Preferential solvation of *p*-nitroaniline in alcohol-dioxan binary solvent mixture

A Dissertation
Submitted for the partial fulfillment

FOR THE DEGREE OF
MASTER OF SCIENCE IN CHEMISTRY

Under Academic Autonomy
NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

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CERTIFICATE

This is to certify that the dissertation entitled "**Preferential solvation of p-nitroaniline in alcohol-dioxan binary solvent mixture**" being submitted by **Sukhamoy Gorai** 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. Gorai bears a good moral character.

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ACKNOWLEDGEMENTS

With deep regards and profound respect, I avail this opportunity to express my deep sense of gratitude and indebtedness to Dr. Sabita Patel, Department of Chemistry, National Institute of Technology, Rourkela, for introducing the present project topic and for her inspiring guidance, constructive criticism and valuable suggestion throughout the project work. I most gratefully acknowledge her constant encouragement and help in different ways to complete this project successfully.

I would like to acknowledge my deep sense of gratitude to Dr. R. K. Patel, Head, Department of Chemistry, National Institute of Technology, Rourkela, for his valuable advices and constant encouragement for allowing me to use the facilities in the laboratory.

I would like to thank Ms. Sarita Garnayak with immense pleasure for her valuable guidance and constant encouragements. I wish to thank my lab partner Prakash and other friends for their help and valuable suggestions throughout my project work.

Last but not the least, I remember with gratitude my family members who were always a source of strength, support and inspiration.

(Sukhamoy Gorai)

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Preferential solvation of *p*-nitroaniline in alcohol-dioxan binary solvent mixture

1. Introduction

1.1 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 solvation process, a relatively small amount of solute dissolves in relatively large amount of solvent to form a homogeneous phase through a variety of intermolecular forces such as solvent-solvent interaction, solute-solvent interaction and solute-solute interaction. The solute-solute interactions gradually disappear and replaced by solute-solvent interactions during the dissolving process. 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. If the liberated solvation energy is lower than the lattice energy, then the overall process of dissolution is endothermic and if the solvation energy is higher than the lattice energy, then the overall process is called exothermic.

1.2 Preferential solvation

The solvation phenomena in mixture of solvents e.g binary, ternary etc. is more complicated than in pure solvents. In addition to the different types of interaction between solute and solvent, the interaction between solvent mixtures plays a significant role in the solvation process. This leads to the large deviation from the ideal behavior expected from the Roult'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.
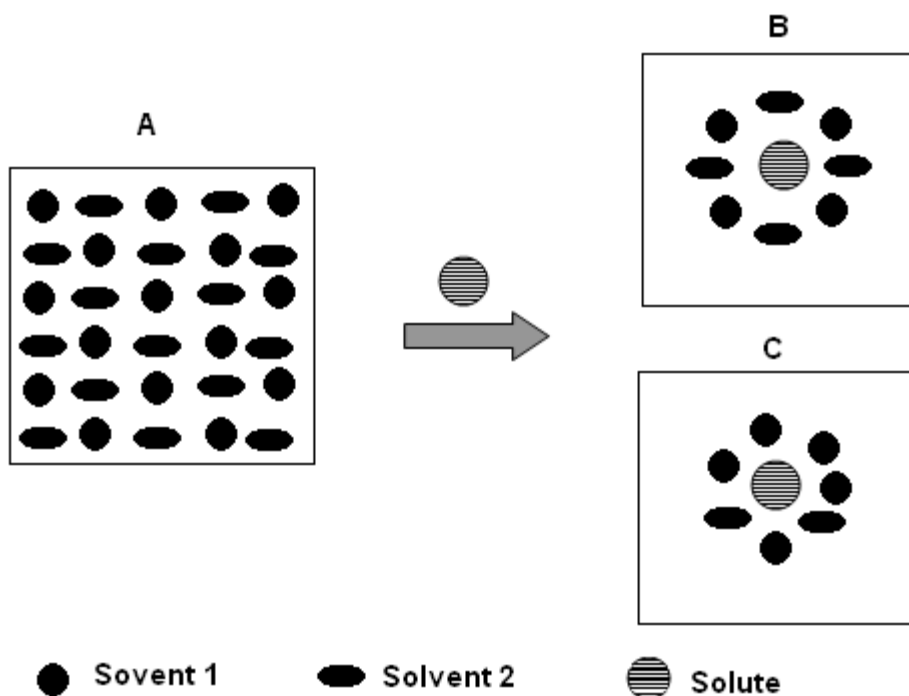

Figure 1: Schematic representation of preferential solvation, A : binary mixture of solvent 1 and solvent 2; B: ideal solvation of the solute; C: preferential solvation of the solute by solvent 1.

