.75	90	0.90	0.30
30	70	0.49	0.51	362	78.98	83.22	-4.25	83	0.83	0.34
20	80	0.36	0.64	359	79.64	84.86	-5.22	78	0.78	0.42
10	90	0.20	0.80	350	81.69	86.85	-5.17	61	0.61	0.41
0	100	0.00	1.00	320	89.34	89.34	0.00	0	0.00	0.00
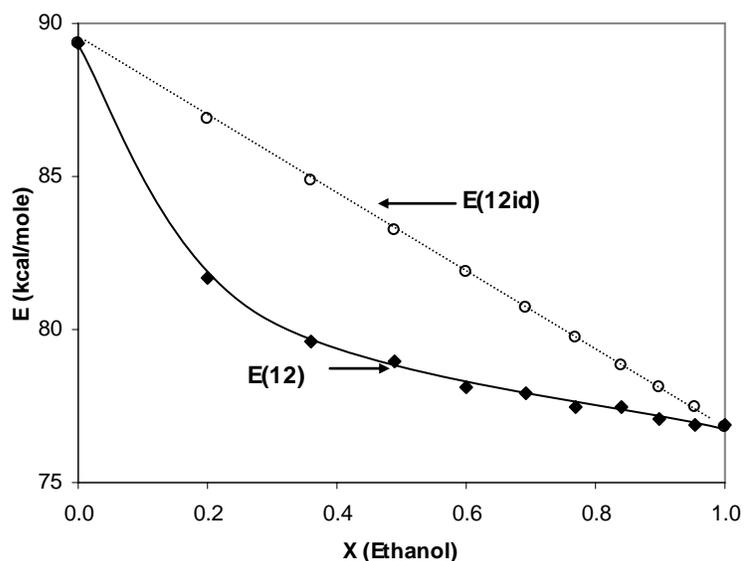
Figure 5: Plot of E, the energy of maximum absorption of the PNA as a function of solvent composition in ethanol+ hexane binary mixture.

Table 4: Wavelength (nm) and energy of maximum absorption(kcal/mole) of PNA and other related parameters as a function of solvent composition in Butanol+Dioxane binary solvent mixture

| Butanol%	Dioxane%	X1	X2	λ	E(12)	E(12id)	Δ	Butanol(l)%	x_1^L	$\delta_1 = x_1^L - x_1$
100	0	1.00	0.00	375	76.24	76.24	0.00	100	1.00	0.00
90	10	0.89	0.11	370	77.27	76.72	0.55	77	0.77	-0.12
80	20	0.79	0.21	368	77.69	77.20	0.49	68	0.68	-0.11
70	30	0.68	0.32	367	77.90	77.66	0.24	63	0.63	-0.05
60	40	0.58	0.42	366	78.11	78.13	-0.01	59	0.59	0.00
50	50	0.48	0.52	365	78.33	78.58	-0.25	54	0.54	0.06
40	60	0.38	0.62	364	78.54	79.03	-0.48	49	0.49	0.11
30	70	0.29	0.71	363	78.76	79.47	-0.71	44	0.44	0.16
20	80	0.19	0.81	361	79.20	79.91	-0.71	35	0.35	0.16
10	90	0.09	0.91	358	79.86	80.34	-0.48	20	0.20	0.11
0	100	0.00	1.00	354	80.76	80.76	0.00	0	0.00	0.00
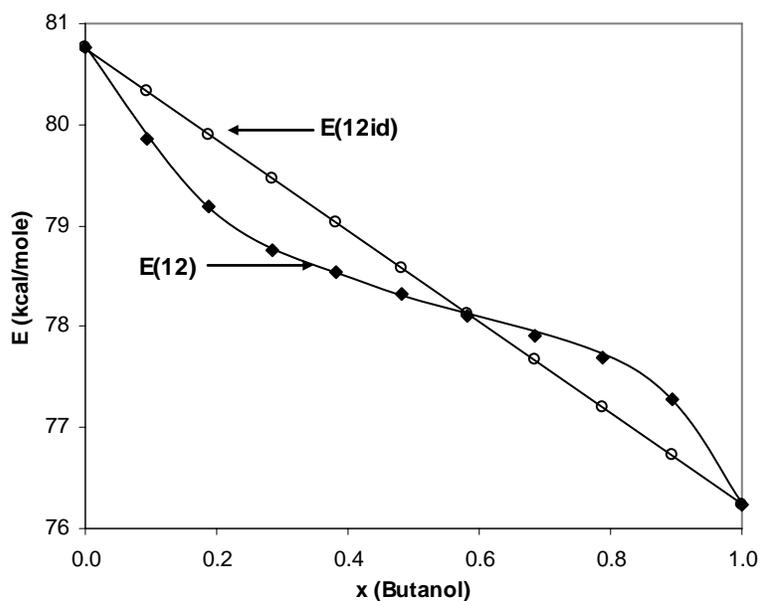
Figure 6: Plot of E, the energy of maximum absorption of the PNA as a function of solvent composition in Butanol+ Dioxane binary mixture.

