

Preferential solvation of *p* - nitrophenol in binary solvent mixtures

A Dissertation Submitted for the partial fulfillment

FOR THE DEGREE OF
MASTER OF SCIENCE IN CHEMISTRY

Under Academic Autonomy
NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA



By

Subhasis kar

*Under the Guidance
Of*

Dr. Sabita Patel

Department Of Chemistry
ROURKELA – 769008, ODISHA
NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

Dr. Sabita Patel
Assistant Professor
Department of Chemistry
National Institute of Technology
Rourkela-769008, India



CERTIFICATE

This is to certify that the dissertation entitled “ **Preferential solvation of *p*-Nitro phenol in binary solvent mixtures** ” being submitted by **Subhasis Kar** to the Department Of Chemistry, National Institute 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. Subhasis Kar bears a good moral character.

NIT-Rourkela
Date:

(Sabita Patel)

ACKNOWLEDGEMENT

I stand with overwhelming satisfaction on a work done to my heart contents with heart felt thanks to all those loving hearts that I met enroute my endeavor. Indeed, first and foremost, I thank Lord Mahadev for the miraculous ways he led me throughout this crucial journey. Without his presence, this would not have been possible. His grace and strength, love, care, and all the blessings are uncountable in the untrodden path.

At the outset, I wish my sincere gratitude, respect and affection to my guide Dr. Sabita patel, professor of dept. of Chemistry who guide me with his valuable contribution, suggestions and constructive criticisms in the most appropriate way. I keep green in mind this record as a sign of debt that can never be repaid in my life.

I also equally owe a great debt of gratitude to Dr. B.G. Mishra, professor of dept. of Chemistry, N.I.T. Rourkela

My special heartfelt thanks to my elder brother Prakash Kumar Malik, PhD Scholar of organic lab.

I record my deep gratitude to Ms. Sarita Garnayak, I am also grateful all other research scholar of organic lab. I bring their contribution on record and express my gratitude.

I take an opportunity to express my thanks to my friends and colleagues who were always there to encourage and support me during my good and bad time in my institute.

I am also thankful to all the staff members for their help.

Last but not least I would like to owe the credit of my work to my beloved parents.

Subhasis Kar

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1. Introduction

1.1 Solvation

Solvation refers to surrounding of the solute molecules or ions by solvent molecules. The solute molecules are either more or less tightly bound with the solvent molecules by intermolecular forces leading to decrease in free energy, termed as solvation energy. The region around the solute, up to which the solvent molecules are reoriented due to the force created by solute is known as solvation shell or cybotectic region. Figure 1 shows a typical solvation shell and how the solvent molecules are reoriented themselves to form the solvation shell.

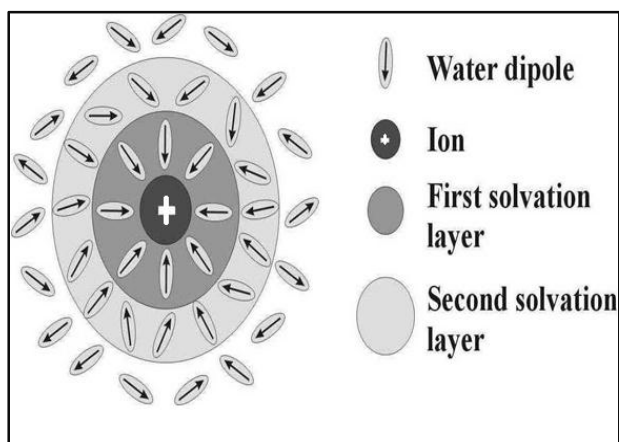


Fig 1. A schematic representation of solvation shell

During the solvation process, when a solute dissolves in a solvent, solute-solute interactions and solvent-solvent interactions are being replaced by solute-solvent interactions to form a solution. The solute molecules enter into solution, will disturb the structure of the solvent, and forming some more or less ordered solvation shell around themselves. If the solvation

energy which is liberated is lower than the lattice energy, then overall dissolution process is endothermic and if the solvation energy is higher than the lattice energy, then the overall process is said to be exothermic process. For the spontaneity of the dissolving process the dissolution process should be endothermic.

