

Preferential solvation of 4-(4-nitrophenylazo) aniline in alcohol-dioxane binary solvent mixture

A Dissertation Submitted for the partial fulfilment

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 4-(4-nitrophenylazo) aniline in alcohol-dioxan binary solvent mixture” being submitted by Anupam Sahoo & Susanta Kumar Behera 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 them 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 Anupam Sahoo & Mr Susanta Kumar Behera bear good moral character.

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(Sabita Patel)

Date:

ACKNOWLEDGEMENT

We owe cordial gratitude to our respected teacher and supervisor Dr. Sabita Patel, Assistant Professor, Department of Chemistry, National Institute of Technology, Rourkela, whose splendid guidance, authentic supervision, assiduous cooperation, moral support and constant encouragement enabled us to make our research work in the present form.

It is our great pleasure to acknowledge to Prof. B.G. Mishra, Head of the Chemistry Department, National Institute of Technology, Rourkela for providing us the necessary facilities for making this research work a success.

We are highly indebted to all the teachers of this department for their kind help and expert suggestions.

We express our profound gratitude to Mr. Prakash Kumar Malik & Ms. Sarita Garnayak for their ceaseless encouragement, immense help and hearty encouragement during our project work.

We wish to thank all our friends for making our stay in this institute a memorable experience.

Finally, we must record our special attention to our Parents and GOD who have always been a source of our strength, inspiration and achievements.

Anupam Sahoo

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CONTENTS

1. Introduction

2. Experimental

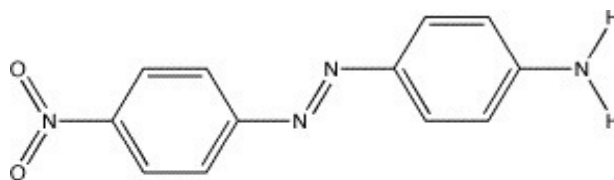
3. Results and Discussion

4. Conclusion

5. References

ABSTRACT:

Electronic spectroscopy is 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 binary solvent, the composition of liquid mixture around the solute (solvation shell) is different from that of the bulk. The inhomogeneity created by the solute molecule in the solvation shell is known as preferential solvation. Owing to the applicability of various azo dyes and the importance to study solute-solvent interaction, herein we have made an attempt to study the preferential solvation of 4-(4-nitrophenylazo) aniline (NPA) in binary solvent mixtures of alcohol with dioxane.



4-(4-nitrophenylazo) aniline

With increase in solvent polarity, the maximum spectroscopic absorption of NPA experience a red shift (bathochromic shift) indicating a positive solvatochromism. These facts can be explained in terms of the greater stabilization of the 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.

In all the case, the molecule of solute is preferentially solvated by alcohols over dioxane due to (i) hydrogen bonding (ii) dipole- dipole interaction and (iii) apolar/hydrophobic interaction In some cases, synergism is observed due to higher solvent-solvent interaction than solute-solvent interaction. The balancing of both polar and apolar characetrisitcs in the solvent cage show significant solvatochromism.

Key words: 4-(4-nitrophenylazo) aniline, preferential solvation, solvatochromism, apolar interaction

1. Introduction

The solvation of ions and molecules in solvent mixtures is more complicated than solvation in neat solvent due to increase in number solute solvent interactions and solvent-solvent interactions. It has been seen that the solvation of ions and dipolar molecules, the composition of solvent mixtures around the solute (solvation shell) can be different from that in the bulk solution. Generally the solute is surrounded preferably by the component of the mixture which leads to the more negative Gibbs energy of solvation, G_{solv}° . This phenomenon that the solvent shell has a composition other than the bulk is termed as selective or preferential solvation.[1-6]

2. Experimental

Electronic spectroscopy provides a suitable method for studying preferential 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 4-(4-nitrophenylazo) aniline as a solvatochromic indicator, in different alcohol (an amphiprotic solvent) and dioxane (hydrogen bond acceptor solvent) binary solvent mixtures.

