Effect of solvent in azo-hydrazone tautomerism of 1-phenylazo-2-naphthol (Sudan I)

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CERTIFICATE

This is to certify that the dissertation entitled "Effect of solvent in azo- hydrazone tautomerism of 1-phenylazo-2-naphthol (Sudan I)" being submitted by Madhabi Seth & Chitta Ranjan Biswal 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 Ms. Madhabi Seth and Mr. Chitta Ranjan Biswal bears a good moral character.

NIT-Rourkela   **(Sabita Patel)**

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ABSTRACT:

The increasing usage of azoic dyes in textile, food, paper printing and cosmetic industries, in electronic industry, such as colorimetric sensors, nonlinear optical (NLO) devices and liquid crystalline displays (LCDs) has attracted much attention in the study of synthesis and properties of different azo dyes. The azodyes with atleast one protic group in conjugation with azo linkage shows azo-hydrazone tautomerism. The importance and various applications of azo dyes promted us to study the solvent effect of 1-phenylazo-2-naphthol (Sudan I) in neat and binary mixture of solvents. Sudan I was synthesized purified and characterized. Absorption spectra of Sudan I in different binary hexane-alcohol mixtures were recorded spectrophotometrically by using a Shimadzu model UV-Visible spectrophotometer. Effect of solvent in azo-hydrazone tautomerism of Sudan-I is studied using UV-Vis spectroscopic method. The percentage of tautomers in neat solvent and binary solvent mixtures of hexane with alcohols were calculated from the absorbance data and correlated with various solvent parameters. In highly nonpolar solvents like hexane, both the forms contribute equally to the equillibrim mixture. With increase in polarity and hydrogen bonding ability, the stability of hydrazone form increases. The contribution of different parameter have been calculated using multiparametric regression equation and explained considering specific solute-solvent interaction and through cooperative hydrogen bonding. In binary mixtures of hexane-alcohol, the change in amount of tautomers with change in volume percent of alcohols is explained through preferential solvation.

Key words: Solvation, preferential solvation, azo-hydrazone tautomerism, Sudan I, binary mixtures

1. Introduction

The increasing usage of azoic dyes in textile, food, paper printing and cosmetic industries, in electronic industry, such as colorimetric sensors, nonlinear optical (NLO) devices and liquid crystalline displays (LCDs) has attracted much attention in the study of synthesis characterization purification and application of natural and synthetic dyes and azo dyes as antibacterial [1-41].

The azodyes with atleast one protic group in conjugation with azo linkage shows azo-hydrazone tautomerism (Scheme 1). The azodyes with atleast one protic group in conjugation with azo linkage shows azo-hydrazone tautomerism. This kind of an equilibrium in azo compounds was first postulated by Liebermann in 1883 by assertion of a labile hydroxyl proton in 1-phenylazo-2-naphtol (C.I. Solvent Yellow 14) that is capable of bonding with a nitrogen atom of the azo group [30] .


Azo (A) form   **Hydrazone (H) form**
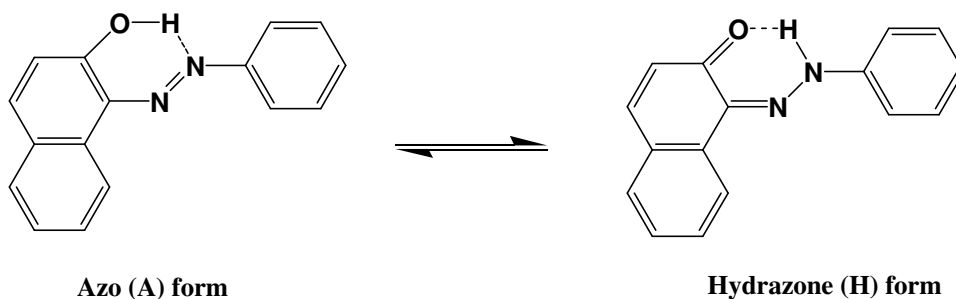
Scheme-1: Azo-hydrazone tautomerism of 1-phenylazo-2-naphtol (Sudan I)

