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Preferential solvation through selective functional group recognition in *p*-nitroaniline

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ABSTRACT

The solvatochromism of the charge transfer band of *p*-nitroaniline (PNA) in different binary solvent mixtures has been investigated from the spectroscopic transition energy (TE). The solvation is proposed to be localized due to the donor and acceptor group and the preference of one solvent above other is due to hydrogen bonding. The preferential solvation has been characterized from the trilinearity of molefraction–TE curves of the binary mixtures. In alcohol–dioxane mixtures, dioxane prefers to solvate amino group while the alcohols preferentially solvate the nitro group through hydrogen bonding. The IR spectral characteristics of PNA in dioxane and butanol also support the preferential solvation model. The thermodynamic parameters have been determined for the solvation process.

1. Introduction

In binary mixture of solvents, solute may induce a change in the composition of the solvents in the immediate neighborhood, i.e. in the solvation sphere, compared to that in the bulk leading to preferential solvation. Solute with a dipole may preferentially be solvated at two different loci with different compositions of the binary mixture. This type of selective solvation has been suggested for the solubilization of chloro-oxalato-tripyridine rhodium(III) complex, which is neither soluble in water nor in pyridine, but is soluble in 1:1 mixture of the two solvents by selective solvation of different units, i.e. the pyridine unit of the complex by pyridine and the oxalate unit by water [1]. Recently Cook et al. have reported the preferential solvation (PS) of a complex (**1**), formed between a strong H-bond accepter and a strong hydrogen bond donor species, by two different solvents with high hydrogen bond donocity (chloroform) and hydrogen bond acceptability (tetrahydrofuran) [2,3]. They explained the variation in the ^{31}P NMR chemical shift of the probe by considering solvation environment of individual functional group by different solvents (Scheme 1). This type of molecular recognition may be occurring in the biological systems for enzymatic reactions and may find wide applications in (1) the absorption of drugs and nutrients in biological systems [4,5], (2) molecular recognition [2,3,6–8], (3) the behavior of pollutants in the natural environment [9,10], and (4) the analysis and optimization of analytical separations [11,12]. Herein, we have made an attempt to investigate the PS through functional group recognition in an intra-molecular system.

PNA, a polarity-sensitive indicator, has been used extensively as a probe for characterizing binding environments in individual solvents [13], in micelles [14], in supercritical water [15] and in binary mixtures [16]. The charge transfer characteristics of PNA (Scheme 2) stimulate the solvatochromism.

In 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 ideal solvation, any observed property (P) of a probe in the solvent mixture is the averaged contribution of the component solvents (Eq. (1)) [17]. Any deviation from Eq. (1) indicates the existence of preferential solvation of the probe.

$$P = \sum x_i P_i \quad (1)$$

where x_i denotes the molefraction of ith solvent.

Maitra and Bagchi have extensively studied the PS of some ketocyanine dyes by binary and ternary solvent mixtures using spectroscopic transition energy (TE) [18]. From the deviation from the ideality of the solvent mixture, they proposed a two phase solvation model consisting of local region or solvation shell, where the solvent molecules experience the field due to solute and outside the local region, termed as bulk. The solvent composition is different in the solvation shell compared to that of bulk. A positive deviation

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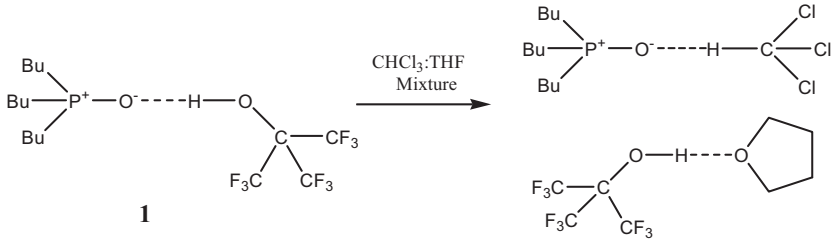


Preferential solvation of complex 1 in chloroform: tetrahydrofuran mixture

Scheme 1.

in TE indicates a PS by the cosolvent with higher spectroscopic TE and vice versa.

In the present work we have studied the solvation of PNA as a solvatochromic indicator, in different binary solvent mixtures. PNA exhibits a quite large solvatochromic shift because of its large dipole moment and significant difference between the ground (6.1*D*) and excited state (15*D*) dipole moment [15]. The longest wavelength absorption band of PNA originates because of an intra-molecular charge transfer (ICT) from the N atom of the amino group to the O atom of the nitro group [19]. The ICT band of PNA shows significant solvent sensitivity, which has generated several solvent polarity scales for organic solvents [13] and micellar system [14].

2. Experimental

The *p*-nitroaniline was purified by crystallizing from hot water, resulted shining light-yellow crystals. All the solvents used were purified using standard methods. Mixed solvents were prepared by carefully mixing the components by volume. Spectral measurements were taken in a Hitachi-U-3010 UV-VIS spectrophotometer. The temperature in the cell was controlled by circulating water by using an INSREF thermostat (India) within a temperature fluctuation of 0.1 K. The position of the band maximum (λ_{max}) was determined from optical density data. All the band maxima in a particular solvent mixture were measured in a number of replicate measurements. The precision of the replicate measurements was ±0.5 nm. Concentrations of the solute in the solutions were in the range 10^{-4}–10^{-3} M. The energy of maximum absorption (E) was calculated from the wavelength maximum (λ_{max}) according to the following formula:

$$E\left(\frac{\text{kcal}}{\text{mol}}\right) = \frac{28590}{\lambda(\text{nm})}$$

3. Results and discussion

Solvatochromism of the intramolecular charge transfer (ICT) band of PNA, which appears at 320–388 nm in solvents with varying polarity (i.e. from hexane to dimethylsulfoxide), is continuous, reversible, and independent of the concentration of the solute. In binary solvents the band does not exhibit any isosbestic point which indicates that the shift of band maximum is not caused by change of equilibrium between two different isolated solvated species in solution.