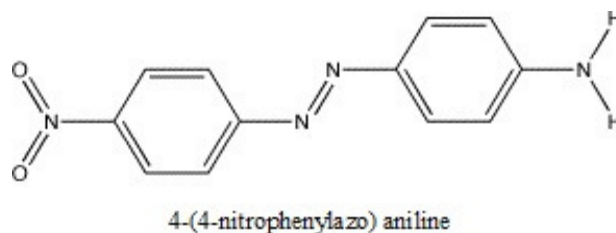
4-(4-nitrophenylazo) aniline is prepared using the method reported earlier [7]. It was purified by recrystallization with ethanol and characterized. The solvents selected are purified following standard procedure. Absorption spectra of NPA in different binary dioxane- alcohol mixtures were recorded spectrophotometrically by using a Shimadzu model UV-Visible spectrophotometer. The binary mixtures were prepared by maintaining various percentage of dioxane (0%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, and 100%) in the NPA

solution. For the purpose, appropriate dioxane- alcohol mixtures were prepared by mixing dioxane and different alcohols and were left as such for 15 minutes. Stock solution of NPA were prepared ($[NPA] = 2.4 \times 10^{-3} \text{ M}$) in dioxane. From this stock solution 0.1 mL was added to 4.9 mL of alcohol so that concentration of the NPA in binary mixture was always maintained at $5 \times 10^{-5} \text{ M}$. Spectra of all the compounds in different solvent compositions were recorded after sometime. The energy of maximum absorption was calculated using the following formula.

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

3. Results and Discussion:

Owing to the applicability of various azo dyes and the importance to study solute-solvent interaction, herein we have made an attempt to study the preferential solvation of 4-(4-nitrophenylazo) aniline (**NPA**) in binary solvent mixtures of alcohol with dioxane.



The maximum spectroscopic transition energy (λ_{max}) of NPA originates due to $\pi \rightarrow \pi^*$ transition, which appears at 391–417nm in solvents with varying polarity (i.e. from benzene to dimethylsulfoxide). Though $\pi \rightarrow \pi^*$ transition generally shows small solvatochromic shift, due the presence of donor (aniline group) and acceptor (nitrobenzene group) moieties, the ground and excited state dipole moment increases showing a large solvatochromic shift. The spectrum 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 rather it is only due to the change in environment.

With increase in solvent polarity, the maximum spectroscopic absorption of NPA experience a red shift (bathochromic shift) indicating a positive solvatochromism. These facts can be explained in terms of the greater stabilization of the 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.

To study the solvation pattern of NPA in binary mixtures of alcohol and dioxane, λ_{\max} of NPA is recorded with varied composition of the solvents. Figure 1-6 show the plots of $E(12)$ (energy of absorption in binary mixture of solvent 1 i.e. alcohol and solvent 2 i.e. dioxane) as a function of mole fraction of alcohol along with the ideal lines. It appears that the experimental data points deviate significantly from the ideal line. The deviation $\Delta(= E(12)-E(12id))$, from the experimental value have been calculated. Other parameters like local mole fraction of the solvents x_1^L and x_2^L , $\delta_i(=x_i^L - x_i)$ which is the measure of the excess or deficit of the i th solvent in the local region compared to that in the bulk are calculated.

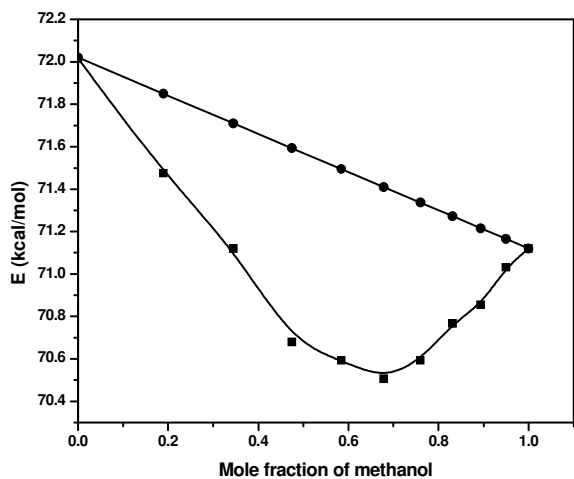


Figure 8: Plot of E, the energy of maximum absorption of the 4-(4-nitrophenylazo) aniline as a function of solvent composition in methanol+ dioxane binary mixture.