2. Experimental

(i)   Synthesis of Sudan I

The dye used in this study was synthesized according to a published procedure [15]. 2-naphthol (78 mg, 0.0005 mole), sodium hydroxide (3M, 0.5 mL) were mixed. The mixture was cooled to 0^oC. A solution of aniline (50 mg, 0.00053 mole), concentrated hydrochloric acid (12 M, 0.25 mL) and 0.5 mL distilled water were warmed and a solution of sodium nitrite (50 mg, 0.00053 mole) in 0.5 mL of distilled water at 0^oC was added and this prepared solution was added to the above cold mixture with good stirring. A blood red solid was formed and reaction left upto 20 min in ice- bath. The crude product formed was filtered, washed with cold water, dried and purified by recrystallization from ethanol. Melting point $= 130^oC$.
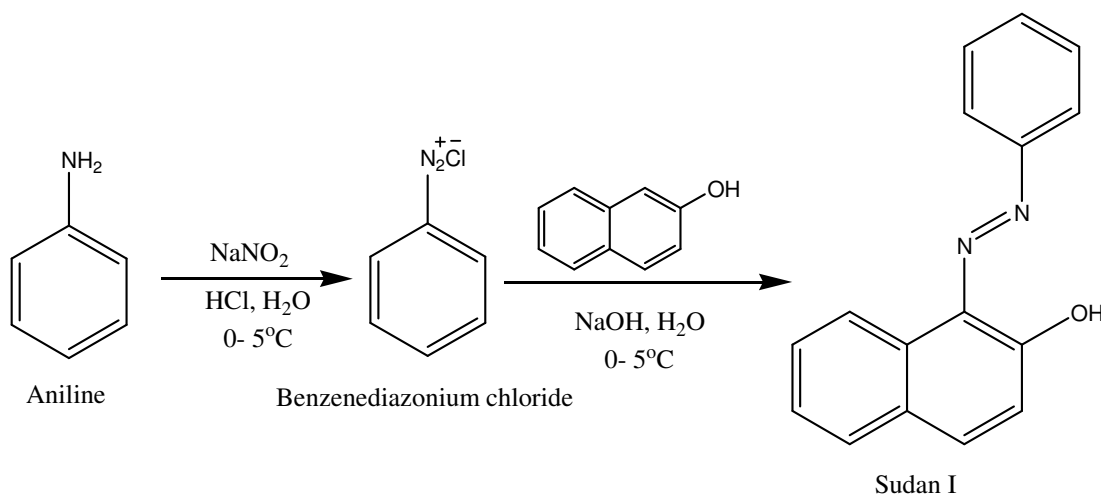
(ii)   Purification of solvents

n-Hexane: for distillation of n-hexane, calcium hydride (CaH_2) was used as drying agent, then it was distilled at 69^0C.

Ethanol: Ethanol was refluxed with fresh lime (CaO) for several hrs, and then it was distilled at 70^0C.

1-Propanol: 1-propanol was refluxed with fresh lime (CaO) for several hrs, and then it was distilled at 97^0C.

n-Butanol: n-Butanol was refluxed with potassium carbonate (K_2CO_3) for several hrs, and then it was distilled at 117^0C.

Pentanol: Pentanol was refluxed with fresh lime (CaO) for several hrs, and then it was distilled at 138^0C.

Hexanol: Hexanol was refluxed with fresh lime (CaO) for several hrs, and then it was distilled at 158^0C.

(iii) *Spectral measurement:*

Absorption spectra of Sudan I in different binary hexane-alcohol mixtures were recorded spectrophotometrically by using a Shimadzu model UV-Visible spectrophotometer. The binary mixtures were prepared by maintaining various percentage of hexane (0%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, and 100%) in the Sudan I solution. For the purpose, appropriate hexane- alcohol mixtures were prepared by mixing hexane and different alcohol s and were left as such for 15 minutes. Stock solution of Sudan I were prepared ([SI] = 2.4 x 10^{-3} M) in hexane. From this stock solution 0.1 mL was added to 4.9 mL of alcohol so that concentration of the Sudan I in binary mixture was always maintained at 5 x 10^{-5} M. Spectra of all the compounds in different solvent compositions were recorded after sometime. The percentage of azo and hydrazone tautomers in different solvents were determined from their corresponding absorbance value.