Considering thirteen different solvents with eight nonpolar and five hydroxylic solvents (Table SI1 of supporting information), the TE values of PNA have been correlated with the polarity scale (π^*) and the correlation coefficient was found to be 0.29 (Eq. (2)). When an *ad hoc* parameter (ahp) was used for hydrogen bonding (one for hydrogen bonding solvent otherwise zero) the correlation has been improved to 0.98 (Eq. (3)) indicating a significant contribution of the hydrogen bonding during solvation. Further, to partition the donocity and acceptability of the hydrogen bonding, α and β parameters, derived by Kamlet et al. [13], were used in the regression analysis. The result indicated that the hydrogen-bond acceptability has significantly more contribution than the hydrogen bond donor ability in solvation of PNA (Eq. (4))

$$\text{TE} = -9.725\pi^* + 86.06, \quad R^2 = 0.29 \tag{2}$$

$$\text{TE} = -8.59\pi^* - 8.03\text{ahp} + 88.62, \quad R^2 = 0.98 \tag{3}$$

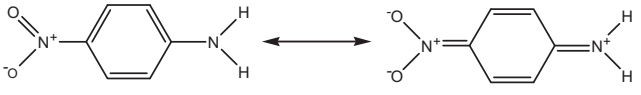
$$\text{TE} = -8.43\pi^* - 1.36\alpha - 8.59\beta + 88.88, \quad R^2 = 0.99 \tag{4}$$

The hydrogen bonding between PNA and solvent molecules may exist as shown in Fig. 1. The hydrogen-bond donor (HBD) solvents can form (i) strong hydrogen bond with the nitro group and (ii) relatively weak bond with the amino nitrogen, while the hydrogen-bond acceptor (HBA) solvents can form strong hydrogen bond with the amino group. As PNA exists as a charge transfer species the amino-nitrogen assumes partial positive charge and hence the second type of hydrogen bonding (ii) is improbable. In nonpolar solvent like hexane, hydrogen bonding does not exist between PNA and the solvent, and the solvation is due to nonspecific dispersive interaction. Addition of ethanol to PNA–hexane solution, replaces hexane from the solvent cage.

As per Eq. (1), in an ideal binary mixture the maximum spectroscopic transition energy, $E(12)_{id}$ of the solute is given by Eq. (5)

$$E(12)_{id} = x_1E_1 + x_2E_2 \tag{5}$$

E_i and x_i represent respectively the maximum energy of absorption (TE) and molefraction of *i*th solvent. Thus, for ideal solvation in a binary solvent mixture, a plot of the observed $E(12)$ values will be linear in molefraction over the entire range. Any deviation from the linearity for the plot of observed TE, $E(12)$ vs. molefraction of the solvents is indicative of the preferential solvation. Thus, the unsym-



Scheme 2.

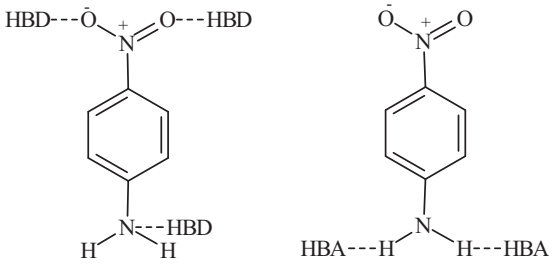


Fig. 1. Different types of hydrogen bonding in PNA.

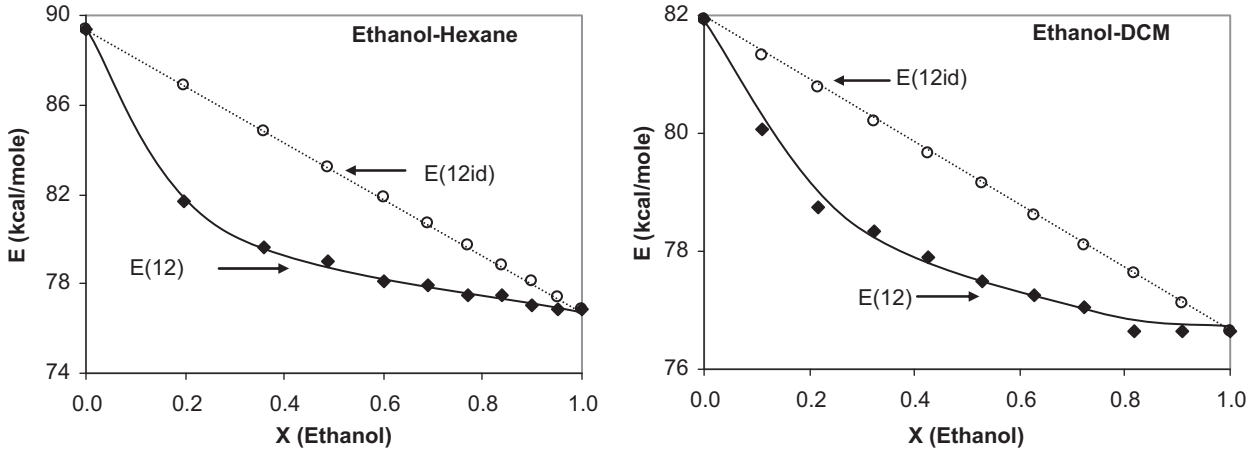


Fig. 2. Plots of spectroscopic transition energy (E) of PNA vs. molefraction (X) of ethanol in ethanol–hexane and ethanol–dichloromethane solvent mixture.