1.2 Preferential solvation

The Solvation process in mixture of two or more solvent is more complicated as compared to pure solvent. With the increase in number of components, number of solute solvent interactions increases. In addition to solute solvent interactions, the interactions between unlike solvent molecules play an important supplementary role leads to large deviations from ideal behavior expected from the Raoult's law of vapor pressure depression of binary mixture. Solute may induced a significant change in the composition of solvent mixture in the solvation sphere than the bulk composition. This is generally known as selective solvation or preferential solvation.[1]

This phenomenon is graphically represented in figure 1.

Preferential or selective solvation is 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.

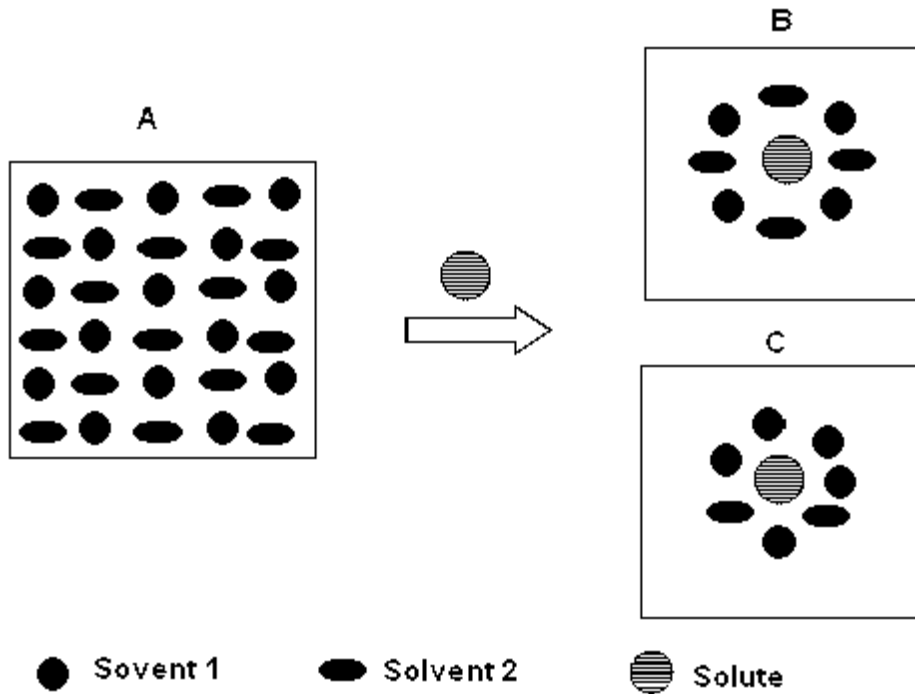


Figure 1: Schematic representation of preferential solvation, A : mixture of solvent 1 and solvent 2 in 1:1 composition; B: ideal solvation of the solute; C: preferential solvation of the solute by solvent 1.

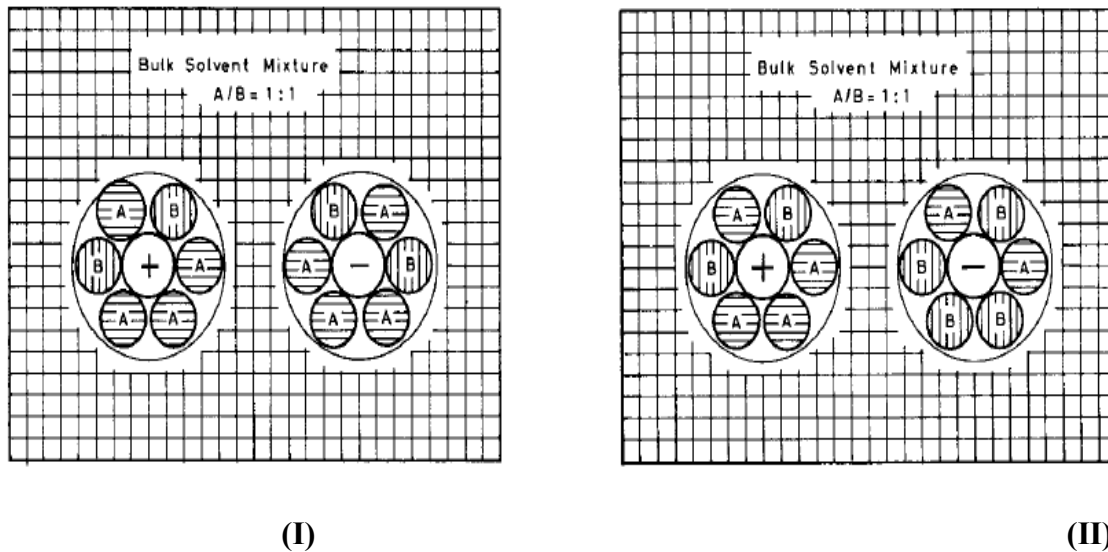


Figure 2: Schematic model for the selective solvation of ions by one component of a binary 1:1 mixture of the solvents A and B (I) Homoselective solvation: both ions are preferentially solvated by the same solvent A. (II) heteroselective solvation: the cation is preferentially solvated by A and the anion by B.[1]