The deviation from ideality of the observed spectroscopic transition energy has often been explained in terms of preferential solvation (PS) of indicator solute by a component solvent.[20-24] In a mixed solvent system, the indicator solute will be solvated by the component solvent molecules. Because of solute-solvent and solvent-solvent interaction, the composition in the immediate neighborhood of the solute may however differ from the bulk composition. The equilibrium composition in the immediate neighborhood of the solute molecule will be determined by the criterion of minimum Gibbs free energy of the solute solvent system. A positive deviation of the measured spectroscopic transition energy (E) from the ideal line indicates PS of the solute by the solvent component having higher E values and vice versa.

To describe solvation in a solvent mixture, a two phase model of solvation has been used. In this model, solvent molecules are assumed to be partitioned in two regions. The region in the neighborhood of the solute molecule, where the solvent molecules experience the field due to the solute, is the local region or the solvation shell, while solvent molecules outside the local region are said to be in the bulk. The maximum energy of absorption E(12) of the solute depends on the composition of solvent mixture in the solvation shell, E(12) can be related to the local mole fractions of the solvents as follows

$$E(12) = x_1^L E_1 + x_2^L E_2$$

where x_1^L and x_2^L are the local mole fractions of the component solvents 1 and 2 respectively and $x_1^L + x_2^L = 1$. The value of x_i^L is in general different from that of x_i. This is because of differential solute-solvent interaction and solvent-solvent interaction. The excess or deficiency of a solvent component in the cybotactic region over that in the bulk can be calculated as follows.

$$\Delta = E(12) - E(12id)$$

$$E(12) = x_1^L E_1 + x_2^L E_2 \text{ and } E(12id) = x_1 E_1 + x_2 E_2$$

$$\Delta = x_1^L E_1 + x_2^L E_2 - x_1 E_1 - x_2 E_2$$

$$\Delta = (x_1^L - x_1)E_1 + (x_2^L - x_2) E_2$$

$$\Delta = \Sigma (x_i^L - x_i)E_i$$

Where the dimensionless quantity $x_i^L - x_i$ is represented as δ_i, which is a measure of the excess or deficit of the i solvent in the local region compared to that in the bulk. In our

calculation, we have chosen the more polar of the two component solvents as the component 1.

Again as $\Delta = (x_1^L - x_1) E_1 + (x_2^L - x_2) E_2$

Thus $\Delta = \delta_1 (E_1 - E_2) ; \Delta = \delta_2 (E_2 - E_1)$

And $\delta_1 = E(12)\text{-}E(12\text{id})/ (E_1 - E_2) ; \delta_2 = E(12)\text{-}E(12\text{id})/ (E_2 - E_1)$

The local mole fraction of component solvents in a binary solvent mixture (1 + 2) is given by $x_i^L = \delta_i - x_i$

or $x_1^L = E(12)\text{-}E_2 / (E_1 - E_2)$

The values of Δ, δ_1 and x_1^L are tabulated at various solvent compositions.