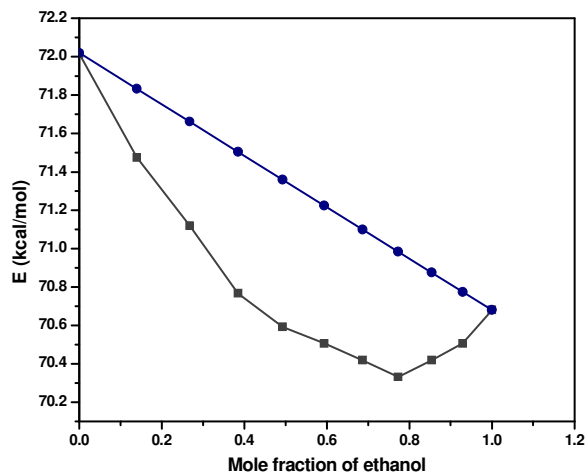


Figure 9: Plot of E, the energy of maximum absorption of the 4-(4-nitrophenylazo) aniline as a function of solvent composition in ethanol+ dioxane binary mixture.

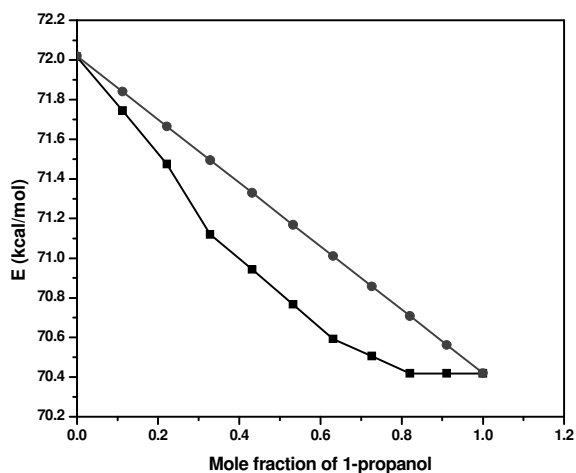


Figure 10: Plot of E, the energy of maximum absorption of the 4-(4-nitrophenylazo) aniline as a function of solvent composition in 1-propanol+ dioxane binary mixture.

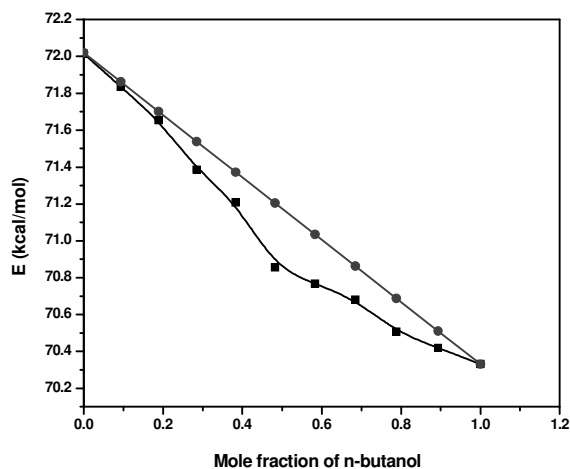


Figure 11: Plot of E, the energy of maximum absorption of the 4-(4-nitrophenylazo) aniline as a function of solvent composition in n-butanol+ dioxane binary mixture.

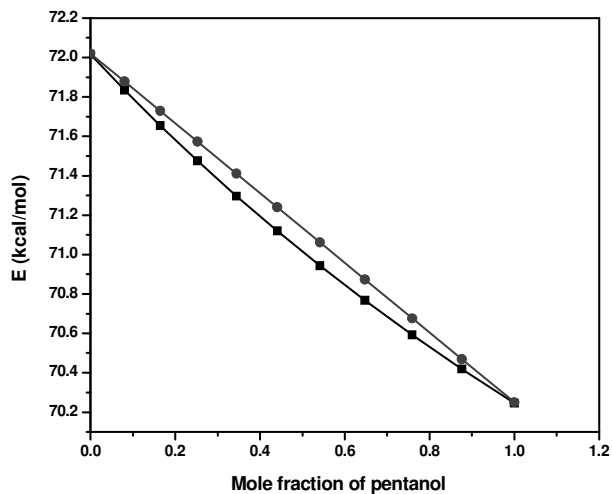


Figure 12: Plot of E, the energy of maximum absorption of the 4-(4-nitrophenylazo) aniline as a function of solvent composition in pentanol+ dioxane binary mixture.