When in a mixture of two solvents, both ions of a dissolved molecule or salt are solvated preferentially by same solvent, then *Homoselective solvation* occurs. Similarly, the preferential solvation of the cation by one, and the anion by the other solvent, is termed *Heteroselective solvation* (Figure2).

The solvent composition at which the energy maximum lie midway between the values for the two pure solvents is termed as 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 3).[2]

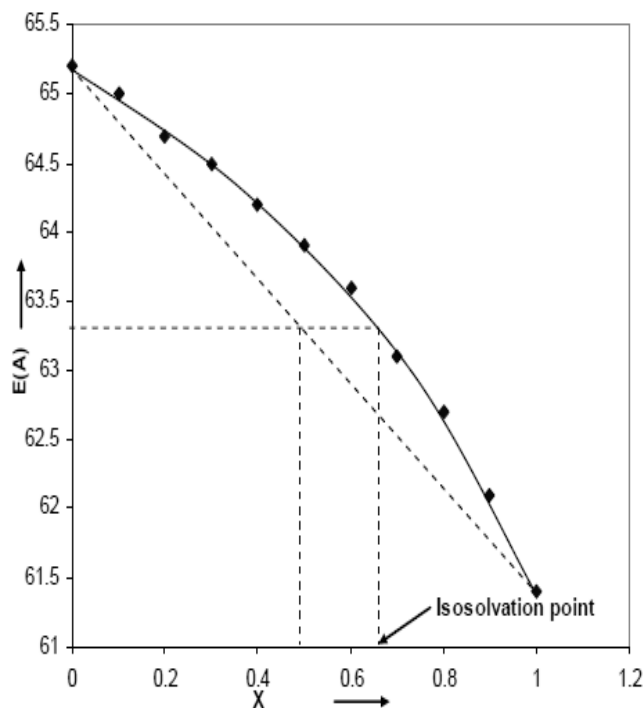


Figure 3: Plots of $E(A)$, the energy of maximum absorption of the ketocyanine dye as a function of solvent composition in mixed binary solvent Water+methanol.[2] Straight line refers to ideal condition without preferential solvation, primary solvation shell of the same composition as the bulk solvent mixture. Curved line: Observed case with preferential solvation of the dye by

methanol and isosolvation point at $X(\text{water}) = 0.66$ or $X(\text{methanol}) = 0.34$, 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

1.3 Different Methods to study preferential solvation

A large number of study have been undertaken both experimentally and theoretically to understand the preferential solvation of solute in different binary and ternary solvent mixtures. Different methods for the study of preferential solvation have been developed namely (i) NMR chemical shift measurements (ii) fluorescence emission measurement (iii) IR absorption shifts and (iv) UV/Vis absorption shifts of solvatochromic dye.

NMR chemical shift method

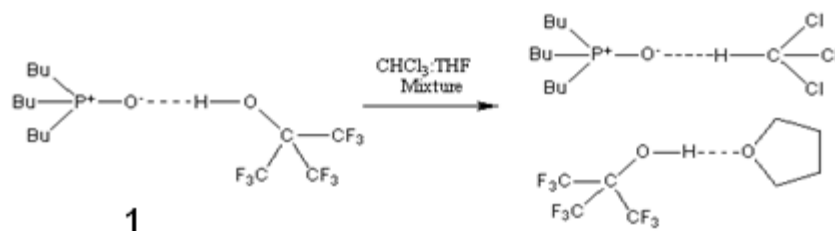
N.M.R method is a very useful method to study the solvation. In this technique the chemical shift values of the probe is determined in different solvent composition. Due to binding of various solvent molecules to the solute or probe, it shows different chemical shifts value from those of the bulk solvent. The chemical shift method can be used only when the solute contains a nucleus which is particularly solvent sensitive.

Frankel et. al. have used NMR chemical shift method to study the preferential solvation of $\text{Co}(\text{acac})_3$ in 1:1 chloroform-carbon tetrachloride binary mixture.[2] From ^{59}Co chemical shift measurement, it was found that $\text{Co}(\text{acac})_3$ is preferentially solvated by chloroform.