Solute with a dipole may preferentially be solvated at two different loci with different composition of the binary mixture. This type of selective solvation has been suggested for the solubilization of chloro-oxalato-tripyridine rhodium(III) complex (**1**),

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 (figure 2).[1]
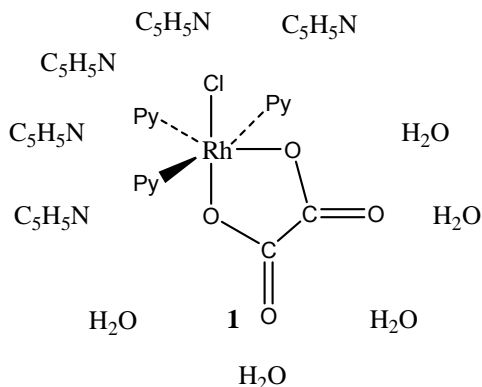
C_5H_5N C_5H_5N

C_5H_5N

C_5H_5N

Cl

Py   Py

H_2O

Py   Rh   O

C_5H_5N O   C=O H_2O

C

H_2O **1**   O H_2O

H_2O

Figure 2: Selective solvation of different parts of complex 1 by pyridine and water

1.3 Different techniques to study preferential solvation

In recent years a large number of study have been undertaken both experimentally and theoretically to understand the preferential solvation of dipolar 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

It 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 solvent molecules to the 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 Co(acac)$_3$ in 1:1 chloroform-carbon tetrachloride binary mixture.[2] From ^{59}Co chemical shift measurement, it was found that Co(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-methylbutyramide (NMBA) in acetonitrile-water and dioxan-benzene solvent mixtures from intermolecular ^{1}H 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 (**2**), 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).
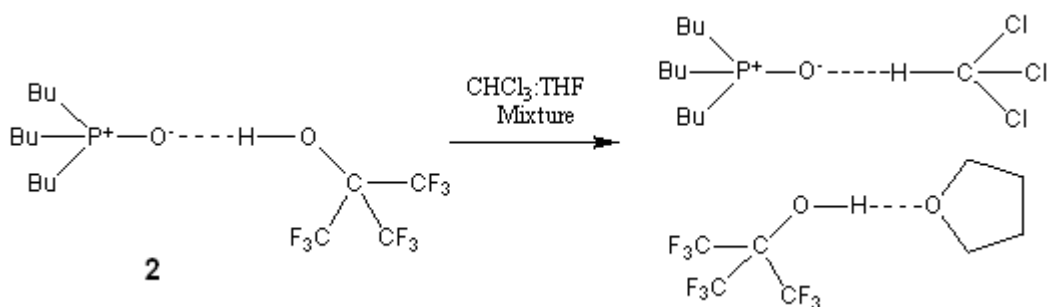
Scheme 1 Preferential solvation of complex 2 in chloroform-tetrahydrofuran binary mixture

Fluorescence emission method

Solvatochromic shift of the fluorescence spectra 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 based on the differential solvation of fluorescent molecule. Reorientations of the solvent molecule can takes place after electronic excitation and in the relaxed excited state solvation equilibrium occur. Petrov has extensively studied and reviewed regarding fluorescence as a method to study preferential solvation in binary solvent mixtyre.[6]

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-DMSO, Acetonitrile-ethanol and benzene-ethanol.[7]

Jozefowicz has studied the preferential solvation of fluorenone and 4-hydroxyfluorenone in binary solvent mixtures (cyclohexane–tetrahydrofuran and cyclohexane–ethanol) using steady-state spectroscopic measurements.[8] 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 solute–solvent 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.[9] 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.

