EFFECT OF SOLVENT POLARITY ON THE ELECTRONIC ABSORPTION SPECTRA OF SOME PHENYL AZO MOIETIES OF 2-NAPHTHOL, RESORCINOL AND 1, 2-DIHYDROXYANTHRAQUINONE.

HAMILTON-AMACHREE A.
AND
MENEGBO LEDESI ISRAEL

ABSTRACT
This paper reports the synthesis of azo compounds by linking diazonium salts obtained from aromatic amines: aniline, 2-aminophenol, 4-aminobenzoic acid and 3-nitroaniline to the coupling components: resorcinol, 2-naphthol and 1,2-dihydroxyanthraquinone through the well-known diazo-coupling reactions. The % yields and melting pointsof the recrystallized azo dyes gave ranges: 65 – 97% and 120 – 230°C respectively. The effect of solvent polarity on the UV-Vis spectral properties of these azo dyes was investigated. The electronic spectral data for the nine azo compounds showed bathochromic red shifts (positive solvatochromism) in the highly polar protic solvent, ethanol and polar aprotic solvent, acetonitrile in contrast to the less polar aprotic solvent acetone.

Keywords: Solvent Polarity, Electronic absorption spectra, Azo compounds.

INTRODUCTION
It is an established fact that chemical processes are influenced by the properties of solvents in which they are carried out. These properties include the dipole moment, dielectric constant, acidity, and refractive index values. The most important property in this regard is the solvent polarity which can alter the position of the absorption or emission band by solvating solute molecules or any other molecular species introduced into the solvent matrix (Reichardt, 1991; 2004)

The extent of this solvation depends on the intermolecular forces between solute and surrounding solvent molecules. Intermolecular forces include nonspecific as well as specific forces. The non-specific forces include purely electrostatic forces arising from the coulomb forces between charged ions and dipolar molecules. Specific forces on the other hand include hydrogen bonding between hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA), electron pair donor (EPD) and electron pair acceptor (EPA) forces. (Reichardt, 1994). Medium effects caused by this differentialsolvation of molecules in the corresponding ground and excited states which induces a shift in the absorption band of electromagnetic radiation has been examined by a number of researchers (Kumar, 2006; Homocianu et al, 2011). Solvent polarity and pH have been observed to have a profound effect on the absorption spectrum of dyes (Mohammad et al, 2008). Tyrosine, for example, increases in absorption maxima and molar extinction coefficient when pH increased from 6 to 13.

Dye molecules which carry charge centers (as an integral part of their structure or because they are derived salts) are prone to absorption changes in various media (Oliveira et al, 2002). The structural complexity of azo dye molecules has drawn the attention of many research groups to understand their behavior in various media (Masoud et al, 1999, 2004; Adeogun, et al; 2007,
The knowledge of these media effects are pertinent in understanding the various physical-organic reactions of these molecules, considering their importance in different fields of pure and applied chemistry. Azo dyes have been studied widely because of their excellent thermal and optical properties in applications such as optical recording medium, toner, ink-jet printing and oil soluble lightfast dye applications (Kandill, 1998). The visible absorption spectra of some novel heterocyclic disazo dyes derived from barbituric acid did not correlate with the polarity of solvents. However, these disazo dyes exist in trisazo forms in the solid state, but in azo-enol forms in solvents. It was also observed that the absorption spectra of these disazo dyes in ethanol were quite sensitive to the addition of a base (Fati and Fikret, 2008). Recent reports on the synthesis, characteristics and solvatochromic properties of some new arylazopyridone dyes show that the wavelength of maximum absorptions and molar extinction coefficients are strongly dependent on the electron donating ability of the substituents on the coupling moiety. The absorption bands of these dyes moved towards longer wavelengths as the polarity of the solvents and electron density of substituents on the coupling moiety increased (Zakers, 2009).

In this study, the effect of solvent polarity on the spectroscopic properties of nine azo dyes prepared by employing the well-known diazotization and coupling reactions is being investigated.

EXPERIMENTAL
Materials and methods.
The chemicals used for this research include Hydrochloric acid, Sodium nitrite and Sodium Hydroxide (BDH), Ethanol, Glacial acetic acid, Acetone, Acetonitrile, Aniline, 2-Aminophenol, 4-Aminobenzoic acid, 3-Nitroaniline (Aldrich), 2-Naphthol, 1,2-Dihydroxyanthraquinone, Resorcinol (Sigma). Melting points of all the synthesized compounds were determined by open capillary method. The electronic absorption spectra of the various azo compounds in the respective solvents employed were recorded using Pye-Unicam Model Sp500 spectrophotometer within the wavelength region of 200-600 nm. Purification of the crude azo compounds was achieved by means of recrystallization.