metrical negative deviation from the linearity in ethanol:hexane mixture (Fig. 2) indicates preferential solvation of PNA by ethanol.

PNA, when solvated by ethanol, the orientation of the solvent molecules may be guided by the hydrogen bonding experienced by the different parts of the molecule. The interaction of ethanol (i) in nitro group is due to its hydrogen bond donor, (ii) in amino group as acceptor and (iii) around the benzene unit may be due to its Van der Waal or dispersive interaction. The weak PNA–hexane interaction (iii type) seems to be difficult to overcome the relatively strong PNA–ethanol (i and ii) interactions. The change in TE with the addition of hexane to PNA–ethanol species up to its molefraction of 0.78 may be attributed to the effect of bulk ethanol–hexane mixture on PNA–ethanol species. However, the possibility of exchange of ethanol by the cosolvent at the benzene site cannot be ruled out. The proposition of selective PS gets further support from the investigation on the change in TE due to the addition of dichloromethane and dioxane to PNA–ethanol species. Dichloromethane, being more polar than hexane, should have more polar effect due to its mixture on the solvated PNA species. The sensitivity of the change in TE of PNA–ethanol species due to the change in the molefraction of the cosolvent (up to 0.75) is found to be more for hexane (4.35: TE = $-4.3542X_1 + 81.012$, $R^2 = 0.9696$) than dichloromethane (3.48: TE = $-3.4826X_1 + 79.46$, $R^2 = 0.9541$) which indicates a selective exchange of ethanol at benzene site by the cosolvent (Fig. 2). Above the molefraction of 0.75, dichloromethane starts replacing ethanol from the binding site at nitro group and amino group. Thus, in addition to hydrogen bonding, hydrophobicity of the solvent has a significant contribution in the solvation of PNA. A clear picture of this phenomenon can be visualized with dioxane (HBA solvent) as the cosolvent. With increase in dioxane molefraction the TE–molefraction plot experiences a positive deviation followed by a negative deviation with crossover point at 0.18 of dioxane (Fig. 3). The positive deviation may be attributed to PS by dioxane through functional group recognition. This may be conceived for an exchange in the amino site, where the solvents are bonded through hydrogen bond acceptor ability.

With further increase in dioxane content in the mixture the TE increases with a relatively lower trend than the ideal behavior up to a molefraction of 0.6. This nonideality may be attributed to the presence of both the solvents in the solvent cage in different proportions. With higher molefraction of dioxane (>0.6) the exchange of ethanol in nitro group may be due to a mixture of ethanol–dioxane.

To have a better insight into this solvation phenomenon, a series of binary mixture of alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, isobutanol, 1-hexanol, cyclohexanol and 1-octanol) and dioxane have been used to solvate PNA. In all the binary mixture, alcohol is represented as solvent 1 and the other component in the mixture is considered as solvent 2. The observed spectroscopic transition energy $E(12)$, calculated ideal transition energy $E(12)_{id}$ and the deviation Δ (=$E(12) - E(12)_{id}$) values at various solvent compositions for all the binary mixture are listed in Tables SI2–10 of supporting information and the corresponding plots of $E(12)$ vs. molefraction of alcohol are plotted (Fig. 4). With increase in the molefraction of alcohol in the binary mixture, TE experiences a negative deviation followed by positive deviation from the ideality. However in the octanol–dioxane mixture the trend is reverse, i.e. a positive deviation followed by a negative deviation. The local molefraction, X_1^L of the alcohol has been calculated by using Eq. (6) [18].

$$X_1^L = \frac{E(12) - E_2}{E_1 - E_2} \tag{6}$$

The existence of both positive and negative deviation in all the plots of TE vs. molefraction (Fig. 4) is attributed to the specific solute–solvent, solvent–solvent interaction and functional group recognition. This phenomenon can be explained by considering the TE–molefraction plot to be trilinear with different transition points and crossovers on ideal behavior at different molefractions of the cosolvents. Let the three lines (Fig. 5, Fig. SI1a–h) be AB, BC and CD with point A for neat dioxane and D for neat alcohol. Point 'B' and 'C' are the two break points in the TE–molefraction trilinear plots and refer to the point of maximum negative deviation and maximum positive deviation respectively. Point 'E' is the intersec-

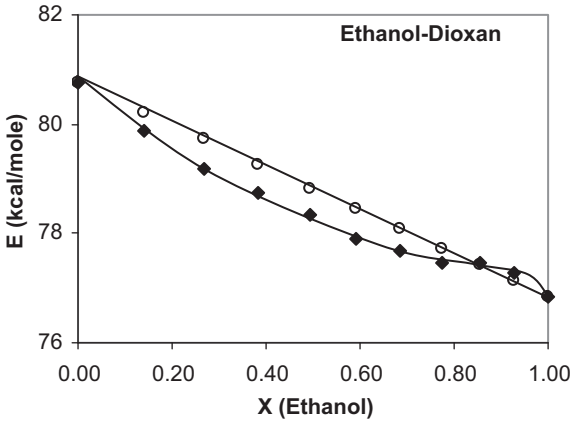


Fig. 3. Plot of spectroscopic transition energy (E) of PNA vs. molefraction (X) of ethanol in ethanol–dioxane solvent mixture.