Bango et. al.[3] also studied the preferential solvation of neutral organic compound like phenol in acetonitrile-water, DMSO-water, diethyl ether-dichloromethane and N-methyl butyramide (NMBA) in acetonitrile-water and dioxan-benzene solvent mixtures from intermolecular ^1H NOESY measurements. By using the Macura-Ernst theory they interpreted the preferred solvent

over the other. In acetonitrile-water binary solvent NMBA was preferentially solvated by acetonitrile and in 1,4 dioxane -benzene binary mixture, it was preferentially solvated by benzene. Phenol in acetonitrile-water and in DMSO-water is preferentially solvated by the organic cosolvent and in dichloromethane ether binary mixture it prefers ether.

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).[4,5] They explained the variation in the ^{31}P nmr chemical shift of the probe by considering solvation environment of individual functional group by different solvent (Scheme-1).



Scheme 1 Preferential solvation of complex 1 in chloroform-tetrahydrofuran binary mixture

The solvation of some neutral and charged organic molecules (phenol, nitroanilines, tetraalkylammonium) in binary solvent mixtures was investigated by means of intermolecular ^1H -NOESY NMR spectroscopy. [6] In most of the cases the solutes are preferentially solvated by one of the solvent in the mixture. The origin of preferential solvation is discussed in terms of solute-solvent interactions and microheterogeneity in the solvent mixture.

Homonuclear and heteronuclear intermolecular NOE measurements were applied to study the solvation of a short model tetrapeptide, NAc-Ser-Phe-Val-Gly-OMe, dissolved in water, in

trifluoroethanol (TFE) and in mixtures of both. [7] Preferential solvation of the peptide by TFE in water-TFE mixtures was demonstrated by a significant decrease in water-peptide interaction and a concomitant buildup of heteronuclear NOE between the fluorine atoms of TFE and the peptide.

Frankel et al. [8] has determined the relative concentrations of water and dioxane, dimethylformamide, or dimethylsulfoxide in the inner coordination spheres of Co^{2+} and Ni^{+} ions in the binary solvent mixtures by examining paramagnetic broadening of solvent proton n.m.r. signals. The results indicate that dimethylsulfoxide and dimethylformamide are good competitors for coordination sites but that dioxane is excluded by water.

Preferential solvation of phenol in equimolar acetonitrile water and ethanol water binary mixtures has been studied by using intermolecular ^1H NOESY experiments by Dahlberg and Laaksonen. [9] Molecular dynamics computer simulations were carried out to study the preferential solvation of phenol on the same systems. In the case of acetonitrile water the local mole fraction obtained from simulations agrees quite well with experiments. In the case of ethanol water there was a qualitative difference.

Fluorescence emission method

In fluorescence spectra the solvatochromic shift of the of fluorophores (probe) dissolved in binary solvent mixture is a suitable method to study preferential solvation. Fluorescence usually occurs from the electronic transition by emission of photons. Solvent effects on fluorescence spectra are based on the differential solvation of fluorescent molecule. Reorientations of the solvent molecule can take place after electronic excitation and in the relaxed excited state solvation equilibrium occurs. Petrov has studied and reviewed regarding fluorescence as a method to study preferential solvation in binary solvent mixture. [10] Using both the absorption and

fluorescence measurement the preferential solvation of 1,5-diamino anthraquinone have been studied in binary liquid mixtures of acetonitrile- DMF, acetonitrile-ethanol, acetonitrile-DMSO and benzene-ethanol.[11] Jozefowicz has studied the preferential solvation of fluorenone and 4-hydroxyfluorenone in binary solvent mixtures (cyclohexaneótetrahydrofuran and cyclohexaneó ethanol) using steady-state spectroscopic measurements.[12] The solvation of the fluorenones, both in the ground and in the excited states, exhibits a non-linear solvatochromic shifts as a function of polar component in the binary solvent mixtures indicating preferential solvation by the polar component of the mixture. From the spectroscopic measurements it was found that, the first solvation shell of the probe contains different number of polar component. These different features are explained by the absence and presence of specific soluteósolvent interactions (hydrogen bond) in the solvent mixtures.