IR spectroscopy method

An infrared spectra is markedly affected by environmental factors of the solute molecule. Solvent plays an important role on IR spectrum. Increasing the solvent polarity the absorption band comes to the lower wave length. This is because of the interaction between the polar solvent and polar moiety of the solute through hydrogen bonding and dipole-dipole interaction.

Kwak et. al.[10] 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, CCl_4, mesitylene (1, 3, 5 trimethylbenzene), and the mixed solvent of mesitylene and CCl_4 (0.83 mole fraction CCl_4), 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 mixed solvent's mole fraction.

Steady-state and time-resolved infrared spectroscopy of the azide (N_3^-) anion has been used to characterize aqueous mixtures both with the ionic liquid (IL) 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]) and with dimethyl sulfoxide (DMSO). The results are discussed in terms of preferential solvation and the degree of water association in the mixtures. [11]

UV-visible spectroscopy method

Uv-vis absorption spectra of molecule are highly dependent on polarity of the used solvent. The intensity, position and shapes of the absorption bands often change with the polarity of the solvent. 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 ground state and the excited state. This solvent effect on spectra of the compound, resulting a hypsochromic (or blue) shift with increasing the solvent polarity is usually called negative solvatochromism. The corresponding bathochromic (or red) shift is termed positive solvatochromism. From a number of literature survey, the UV-visible study provides a new opportunity to investigate how solute could be preferentially solvated in binary mixture solvents through the specific and non-specific interactions.

Oka and Kajimoto proposed a model to estimate of the number of solvent molecules solvating to the solute using 4-(N-N′methylamino) benzonitrile in super critical CF_3H with UV absorption utilizing the solvatochromic shift.[12] Bagchi and co-workers[13-19] 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 solute-solvent and solvent-solvent interaction. H-bonding is the major factor for preferential solvation. They also suggested three parameters like solvent polarity-polarizability, H-bond donation (HBD) ability and H-bond acceptor (HBA) capability for the difference in solute-solvent interaction.

2. Experimental

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-nitro aniline (PNA) as a solvatochromic indicator, in different alcohol (an amphiprotic solvent) and dioxan (hydrogen bond acceptor solvent) binary solvent mixtures monitoring the absorption band of PNA.

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 (Shimadzu) 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 ±0.5 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 Discussions

The longest wavelength absorption band in electronic spectra of PNA appears due to intermolecular charge transfer (ICT) from -NH$_2$ to –NO$_2$ group.[23]   With change in solvent polarity the ICT band exhibits a positive solvatochromism (Table 1). The charge separated excited state of PNA is more polar than the ground state, thus stabilized more with increase in solvent polarity compared to the ground state which reduces the energy difference between ground and excited state intern reducing the maximum energy of absorption resulting in a positive solvatochromism (Figure-3).[12]

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

| Sl.No.	Solvent	λ_{max} in nm	Sl.No.	Solvent	λ_{max} in nm
1	Hexane	320	11	Methanol	370
2	Toluene	340	12	Ethanol	372
3	Benzene	344	13	1-Propanol	375
4	Dichloromethane	349	14	2-Propanol	376
5	Dioxan	354	15	1-Butanol	375
6	Diethylether	349	16	*iso*-Butanol	376
7	Ethylacetate	358	17	Hexanol	370
8	Acetone	366	18	Cyclohexanol	379
9	Tetrahydrofuran	364	19	Octanol	365
10	Dimethylsulphoxide	389	20	Water	380
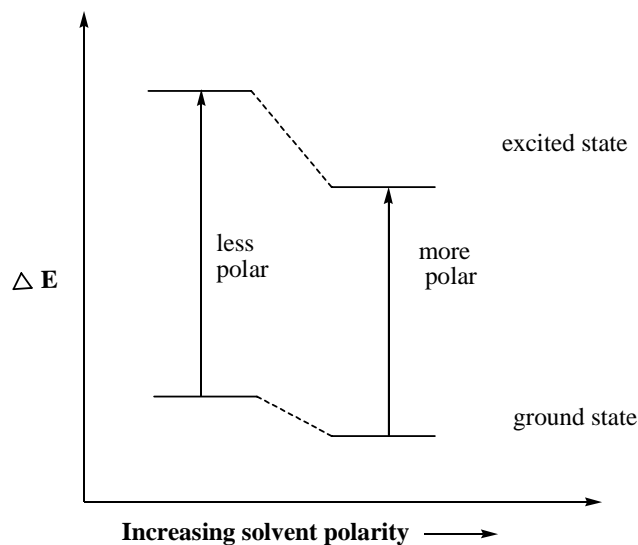
Figure 3: schematic representation of solvent effects on the electronic transition energy of PNA; Illustration of positive solvatochromism.