Synthesis of phenyl azo moieties of 2-Naphthol, Resorcinol And 1, 2-Dihydroxyanthraquinone using the standard methods of diazotization and coupling

0.70 g (0.01 mol) of dry sodium nitrite was dissolved in 5 ml of distilled water and cooled to < 5°C in an ice bath. The resultant solution was added drop-wise to an ice cold solution of acidified aniline (0.011 mol, 1.02 ml). The cold diazonium salt solution was then coupled with a slightly alkaline solution of 2-Naphthol (0.01 mol, 1.67 g). The reaction mixture was stirred for a period of 1 h at a temperature of < 5°C. The colored crystals obtained were filtered, washed, with cold distilled water and dried at 40°C. The crude crystals obtained were purified by recrystallization using Glacial acetic acid. The percentage yield was calculated and melting point was determined. The same standard procedure was repeated for the preparation of the respective diazonium salts.
using the designated aromatic amines: 2-aminophenol, 4-aminobenzoic acid and 3-nitroaniline. The corresponding coupling reactions were carried out with the resultant diazonium salts and the coupling components: 2-naphthol, resorcinol and 1,2-dihydroxyanthraquinone (Vogel, 1979 and Carey, 2003). The equations for the preparation of the phenyl azo moieties of the respective azo compounds are presented in Schemes 1 and 2.
1- phenylazo-2- naphthol

4-(4'- carboxy phenylazo)-1,2- dihydroxy anthraquinone

1-(4'- carboxy phenylazo)-2- naphthol
Effect Of Solvent Polarity On The Electronic Absorption Spectra Of Some Phenyl Azo Moieties Of 2-naphthol, Resorcinol And 1, 2-dihydroxyanthraquinone.

aniline diazonium salt + alizarine → 4-phenylazo-1,2-dihydroxyanthraquinone

3- nitro phenyl diazonium salt + 2-naphthol → 1-(3-nitro phenylazo)-2-naphthol

aniline diazonium salt + resorcinol → 4-phenyl-3-hydroxy phenol
Scheme 2: Equations for the coupling reactions of diazonium salts to the designated coupling components

RESULTS AND DISCUSSION
Nine azo compounds (dyes 3a-3i) based on the coupling components: 2-naphthol, resorcinol, and 1,2-dihydroxyanthraquinone were prepared following the standard synthetic pathways (Vogel, 1979; Carey, 2003) for the diazotization and coupling as presented in schemes 1 and 2.

TABLE 1: Physical properties and percentage yields of the Azo dyes 3a-3i.

<table>
<thead>
<tr>
<th>Dyedesignation</th>
<th>Dyes</th>
<th>MeltingPoint</th>
<th>Colour</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>1-Phenylazo-2-Naphthol</td>
<td>120-122°C</td>
<td>Deep Pink</td>
<td>73%</td>
</tr>
<tr>
<td>3b</td>
<td>4-Phenylazo-1,2-dihydroxy Anthraquinone</td>
<td>160-162°C</td>
<td>Brownish Orange</td>
<td>95%</td>
</tr>
<tr>
<td>3c</td>
<td>4-Phenylazo-3-hydroxyphenol</td>
<td>127-128°C</td>
<td>Orange Red</td>
<td>80%</td>
</tr>
<tr>
<td>3d</td>
<td>1-(2-Hydroxyphenylazo)-2-Naphthol</td>
<td>174-176°C</td>
<td>GrayishPurple</td>
<td>69.8%</td>
</tr>
<tr>
<td>3e</td>
<td>1-(4-carboxyphenylazo)-2- Naphthol</td>
<td>180-200°C</td>
<td>ReddishOrange</td>
<td>69%</td>
</tr>
<tr>
<td>3f</td>
<td>4-(4'-Carboxyphenylazo)- 1,2-dihydroxyAnthraquinone</td>
<td>218-220°C</td>
<td>LightBrown</td>
<td>91%</td>
</tr>
<tr>
<td>3g</td>
<td>4-(4'-phenylazo)-3-hydroxyphenol</td>
<td>248-250°C</td>
<td>ReddishBrown</td>
<td>97%</td>
</tr>
<tr>
<td>3h</td>
<td>1-(3-Nitrophenylazo)-2- Naphthol</td>
<td>200-202°C</td>
<td>Brick Red</td>
<td>65%</td>
</tr>
<tr>
<td>3i</td>
<td>1-(3-Nitrophenylazo)-1,2-dihydroxyanthraquinone</td>
<td>229-230°C</td>
<td>Saddle</td>
<td>71%</td>
</tr>
</tbody>
</table>
The appreciable product yields of the dyes (65%-95%) as presented in Table 1 depict the satisfactory nature of the synthesis. This could be attributed to the coupling components, having positions of high electron densities which facilitated the rate of coupling. A good control over some reaction conditions like temperature which was maintained below 5°C may have also contributed to the yields recorded. The recrystallized compounds with well-defined melting points are characteristic of relatively pure compounds but the dependence of melting points on a number of factors such as geometry, interactions etc. however, limits detailed explanation of these values (Maradiya, 2002).