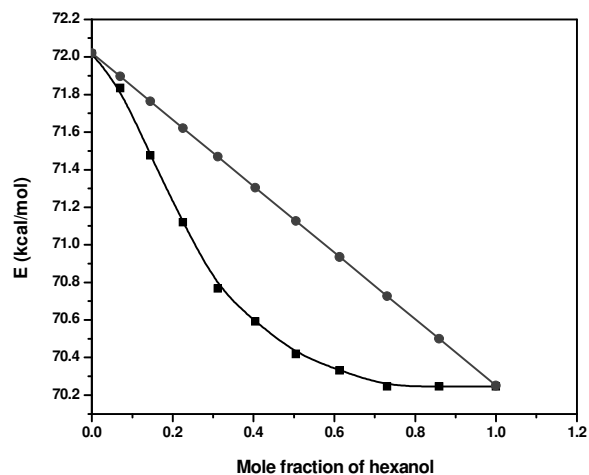


Figure 13: Plot of E, the energy of maximum absorption of the 4-(4-nitrophenylazo) aniline as a function of solvent composition in hexanol+ dioxane binary mixture.

In all the alcohol-dioxane binary solvent mixtures, NPA is preferentially solvated by alcohol. Polarity of alcohols is not the only reason for preferential solvation as the polarity of dioxane is more than that of butanol, pentanol and hexanol. Thus the specific interaction (H-bonding) is playing a major role in the solvation of NPA due to hydrogen bond donor and higher hydrogen bond acceptor properties of alcohols than dioxane.

The extent of preferential solvation in the alcohol series, $\delta_1 (= x_1^L - x_1)$, which is a measure of the excess or deficit of the alcohol in the local region compared to that in the bulk, is compared. In all the cases from methanol to hexanol, δ_1 was found to be positive. The point of maximum δ is considered for comparison of the extent of preferential solvation. δ_1 or the extent of PS decreases with decrease in polarity and with increase in hydrophobicity up to pentanol while for hexanol the trend is reverse. Further, with increase in α (hydrogen bond donor acidity)⁸ of the alcohols extent of PS increases, whereas with increase in β (hydrogen bond acceptor basicity)⁹ PS decreases (figure 16). As in the solvation of NPA both HBA and HBD ability of the solvents are important, the decrease of PS with increase in β can be attributed to simultaneous increase in the hydrophobicity of the solvents.

Due to the donor-acceptor characteristics of the chromophoric group, it may be assumed that the polar part, like ethereal oxygen of dioxane, hydroxyl group of alcohols will be oriented toward the probe and stabilise both the ground and excited state of the probe through hydrogen bonding and dipole-dipole interaction. Alcohol forms H-bond with both the $-NH_2$ and $-NO_2$ group as hydrogen bond acceptor and hydrogen bond donor respectively. Increase in hydrophobic units in the alcohols will decrease the binding of these groups with the probe as evident from the plot of $\log P$ vs. δ with concomitant decrease in preferential solvation. Further,

positive solvatochromism with increase in methylene units in the alcohol component is due to a balance of polar and nonpolar groups of the solvent in the solvation process as well as to the orientation of solvent molecule around the probe. In case of hexanol, the reverse trend is may be due to its higher hydrophobicity compared to HBA or HBD ability. Thus the probe, NPA though having polar groups like $-\text{NH}_2$, $-\text{NO}_2$ and $-\text{N}=\text{N}-$, the presence of two hydrophobic benzene ring compensates the polarity and the solvents are orientated in such a way that both the hydroxyl and alkyl groups remain close to the chromophoric unit solvating through both polar and apolar characteristics.

4. Conclusion

The preferential solvation of 4-(4-nitrophenylazo) aniline in binary mixture of dioxane and different alcohol has been studied by using UV-Vis absorption technique. In all the case, the molecule of solute is preferentially solvated by alcohols over dioxane due to (i) hydrogen bonding (ii) dipole- dipole interaction and (iii) apolar/hydrophobic interaction In some cases, synergism is observed due to higher solvent-solvent interaction than solute-solvent interaction. The balancing of both polar and apolar characetrisitcs in the solvent cage could show significant solvatochromism.

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