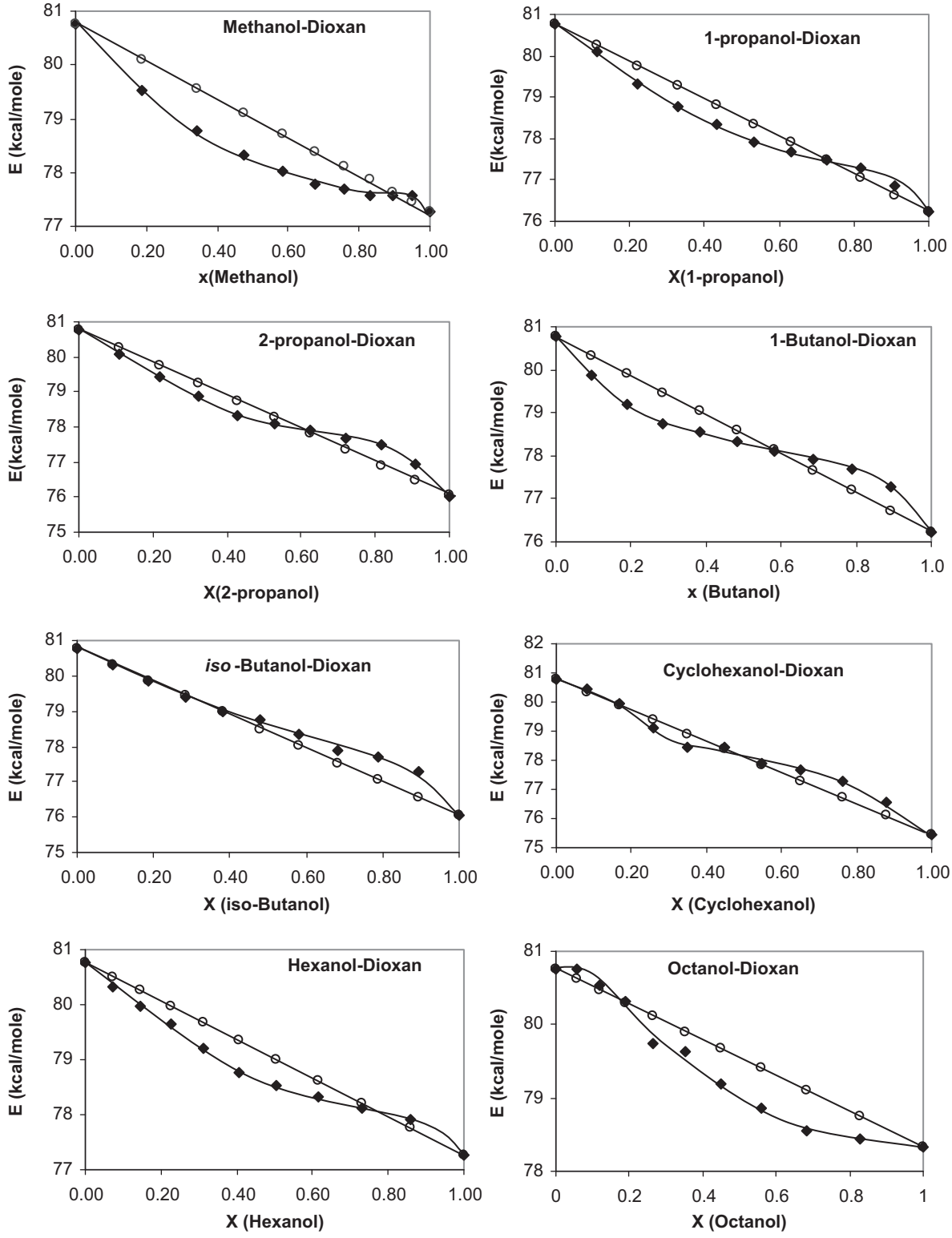


Fig. 4. Plot of spectroscopic transition energy (E) of PNA vs. molefraction (X) of alcohols in alcohol–dioxane binary mixture. The straight lines represent ideal solvation.

tion point between the ideal line and the experimental curves. The molefractions of alcohols at points B, C and E were obtained from the trilinear plots (Fig. 5, Fig. SI1a–h) and also from the plots of deviation (Δ) vs. molefraction of alcohols.