The fluorosolvatochromism of 4-[(1-methyl-4(1*H*)-pyridinylidene)-ethylidene]-2,5-cyclohexadien-1-one (Brooker's merocyanine) was studied in pure and mixed solvent system.[13] The fluorescence emission band of the dye was dependent on the medium. The behavior of the probe in binary mixtures including a hydrogen-bond accepting solvent (acetonitrile, *N,N*-dimethylformamide, and dimethylsulfoxide) and a hydroxylic solvent (water, methanol, ethanol, propan-2-ol, and butan-1-ol) was also investigated by this method.

IR spectroscopy method -

Solvent plays an important role on IR spectrum. With increase in the solvent polarity the absorption band comes to the lower wave length. This is due to the interaction between the polar solvent and polar moiety of the solute through hydrogen bonding and dipole-dipole interaction. Kwak et. al. [14] have used ultrafast 2D-IR vibrational echo experiments, IR pump-probe experiments, and FT-IR spectroscopy of the hydroxyl stretch of phenol-OD in three solvents,

CCl₄, mesitylene (1, 3, 5 trimethylbenzene), and the mixed solvent of mesitylene and CCl₄ (0.83 mole fraction CCl₄), to study solute-solvent dynamics and preferential solvation. The experimental results and MD simulations indicate that the solvent structure around the solute may be different from the mole fraction of mixed solvent. Steady-state and time-resolved infrared spectroscopy of the azide (N₃⁻) anion has been used to characterize aqueous mixtures both with the ionic liquid (IL) 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) and with dimethyl sulfoxide (DMSO). The results are discussed in terms of preferential solvation and the degree of water association in the mixtures. [15]

UV-visible spectroscopy method

UV-vis absorption spectra of molecules depend on the polarity of the used solvent. With change in the polarity of the solvent, the intensity, position, and shapes of the absorption bands are also changed. This is because with changing the polarity of the medium, the intermolecular interactions of the chromophore are changed, which leads to the change of the energy difference between the ground state and the excited state. This solvent effect on the spectra of the compound, resulting in a blue shift (hypsochromic effect) with increasing solvent polarity, is usually called negative solvatochromism. The corresponding red shift (bathochromic effect) is termed positive solvatochromism. From the literature survey, the UV-visible study provides a new opportunity to investigate how a solute could be preferentially solvated in binary mixture solvents through specific and non-specific interactions. Oka and Kajimoto proposed a model to estimate the number of solvent molecules solvating the solute by using 4-(N,N-methylamino) benzonitrile in supercritical CO₂ with UV absorption utilizing the solvatochromic shift. [16]

Bagchi and co-workers[17-23] have used UV-vis absorption techniques to the study of preferential solvation of different solvatochromic dyes in various binary and ternary solvent mixtures. From all these experiments they have interpreted that the origin of preferential solvation is due to the different solvent-solvent interaction and solute-solvent interaction. H-bonding have also main role in preferential solvation. They also suggested three parameters like solvent polarity polarizability, HBD or H-bond donation ability and HBA or H-bond acceptor capability for the difference in solute-solvent interaction.

The microscopic feature of solvent systems resulting from the basis of binary mixtures formed by a protic molecular solvent (methanol, ethanol, propan-1-ol, propan-2-ol, and 2-ethoxyethanol) and a 1-butyl-3-methylimidazolium (bmim)-based ionic liquid (IL) cosolvent composed of different anions (tetrafluoroborate, hexafluorophosphate, chloride, and bromide) have been analysed by Fortunato et al. [24] The behavior of the solvent systems was analyzed according to their deviation from ideality. The ion-pair character of the ionic liquids affects their interactions with a solute or a molecular solvent. They have explored the possibility of formulating mixtures having a particular property for particular purpose paying particular attention to the most remarkable microscopic properties, the acidity and the basicity, in order to propose new solvents. Thus, the solvating feature can be tailored selecting the molecular and/or the ionic component at a particular composition.

Structural and intermolecular interactions of solvatochromic probes 4-nitroaniline, 4-nitroanisole, and Reichardt's dye were investigated in the binary mixtures of 2-hydroxy ethylammonium formate as an ionic liquid with N,N-dimethyl formamide, dimethyl amine, and dimethyl sulfoxide. [25] Synergistic solvation behavior for some mixtures was observed. Preferential solvation model was applied to study solvent mixtures effects on solvation of

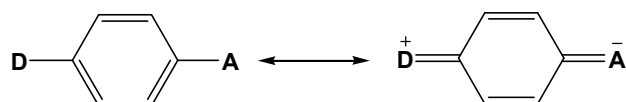
indicators, and from these information solute-solvent and solvent-solvent interactions were interpreted. Preferential solvation (specific solute-solvent interactions) or the solvent-solvent interaction is the reason for deviation from ideal behavior of probes.