3. Results and Discussion

The present study aims to elucidate the solvent effect on the azo-hydrazone tautomerism of 1-phenylazo-2-naphthol (Sudan I) using UV-Vis spectroscopic method and to investigate the factors controlling the preference of one tautomer over the other. Solvent polarity scales are used to correlate the properties of solvent and amount of different tautomers in neat and binary solvent mixtures. Due to the presence of hydroxyl group in conjugation to the azo bridge in Sudan I leads to a prototropic equilibrium generally referred to as the azo-hydrazone tautomerism.

In Sudan I, the two tautomeric forms are isoenergetic in gas phase with energy difference of 1.1 kcal/mol [42]. . This is also true for highly non-polar solvent like hexane as evident from the absorbance in UV-Vis spectrum. Sudan I shows a peak around 460-500 nm for hydrazone form and a peak around 420-430 for azo form. From the absorbance in UV-Vis spectrum the percentage of azo and hydrazone tautomers are found to be 48.9 and 51.1 respectively in hexane. The change in the composition of tautomers with change in solvent is explained by correlating with different solvent parameters. On correlating the % of tautomers with ET(30) of the 19 selected solvents it is found that percentage of hydrazone form increases. Except for some solvents like chloroform, dichloromethane, acetone, dioxane and acetophenone, the plot of ET(30) versus amount of H-form is linear with correlation coefficient of 0.97, which delineate that with increase in polarity amount and stability of hydrazone form increases (Figure 1). The plot of % of H-form vs. logP and plot of % of H-form vs. π^* show decrease in stability of H-form with increase in hydrophobicity (figure 2). For azo form reverse is the trend in all the cases. The presence of two straight line, demarcate the solvents in two categories contributing differently to the stability of the tautomers. Alcohols with both HBD and HBD ability form one category while other category includes HBA solvents like ethylacetate, DMF, DMSO etc.
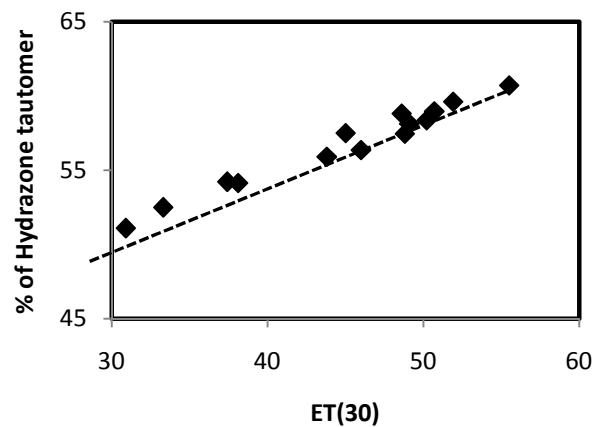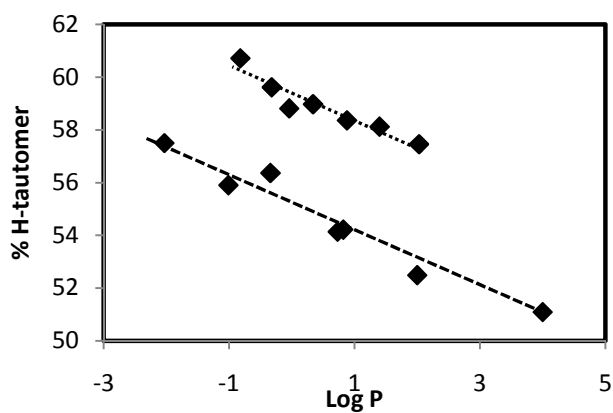
Figure 1: Plot of % of H-form versus ET(30) of solvents.