In the solvation of PNA by dioxane, the N–H sites will be strongly solvated through hydrogen bonding, while for the rest, the solvation may be due to nonspecific interactions. Addition of alcohol as a cosolvent changes the solvation pattern of PNA. With a slight increase in the molefraction of alcohol, a sharp negative deviation in the TE from ideality (AB line in Fig. 5) is observed indicating a PS by alcohol through hydrogen bonding with nitro group. Fig. 6 depicts the change in local molefraction of methanol, ethanol, 1-propanol and 1-butanol due to change in molefraction of these alcohols in dioxane solvated PNA. From the figure it is clear that with increase

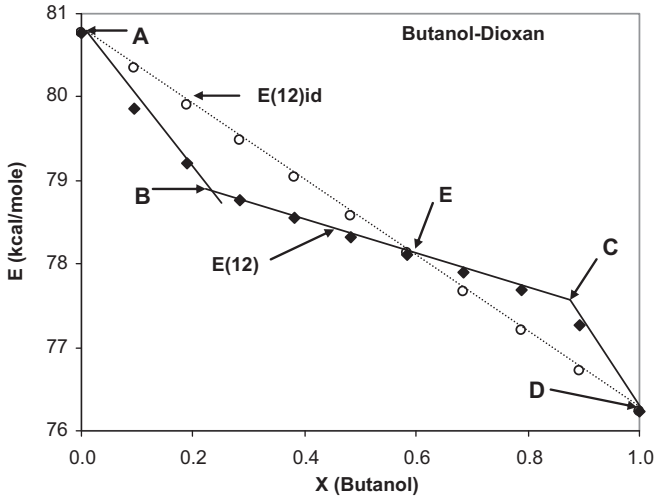


Fig. 5. Tri-linear dependence of maximum energy of absorption as a function of solvent composition in butanol–dioxane binary mixture.

in the hydrophobicity of the solvent, the amount of alcohol to reach the maximum deviation from ideality (point B) decreases. Thus, besides the hydrogen bond donocity, hydrophobicity has also a major role to play in the replacement of dioxane from the solvation shell. Among the solvent parameters, log *P* [20], the logarithm of partition coefficient of the substrate between octanol and water, has the intrinsic characteristics of both hydrophilicity (partition from or to water) and hydrophobicity (partition from or to octanol). The plot of log *P* of alcohols obtained from literature (Table SI11) [20] against the molefraction at point B (x_B) (Table 1) is found to be bilinear indicating a balanced contribution from both the factors (Fig. 7). A minimum of butanol in the plot of Fig. 7 indicates a hydrophobic switch, which balances the polarity and hydrophobic contributions of the solvents. With shorter chain length than butanol, polarity (hydrophilicity) of the medium predominates over hydrophobicity (apolar interaction) and with longer chain length hydrophobicity predominates. This type of observation is also reported by Martins et al. [21] in the study of thermosolvatochromism of merocyanine dyes in aqueous–alcohol binary mixture. They have observed a PS of alcohol over water and the PS is found to be more in propanol than methanol indicating a significant contribution of hydrophobicity.

With a view to separate the contribution of these two factors, from the bilinear plot it was assumed that alcohols up to butanol

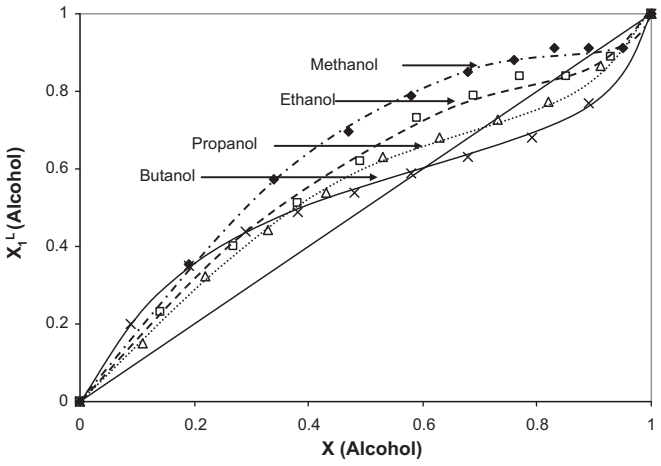


Fig. 6. Plot of local molefraction vs. bulk molefraction of alcohol in the solvation of PNA in alcohol–dioxane binary mixture.

Table 1
Molefraction of alcohol at point B and point E in the alcohol–dioxane binary mixture.

Sl. no.	Alcohol	Molefraction of alcohol	
		At point B (x_B)	At point E (x_E)
1	Methanol	0.5	0.9
2	Ethanol	0.4	0.85
3	1-Propanol	0.32	0.73
4	2-Propanol	0.38	0.58
5	Isobutanol	0.18	0.33
6	1-Butanol	0.22	0.58
7	Cyclohexanol	0.31	0.42
8	1-Hexanol	0.42	0.89
9	1-Octanol	0.64	0.19

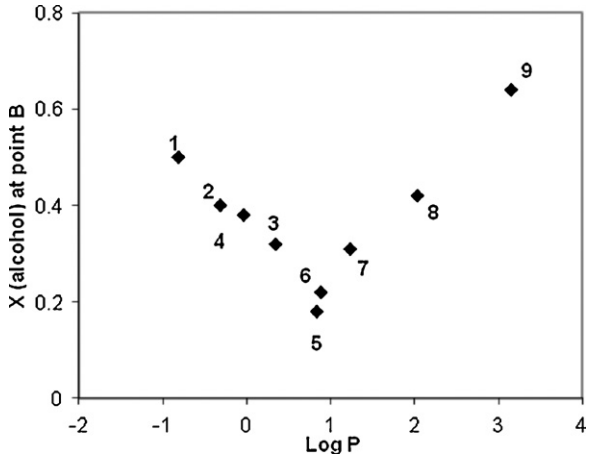


Fig. 7. Plot of molefraction vs. log *P* of alcohols at point B in alcohol–dioxane binary mixture (numbers in the figure indicate the serial number in Table 1).