With increase in solvent polarity, the maximum spectroscopic absorption of PNA experience a red shift (bathochromic shift) indicating a positive solvatochromism. These facts can be explained in terms of the greater stabilization of the charge separated excited state compared to the ground state by greater solvating power of polar solvents through specific (hydrogen bonding) and nonspecific (dipole-dipole) interaction, which reduces the energy difference between ground and excited state intern reducing the maximum energy of absorption (Figure 7).
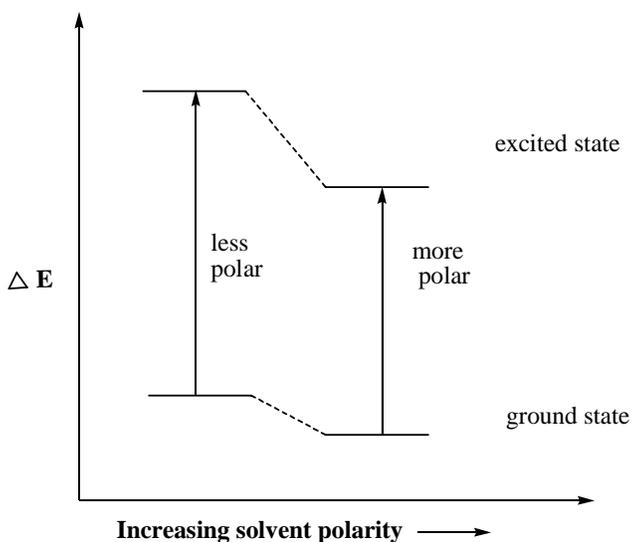

Figure 7: schematic representation of solvent effects on the electronic transition energy of PNA a dipolar solutes; Illustration of positive solvatochromism.

In binary solvent mixture of ethanol+hexane and ethanol+dichloromethane, negative deviation (Figure 4 and 5) indicate that the PNA prefers ethanol over hexane and DCM. The extent of preferential solvation δ_i for both the cases has been calculated (table-2 and 3). These results can be explained in terms of the higher polarity of the ethanol. It is known that ethanol interacts with the molecules of the solutes specifically through hydrogen bonding interaction. Thus the preference of ethanol over hexane and dichloromethane can be rationalized in terms of a difference in the specific interaction (through hydrogen bonding) of the solute molecule with the component solvents (figure 8). The nitro group is solvated by type-A hydrogen bonding interaction i.e. hydrogen bond donation from solvent to solute. Conversely amino group is solvated via type-B hydrogen bonding interaction i.e. hydrogen bond donation from solute to solvent.
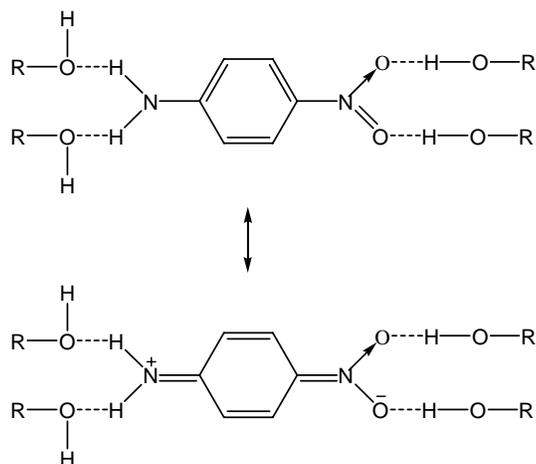

Figure 8: Solvation of PNA in amphiprotic solvents; both type-A (solvent to substrate) and type-B (substrate to solvent) hydrogen bonding leads to lowered electronic transition energy.