Mishra and coworkers [26] have studied the preferential solvation of N-alkyl(methyl, hexyl, and hexadecyl)-4-[(4-N,N-dimethylamino)styryl]pyridinium halides in binary solvents using UV-Vis spectroscopic technique. The probes have a donor-acceptor system and the corresponding absorption bands are found to be solventsensitive. In neat solvents, excluding a few, reversal in solvatochromism was observed, identifying a polarity scale for solvatochromic switch, which appears around 45-50 $E_T(30)$ scale. There is not much effect of the change in the apolar characteristics by changing the alkyl chain of the probe, which confirmed the preferential solvation is mainly due to the chromophoric group. Due to solvent-solvent interactions, in some cases, hypo- and hyperpolarity in the solvent cage were observed. The preferential solvations of the dyes by these solvents were analyzed by consideration of the interactions of solvents with hydrophilic and hydrophobic groups of the probes. The orientations of the solvent molecules around the probes were proposed. Disorder of the solvents around the probes was also considered for preferential solvation phenomena.

The preferential solvation of p-nitroaniline in binary mixture of alcohol and dioxane has been studied by Patel et al. [27]. They proposed a localized solvation of p-nitroaniline due to specific solute solvent interactions. They proposed a solvation model where, alcohol preferentially solvate the nitro part and dioxane preferential solvate the amino site of p-nitroaniline.

2. Experimental

For the study the preferential solvation polarity-sensitive indicators are mainly used. These indicators or probes were generally aromatic molecules and mostly of the A-C₆H₄-D type, where A and D respectively stand for electron-acceptor (such as NO₂) and electron-donor (such as OH) groups.



For studying the solvation Electronic spectroscopy is found to be suitable method. 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, p-nitrophenol (PNP) is used to probe preferential solvation as a solvatochromic indicator organic-organic binary solvent mixtures by monitoring the absorption band of PNP.

The p-nitrophenol was purified by crystallizing it from hot water. All the solvents used were dried over CaCl₂ and distilled before use. All mixed solvents were prepared by carefully mixing the components by volume. The Spectral measurements were taken by using UV-VIS spectrophotometer. The position of the absorption maximum (λ_{max}) was determined by optical density data. The energy of maximum absorption (E) was calculated from the wavelength maximum (λ_{max}) according to the following expression.

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

3. Results and Discussion

P-Nitrophenol shows two forms in the crystalline state. The β -form is colourless pillar. The α -form is yellow pillars, stable at room temperature. It is odourless and soluble in water. The uses of *P*-Nitrophenol is that, it act as intermediate in the synthesis of paracetamol. *P*-Nitrophenol is raw materials for fungicides. The color-changing property makes this compound useful as a pH indicator. Thus the study of the solvation of PNP is essential.

Table 1: Longest wavelength absorption band (λ_{max}) of PNA in different solvent

<u>Solvent</u>	α	<u>logP</u>	π^*	β	λ_{max}
Methanol	0.98	-0.82	0.60	0.62	311.5
Ethanol	0.86	-0.32	0.54	0.77	312.0
1-propanol	0.78	0.34	0.51	0.83	312.0
2-propanol	0.78	-0.04	0.46	0.95	314.0
1-butanol	0.79	0.88	0.46	0.88	312.5
dioxane	0.00	-0.27	0.55	0.37	304.5
THF	0.00	0.82	0.58	0.55	309.5
DMSO	0.00	-2.03	1.00	0.76	321.0
DMF	0.00	-1.01	0.88	0.69	319.0
Ethylacetate	0.00	0.73	0.55	0.45	306.5
benzylalcohol	0.43	1.10	0.98	0.50	319.0
acetonitrile	0.15	-0.34	0.85	0.31	307.5
chloroform	0.34	1.97	0.76	0.00	307.5

The absorption maximum of PNP in 13 different solvents is presented in table 1. From this table it is clear that with increase in solvent polarity positive solvatochromism is observed. On correlating the absorption maximas obtained in different solvents with the solvent parameters such as α , $\log P$, π^* , β etc. the correlation coefficient obtained are very low. The Individual solvent parameters are not able to explain the change in absorption maximum with change in solvent polarity (equation 1, 2) indicating that, the solvation is not due to a single property of the solvent rather it is the combination of all.