solvate PNA through hydrogen bonding only (hydrophilicity) and the rest solvate through apolar interactions (hydrophobicity) only. This assumption was supported by a regression model (Eq. (7)) where the first term with a sensitivity of 0.222 is for the hydrophilic contribution of log *P* ($\log P_{hp}$) towards solvation of PNA, while the second term with a sensitivity of 0.156 is for the corresponding hydrophobic or apolar contribution ($\log P_{ap}$). Further, to establish the hydrophilic contribution is mainly due to hydrogen bonding ability of the solvents, the log *P* values for the lower four alcohols were replaced by hydrogen bond donating parameter (α) and on further regression, the regression coefficient (R^2) was found to improve from 0.81 to 0.96

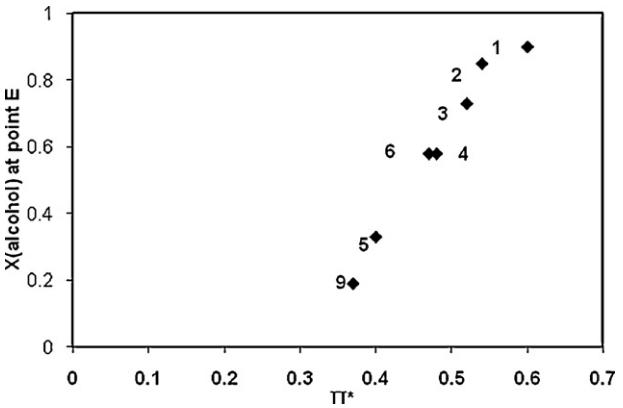


Fig. 8. Plot of molefraction vs. π^* of alcohols at point E in alcohol–dioxane binary mixture (numbers in the figure indicate the serial number in Table 1).

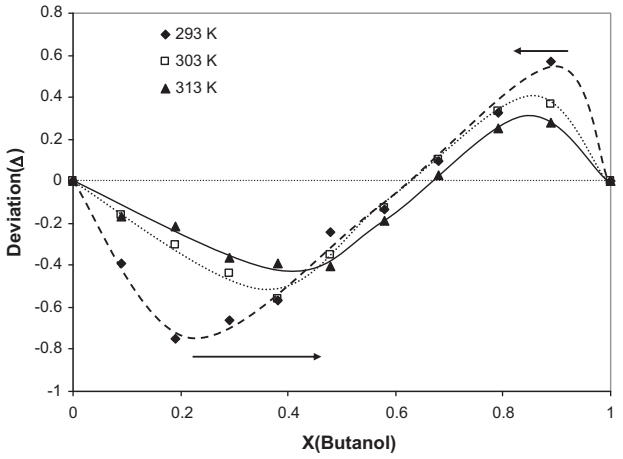


Fig. 9. Plots of deviation vs. molefraction of butanol at three different temperatures.

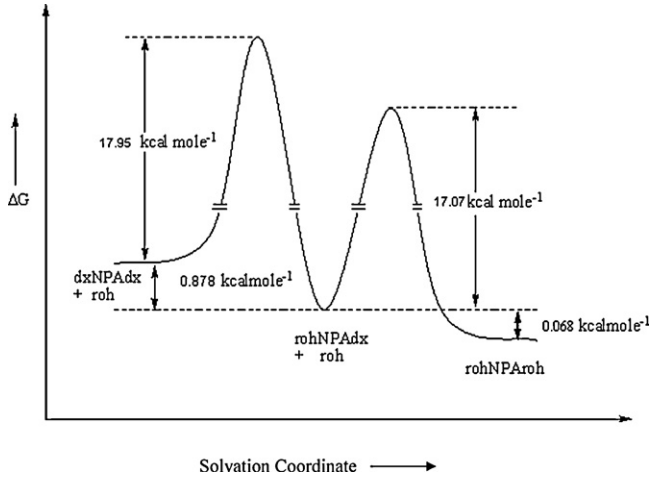


Fig. 10. Free energy diagram for the solvation of PNA in butanol–dioxane binary mixture at 293 K.

(Eq. (8)).

$$x_B = 0.294(\pm 0.035) - 0.222(\pm 0.053)\log P_{hp} + 0.156(\pm 0.026)\log P_{ap}, \quad R^2 = 0.807, \quad F = 12.59 \tag{7}$$

$$x_B = 0.015(\pm 0.0035) + 0.469(\pm 0.048)\alpha + 0.215(\pm 0.019)\mathrm{Log}\,P_{ap}, \quad R^2 = 0.955, \quad F = 64.38 \tag{8}$$

Further, the size of the alkyl group of the small alcohols also contributes to the PS. With similar hydrogen bonding site in alcohol with the nitro group of PNA, and with same dimension of the solvent shell around PNA, it is found that with increasing size of the alkyl groups, the local molefraction decreases. In a similar investigation with a series of alcohols on preferential solvation within a solvation domain (hydrophilic nanocavity) Zhao et al. observed that PS depends critically on the size and structure of the solvents [22].