<table>
<thead>
<tr>
<th>Dye Designation</th>
<th>Ethanol $\lambda_{max}$ (nm)</th>
<th>Acetonitrile $\lambda_{max}$ (nm)</th>
<th>Acetone $\lambda_{max}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>460</td>
<td>440</td>
<td>400</td>
</tr>
<tr>
<td>3b</td>
<td>420</td>
<td>420</td>
<td>400</td>
</tr>
<tr>
<td>3c</td>
<td>460</td>
<td>460</td>
<td>420</td>
</tr>
<tr>
<td>3d</td>
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<td>3e</td>
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<td>3g</td>
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<td>3h</td>
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<tr>
<td>3i</td>
<td>460</td>
<td>440</td>
<td>400</td>
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</tbody>
</table>

The solvatochromic behavior of dyes 3a-3i was examined using a highly polar protic solvent, ethanol and two aprotic solvents, acetonitrile and acetone. The electronic spectradata recorded over the wavelength range of 200 nm-600 nm are summarized in Table 2 as well as Figures 1 to 9.

There was no significant change in the absorption spectra of these dyes in ethanol and acetonitrile except for dyes 3a, 3e and 3i. This could be attributed to the relative similarities of these solvents in polarity, depicted by their dielectric constants.
Fig. 2: Spectra of dye 3b in ethanol, acetone and acetonitrile
Effect Of Solvent Polarity On The Electronic Absorption Spectra Of Some Phenyl Azo Moieties Of 2-naphthol, Resorcinol And 1, 2-dihydroxyanthraquinone.

Fig. 3: Spectra of dye 3c in ethanol, acetone and acetonitrile

Fig. 4: Spectra of dye 3d in ethanol, acetone and acetonitrile
Fig. 5: Spectra of dye 3e in ethanol, acetone and acetonitrile

Fig. 6: Spectra of dye 3f in ethanol, acetone and acetonitrile
Effect Of Solvent Polarity On The Electronic Absorption Spectra Of Some Phenyl Azo Moieties Of 2-naphthol, Resorcinol And 1, 2-dihydroxyanthraquinone.

Fig. 7: Spectra of dye 3g in ethanol, acetone and acetonitrile

Fig. 8: Spectra of dye 3h in ethanol, acetone and acetonitrile
Fig. 9: Spectra of dye 3i in ethanol, acetone and acetonitrile

The spectra of these azo dyes in the three solvents used for this study shows a bathochromic effect (Red shift) of the absorption band in ethanol and acetonitrile, which is in contrast to that observed in acetone. Polar solvents like ethanol and acetonitrile with relative high dielectric constants of 30 and 37.5 respectively, lowered the excited state energy of the dye molecules due to π-π* transitions induced by dipole-dipole interactions and hydrogen bonding, hence shifting the absorption band to longer wavelengths. On the other hand, in acetone, only a weak transition of the oxygen lone pair (π→ π* transitions) showed a solvent effect which shifts the absorption band to shorter wavelength due to lesser extent to which it can hydrogen-bond with the molecules in their excited states. (Homocianu et al, 2011; Masoud et al, 2004)

Hence, solvent effect on the absorption band of dye molecules depend on the overall solvation capability of the solvent. This in turn depends on the action of all possible non-specific and specific intermolecular interactions between the dye molecules and the solvent molecules. However, this excludes those interactions leading to definite chemical alterations of the dye molecules such as oxidation, reduction or chemical complex formations.

**CONCLUSION**

The synthesis and solvatochromic properties of nine azo dyes and their preliminary characterization were investigated. Well defined melting points were recorded on the compounds purified by recrystallization in a suitable solvent: Glacial acetic acid. It was found that the absorption maxima of these dyes are dependent on solvent polarity. Solvation of dye molecules probably occur via dipole-dipole interaction in non-hydrogen donating solvents,
whereas in hydrogen-bond donor solvents such as ethanol, the phenomenon is more hydrogen bonding in nature.

REFERENCES