In case of butanol + dioxane binary solvent mixture, PNA is preferentially solvated by butanol up to mole fraction of 0.6 (60% of butanol concentration). However with increase in mole fraction of butanol after 0.6 (> 60%) PNA is preferentially solvated by dioxane (Figure 6; table 4). The maximum negative deviation is at mole fraction 0.22 and the maximum positive deviation is at mole fraction 0.86 (Figure 9).
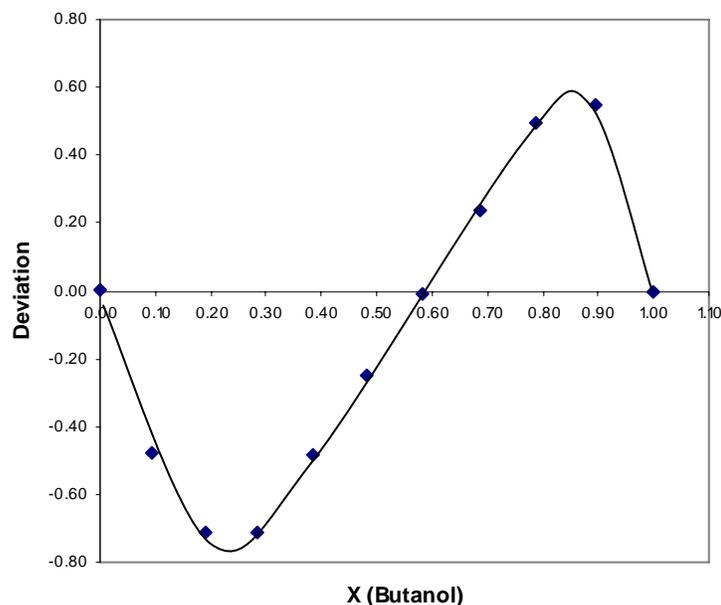
Figure 9: Plot of deviation as a function of solvent composition in butanol+dioxane binary mixture

The existence of both positive and negative deviation is attributed to the specific solute-solvent and solvent-solvent interaction. This phenomenon can be explained by means of a tri-linear solvation plot AB, BC and BD (Figure 10)**.** In this binary mixture, butanol acts as a amphiprotic solvents (both HBD and HBA) while dioxane acts as a HBA solvent. In this figure point 'A' (100% dioxane) corresponds to the dioxane solvated PNA molecule. A slight increase in the concentration of butanol in the bulk medium causes a significant decrease in the energy of absorption, represented by 'AB' line. This decrease is attributed to the increase in the concentration of butanol in the local region due to specific solute-solvent interaction and preferential solvation of nitro group. The HBD ability of butanol stabilizes the charge separated excited states to a larger extend compared to the ground state thus decreasing the energy of absorption.   The maximum deviation point 'B' may be correlated with the solvated molecule where the amino group is preferentially solvated by dioxane a HBA solvent, and nitro group is preferentially solvated by butanol a HBD solvent, thus stabilizing the excited state (Chart B, Figure 11).