If the binary mixture is ideal in nature then the maximum spectroscopic transition energy, E(12id) in two different solvents 1 and 2 will be as per eqn (1)[24]

$$E\,(12id) = x_1E_1 + x_2E_2 \tag{1}$$

Where E_i and x_i represent respectively the maximum transition energy of absorption (TE) and mole fraction of ith solvent. Thus, for ideal solvation in a binary solvent mixture, a plot of the observed transition energy (E(12)) values will be linear in mole fraction 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.[13-19] To study the solvation mechanism of PNA in alcohol-dioxan binary solvent mixture, we have taken different alcohols such as methanol, ethanol, propanol, 2-propanol, butanol, iso-butanol, hexanol, cyclohexanol and octanol with varied polarity and hydrophobicity. The λ_{max}, E(12), E(12id), the deviation from Δ (Δ= E(12)- E(12id))[19] have been calculated and E(12)

vrs. mole fraction of the component solvent has been plotted. Figure 4 shows a reprentative plot of E(12) vrs. mole fraction of alcohol in alcohol-dioxan binary mixture. From all the plots it is clear that the observed transition energy deviate significantly from the ideality which indicates the presence of preferential solvation of PNA in the medium. The observed E(12) of the solute depends on the compositions of the solvent mixture in the solvation shell, thus E(12) can be related to the local composition 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 local mole fraction X_1^L of the solvent 1 can be calculated by using equation 2[19]

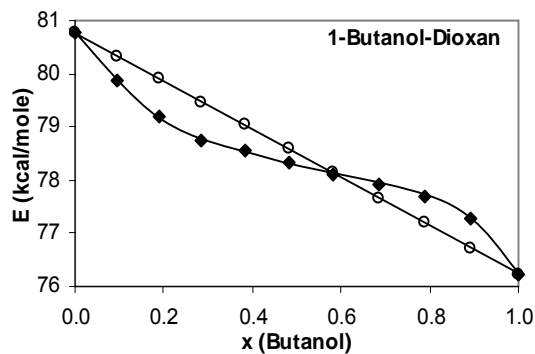$$x_1^L = E(12)-E_2 / (E_1 - E_2) \tag{2}$$

Figure 4: Plot of spectroscopic transition energy (E) of PNA vs. molefraction (X) of butanol in butanol-dioxan binary mixture. The straight lines represent ideal solvation.

In binary solvent mixture of ethanol+hexane and ethanol+dichloromethane, negative deviation is observed which indicates that the PNA prefers ethanol over hexane and DCM. These results can be explained in terms of the higher polarity of the ethanol. 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. In alcohol-dioxan binay mixture, increase in the mole fraction of alcohol 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 existence of both positive and negative deviation in all the plots of TE vs. mole fraction (figure 4) is attributed to the specific solute-solvent, solvent-solvent interaction (hydrogen bonding). Besides hydrogen bonding hydrophobicity has also a major role to play in the replacement of dioxane from the solvation shell.

4. Conclusion

In the alcohol dioxan binary solvent mixture, preferential solvation is mainly due to specific solute-solvent interaction due to hydrogen bonding. Beside hydrogen bonding hydrophobicity of the alcohol has also a major contribution towards the replacement of dioxan from the solvation shell. Thus Information about the local region around a solute in a binary solvent mixture can be obtained by monitoring the electronic spectra of the probe solute.

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