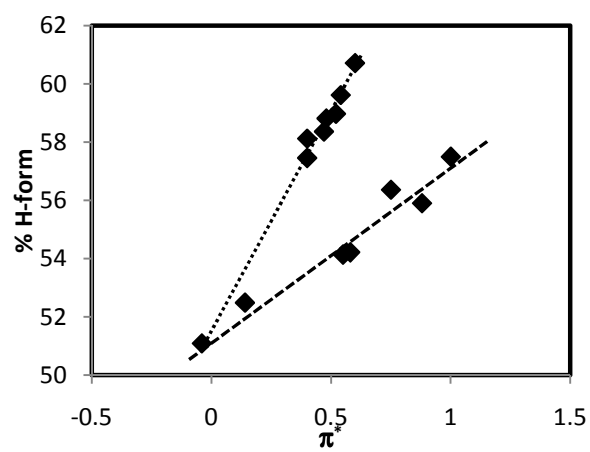**Figure 2:** Plot of % of H-form versus log P of solvents

Figure 3: Plot of % of H-form versus π^* of solvents

To find out the contribution of these parameters towards the stability of the tautomers through solvation, multiparametric regression equation is used (equation 1).

$$\% \text{ H-Form} = -5.44 \; \pi^* - 0.95 \; \text{logP} - 0.45 \; \alpha + 2.09 \; \beta + 0.315 \; \text{ET(30)} + 44.96 \tag{1}$$

$$(R^2 = 0.996)$$

From this regression equation, it is clear that π^*, logP and α has negative contribution while β and ET(30) has positive contribution towards the stability of H-tautomer. It is unexpected that, though π^* is a polarity parameter, a high negative contribution (-5.44) is observed and need to explain. From eq-1 it is found that, increase in HBD ability (α) stability of H-tautomer decreases. In this work we have considered two type of solvents (i) alcohols with both HBA and HBD ability and (ii) solvents with HBA ability. For most of the HBA solvents selected for the project work, the α is zero. Thus considering only the selected alcohols, the stability of H-form increases with increase in α . Further, with increase in HBA ability (β) stability increases. It can be explained through the specific solute-solvent interaction through hydrogen bonding.

In binary mixtures of hexane with alcohols, with increase in alcohol content, percentage of hydrazone form increases (figure 4). Further with increase on polarity and HBD ability of solvents, percentage of hydrazone tautomer increases. At the higher vol % of alcohols, the difference in stability of H- form due to change in alcohols is more compared to lower vol % of alcohols. These facts can be explained through preferential ssolvation of Sudan I with alcohol through specific solute solvent interaction.
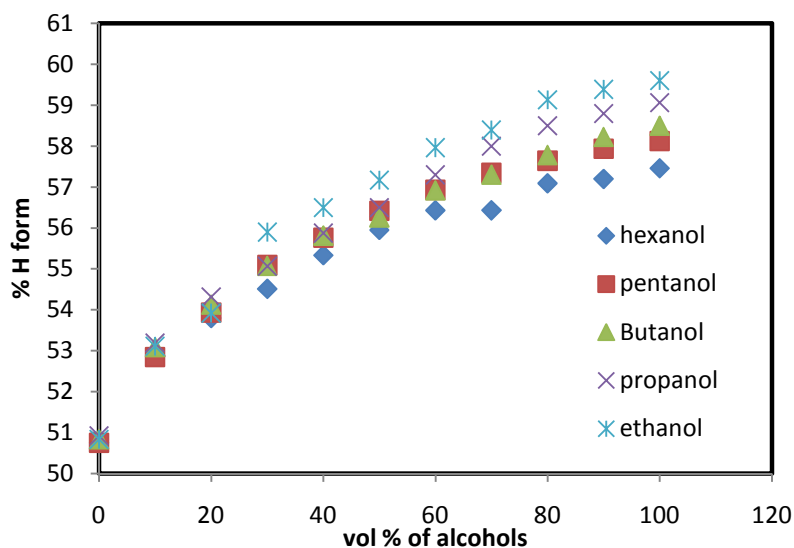
Figure 4: Plot of % H-form vs. vol% of alcohols

4. Conclusion

Effect of solvent in azo-hydrazone tautomerism of Sudan-I is studied using UV-Vis spectroscopic method. The percentage of tautomers in neat solvent and binary solvent mixtures of hexane with alcohols were calculated from the absorbance data and correlated with various solvent parameters. In highly nonpolar solvents like hexane, both the forms contribute equally to the equillibrim mixture. With increase in polarity and hydrogen bonding ability, the stability of hydrazone form increases. The contribution of different parameter have been calculated using multiparametric regression equation and explained considering specific solute-solvent interaction and through cooperative hydrogen bonding. In binary mixtures of hexane-alcohol, the change in amount of tautomers with change in volume percent of alcohols is explained through preferential solvation.

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