With further increase in alcohol molefraction, the deviation decreases from point B, experiencing a crossover to the ideality with a maximum deviation at point C. At the crossover point (E) the local concentration of each solvent is same as that of the bulk and therefore the polarity around PNA is due to the ideal mixture of the solvents. The linear relationship of molefraction at this point with the polarity descriptor (π^*) of the cosolvent also supports the isoenvironment for PNA (Fig. 8). Beyond E, with increasing molefraction of alcohol, the TE experiences a positive deviation with a maximum at point C. From E to D, the PS is due to dioxane through hydrogen bonding at amino group through its hydrogen bond acceptor ability. The transition at point C is due to the exchange of dioxane by alcohol in the amino side of PNA. As both dioxane and alcohol act

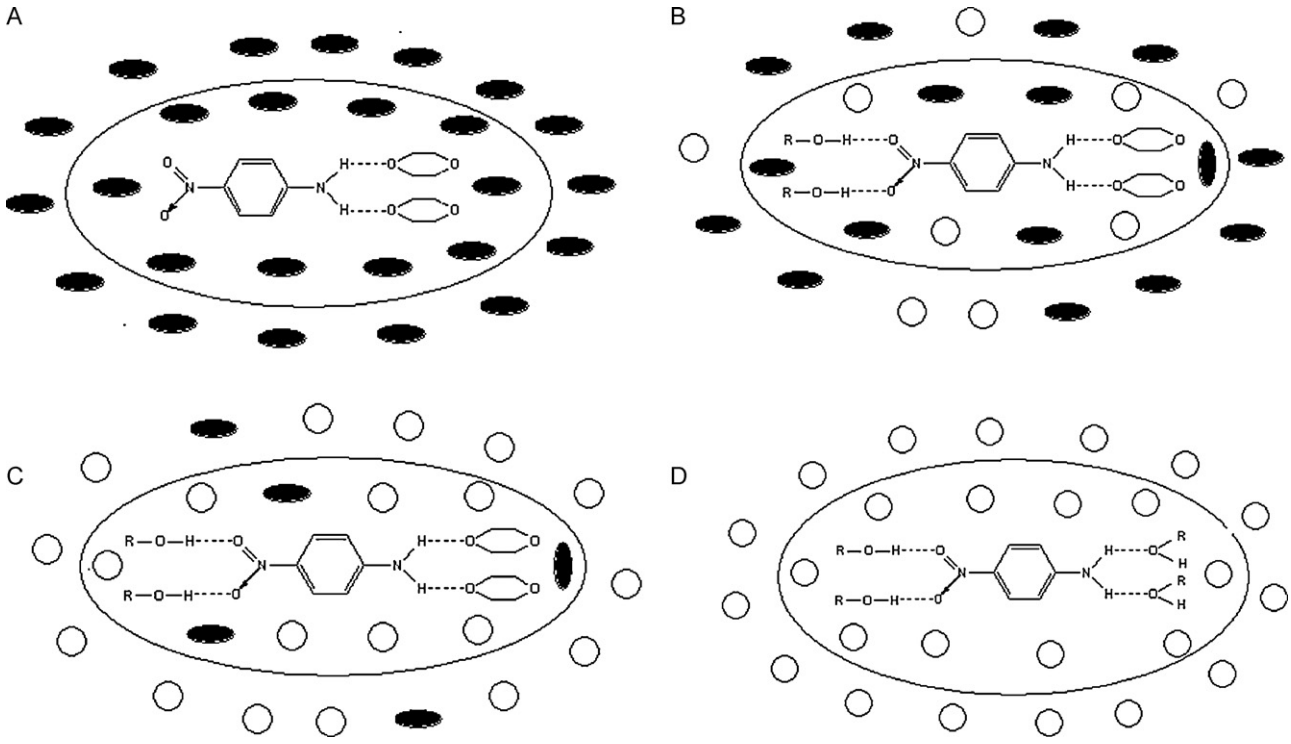


Fig. 11. Schematic diagram of the solvation pattern of PNA in dioxane (O) + alcohol (O) binary mixture at various solvent compositions (inside the ellipse represent local environment around PNA while outside is the bulk).

as hydrogen bond acceptor, the change in the structure of alcohol does not have much effect on the trend of the PS (positive deviation from ideality) and also on the molefraction at point C.

The IR spectral data of PNA recorded in dioxane and butanol also supports the functional group recognized preferential solvation. The absorption peaks due to nitro group in dioxane ($1323\,cm^{-1}$) suffers a shift towards lower frequency up to $1294\,cm^{-1}$ by the addition of butanol due to hydrogen bonding (Figs. SI1–SI3). However the peak due to amino group in dioxane, butanol and in butanol–dioxane mixture remains almost the same ($3481–3479\,cm^{-1}$). In butanol–dioxane mixture the IR spectral patterns are similar to that in butanol.

From the above results a solvent competition model for functional groups may be proposed for the binary mixture of alcohol and dioxane. At point A in Fig. 5, PNA is solvated by dioxane; on line AB, alcohols starts replacing dioxane from the nitro group, at point B the replacement at this site is maximum, on line BC the solvated species has an environment similar to that of the bulk; and at point C, the alcohol starts exchanging dioxane from the amino functional group. As the interaction of dioxane with PNA is dispersive and nonspecific in all sites except the amino site, the ease in replacement of dioxane by alcohol is conceivable and the replacement ratio is more than one. In case of isobutanol the AB line overlaps with the ideal indicating the affinity of both the solvents for nitro group is similar. Though isobutanol has appreciable hydrogen bond donor ability ($\alpha = 0.84$), the hydrophobic contribution of the isobutanol makes the solvent dioxane like towards nitro group. Similar phenomenon has also been observed for cyclohexanol, however, in octanol, addition of cosolvent could not change the environment of the functional groups. Up to a molefraction of 0.2, PNA is preferentially solvated by dioxane and after that it is preferentially solvated by octanol. This observation also supports the proposition that hydrophobic interaction plays an important role in solvating PNA by organic solvents.