$$\lambda_{\max} = 14.48 (\pm 6.58) \pi^* + 302.33 (\pm 4.58) \dots\dots(1)$$

$$N=13, R^2=0.31$$

$$\lambda_{\max} = 10.48 (\pm 4.89) \beta + 305.85 (\pm 3.15) \dots\dots(2)$$

$$N=13, R^2=0.29$$

Multiparametric regression equation is used to describe the solvation of PNP in different solvent. Out of various multiparametric equation, the shift of λ_{\max} is best described by combination parameter π^* and β (equation 3). Both π^* and β have positive contribution towards solvation of PNP.

$$\lambda_{\max} = 21.57 (\pm 2.80) \pi^* + 15.77 (\pm 2.07) \beta + 288.25 (\pm 2.61) \dots\dots(3)$$

$$R^2=0.90$$

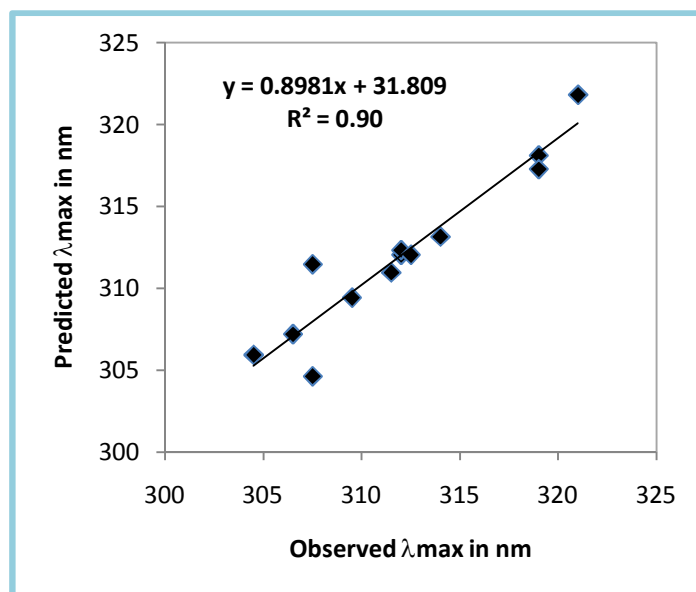
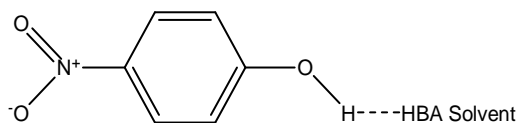


Figure 4 - the plot of predicted λ_{max} vs. observed λ_{max} of PNP in different solvents

From the plot of predicted vs observed λ_{max} (figure 4), it is clear that except chloroform and acetonitrile all other solvents lies in a straight line which proves the validity of the regression model. The presence of chloroform and acetonitrile as outliers in the plot may be explained through the low β value (Chloroform:0 and acetonitrile: 0.31). Thus it can be proposed that hydrogen bond acceptor has a significant contribution in the solvation of PNP. The hydrogen bond acceptor (HBA) solvents can form a single H-bond with the hydroxyl group of PNP (Scheme 2).



Scheme 2: Hydrogen bonding of PNP with HBA Solvent

Excluding Chloroform and Acetonitrile, the correlation coefficient increases from 0.90 to 0.98 (equation 4). The plot of predicted vrs. observed λ_{\max} is presented in figure 5.

$$\lambda_{\max} = 23.09 (\pm 1.45) \pi^* + 17.50 (\pm 1.58) \beta + 286.21 (\pm 1.58) \quad \dots\dots(4)$$

$R^2 = 0.98$ (excluding chloroform ($\beta = 0$) and acetonitrile ($\beta = 0.31$))

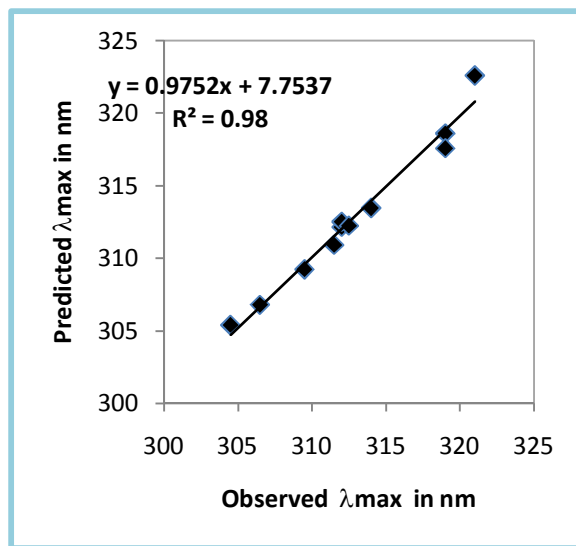


Figure 5 - the plot of observed λ_{\max} vrs predicted λ_{\max} of PNP obtained from regression model equation 4.