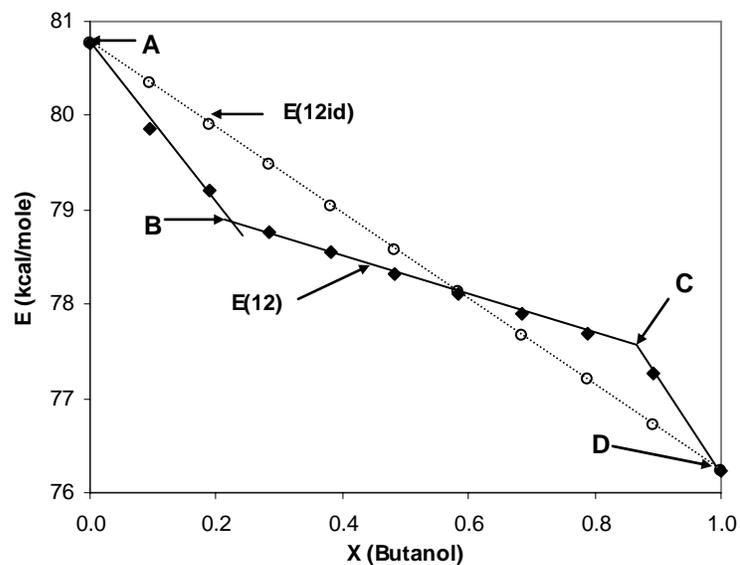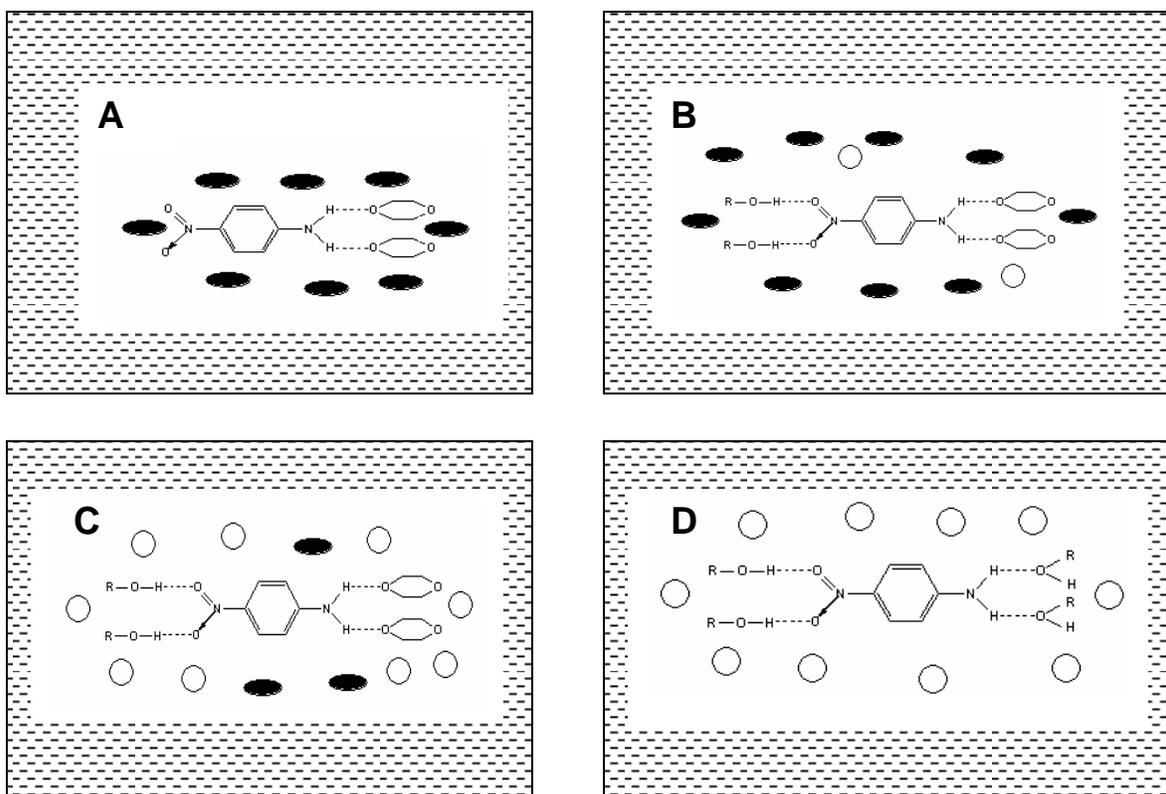**Figure 10:** Tri-linear dependence of maximum energy of absorption as a function of solvent composition.

Figure 11: Schematic diagram of the solvation pattern of PNA in botanol + dioxane binary mixture at various solvent composition A: x (butanol) = 0, B: x (butanol) = 0.22, C: x(butanol) = 0.86, D: x(butanol) = 1.00

The small decrease in the maximum energy of absorption with increase in the composition of butanol 'BC line' may be elucidated through the presence of nonspecific solute-solvent an also specific and non-specific solvent-solvent interaction due to which replacement of dioxane from the solvation shell by butanol is taking place. The maximum positive deviation point 'C' in figure 10 corresponds to the chart C in figure 11 where the most part of the solvation shell is covered by butanol whereas NH_2 is preferentially solvated by dioxane by type A (solvent to solute) hydrogen bonding. With increase in the mole fraction of butanol in the range 0.86 to 1.00 a large decrease in the energy of absorption is observed. This decrease may be due to the replacement of dioxane hydrogen boded to amino group of PNA by butanol. As butanol is having greater HBA ability compared to dioxane, increases the solvation energy and stabilizes the excited state and thus the energy of absorption decreases.

4. Conclusion

Information about the local region around a solute in a binary solvent mixture can be obtained by monitoring the ICT band of p-nitroaniline. The composition of the local region differs from the average composition due to differential solute-solvent and solvent-solvent interaction. The excess or deficit of a solvent component in the local region can be estimated from observed absorption energy maximum. Thus UV-VIS spectroscopic techniques is a better tool to investigate the solute-solvent interaction, preferential solvation and molecular recognition.

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