The effect of temperature has a significant effect on the PS by butanol in butanol–dioxane mixture. This is because of the fact that the hydrogen bond donocity of alcohol has to compete with the nonspecific dispersive interaction of PNA–dioxane. With increasing temperature from 20 to 40 °C, the molefraction at point B shifts from 0.22 to 0.42 with decreasing trend in the deviation from ideality (Fig. 9). With increase in temperature, hydrogen bonding weakens leading to desolvation of the probe [21,23]. However, in the positive deviation, where the PS is due to dioxane, the shift in molefraction at point C is very small, i.e. from 0.89 to 0.86 with same decreasing trend in the deviation with increase in temperature. Within this temperature range the relatively strong hydrogen bonding of N–H with dioxane is not affected much.

The thermodynamics of PS may be investigated by considering the solvation as equilibrium.

$$\mathrm{dxNPAdx} + \mathrm{roh} \rightleftharpoons \mathrm{rohNPAdx} + \mathrm{dx} \quad \text{at point B}$$

$$\mathrm{rohNPAdx} + \mathrm{roh} \rightleftharpoons \mathrm{rohNPAroh} + \mathrm{dx} \quad \text{at point C}$$

where NPA, dx and roh refer to nitro-phenyl-aniline, dioxane and alcohol respectively.

Akin to the free energy of micellization [24] and considering the above equilibrium, the Gibbs energy of PS (ΔG_{PS}) may be obtained from Eq. (9), where $x_{(B/C)}$ being the molefraction of cosolvent.

$$\Delta G_{PS} = RT \ \ln x_{(B/C)} \tag{9}$$

At point B the ΔG_{PS} is determined to be −878, −596 and −537 cal and at point C the value is −67.6, −83.5 and −93.5 cal at 20, 30 and 40 °C respectively.

By considering solute–solute, solvent–solute and solvent–solvent interactions Hunter reported a hydrogen bonding scale of a large number of solutes/functional groups in different solvents [25]. These scales have been used to determine the change in free energy due to change in hydrogen bonding ($\Delta\Delta G_{H\text{-bond}}$ in kJ/mol) during solvation of the solute by using Eq. (10).

$$\Delta\Delta G_{H\text{-bond}} = -(\alpha - \alpha_s)(\beta - \beta_s) \tag{10}$$

where α and β are hydrogen-bond donor and hydrogen-bond acceptor constants for the solute molecules, and α_s and β_s are the corresponding hydrogen-bond donor and hydrogen bond acceptor constants for the solvent. By considering the α values to be 2.1 and 2.7 for $–NH_2$ and –OH and the β values to be 3.7, 5.3, 5.8 and 5.5 for $–NO_2$, $–NH_2$, –OH and –O– respectively, the change in free energy due to change in hydrogen bonding during preferential solvation has been calculated using the above equation. For replacement of dioxane by butanol in the nitro site of PNA (at point B), keeping amino site unaffected, the free energy change was calculated and found to be −1350 cal/mol. Similarly for the addition of dioxane in PNA–butanol, free energy change for replacement of butanol by dioxane in the amino site (at point C) was calculated to be 170 cal/mol, i.e. the energy requirement for replacing dioxane by butanol in the amino site is −170 cal/mol. The deviation in the change in energy from the experimental value may be attributed to the other dispersive interactions between solute and solvent. Thus the theoretical calculation also supports the functional group recognition model.

Considering the solvation as a substitution process, the activation parameters were calculated from the change in the molefraction with temperature [26]. The $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ values for the sequential inclusion of butanol in the nitro side followed by amino side in the dioxane solvated PNA are found to be $5.326\,kcal\,mol^{-1}$, $-43.098\,cal\,K^{-1}\,mol^{-1}$, $17.95\,kcal\,mol^{-1}$ and $-0.268\,kcal\,mol^{-1}$, $-59.195\,cal\,K^{-1}\,mol^{-1}$, $17.076\,kcal\,mol^{-1}$ respectively. Accordingly a potential energy curve may be presented as shown in Fig. 10. The trend in the values also supports the proposition of exchange of cosolvent in the solvent shell preferentially through functional group recognition. The higher change in entropy for inclusion of dioxane in PNA–butanol over the inclusion of butanol in PNA–dioxane indicates more hydrogen bonding interactions in PNA–butanol than PNA–dioxane. The lower value of $\Delta H^{\neq}$ indicates spontaneity in solvation of PNA by dioxane which may be attributed to the induced dipolar–dipolar interaction of dioxane and PNA. Accordingly a preferential solvation of PNA by the solvents has been proposed as shown in schematic diagram (Fig. 11).

Thus, the functional groups in a molecule can orient the solvents and increase the local concentration at specific sites. This phenomenon can find applications in explaining intricate mechanism in drug–enzyme interactions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2011.01.020.

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