Solvation of PNP in Butanol-dioxane binary solvent mixtures

The calculated spectroscopic transition energy for ideal solvation ($E(12id)$), observed transition energy ($E(12)$) and the deviation from ideal behavior (Δ)[27] for the solvation of PNP in butanol-dioxane binary mixture is presented in Table 2. The plot of transition energy vrs mole fraction of butanol is plotted in figure 6.

Table 2: E(12) in kcal/mole of PNP and other related parameters as a function of solvent composition in butanol-dioxan binary mixture

X1	X2	λ	E(12)	E(12id)	Δ
1.00	0.00	312.5	91.49	91.49	0.00
0.89	0.11	312.5	91.49	91.73	-0.24
0.79	0.21	312.5	91.49	91.97	-0.48
0.68	0.32	312.5	91.49	92.20	-0.71
0.58	0.42	311.5	91.78	92.43	-0.65
0.48	0.52	311	91.93	92.66	-0.73
0.38	0.62	310.5	92.08	92.88	-0.80
0.29	0.71	309	92.52	93.10	-0.57
0.19	0.81	307.5	92.98	93.32	-0.34
0.09	0.91	306.5	93.28	93.53	-0.25
0.00	1.00	305	93.74	93.74	0.00

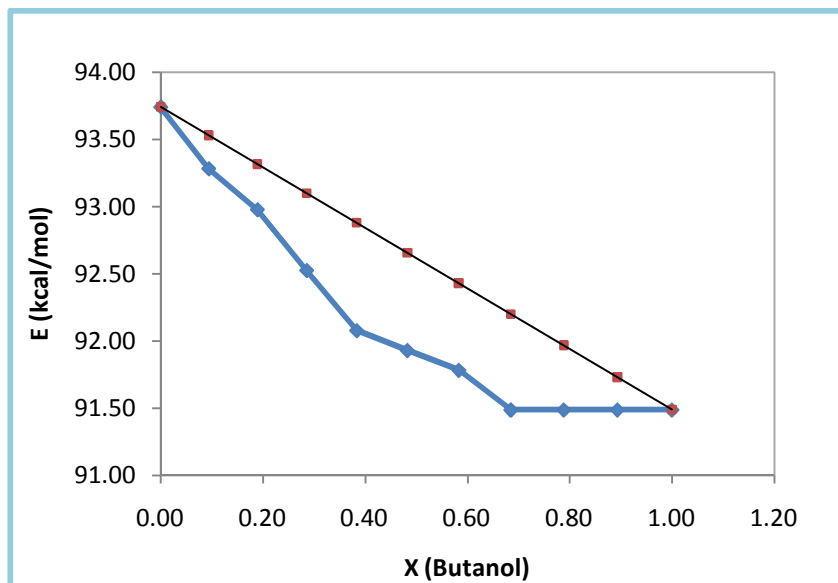


Figure 6: Plot of spectroscopic transition energy (E) of PNP vs. molefraction (X) of butanol in butanol-dioxan binary mixture. The straight lines represent ideal solvation.

From the figure it is clear that, the observed transition energy deviates significantly from the ideal line. IN butanol and dioxane binary solvent mixture PNP prefers butanol over dioxane or in other word the PNP is preferentially solvated by butanol. These result can be explained through the polarity parameter π^* and hydrogen bond accepting parameter β . The values of π^* and β are 0.46 and 0.88 in butanol and 0.55 and 0.37 in dioxane. Though the polarity of dioxane is higher than butanol, due to high difference in β value, PNP is preferentially solvated by butanol.

4. Conclusion

PNP shows positive solvatochromism. The positive Solvatochromism of PNP is explained through polarity and hydrogen bond acceptor ability of the solvent. In butanol-dioxane binary solvent mixture, PNP is preferentially solvated by butanol with higher hydrogen bonding accepting ability. Thus UV-VIS spectroscopic method is suitable way for investigating the preferential solvation, solute-solvent interaction and molecular recognition.

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