The Changes of Absorption Spectra of Azo Dyes in Solvent Mixtures

EERO P. J. ELENIUS

Chemistry Department, University of Turku, Finland

The absorption spectra of some azo dyes were measured in mixtures of hexane and ethanol or ethanol and water. The formation of a new species in solutions of some para substituted azo dyes through intermolecular hydrogen bonds or the disturbance of an intramolecular hydrogen bond of o-methyl red explains one type of changes. The other type, shift of the absorption maximum towards longer wavelengths with increase of OH-group concentration in the solvent, may be due to the action of the dipole field on the dye molecules.

The absorption spectra of dyes in the visible and ultraviolet region are not always the same when measured in different solvents. For example Chako has presented a large number of compounds which have this quality. Often such changes in the absorption spectrum can be explained by certain chemical reactions but solvents of different dielectric constant may cause displacements of absorption bands.

In this work these problems were studied by using a series of solvent mixtures instead of pure solvents. In this manner the whole effect was divided into a large number of small changes in the hope of arriving at a better understanding of these solvent effects.

The addition of water to alcoholic solutions of substituted azobenzenes also has been studied by Brode and coworkers.

EXPERIMENTAL

A. Choice of the solvent. The solution spectra of dyes measured in normal alkanes are most like gaseous spectra of the same dyes. Therefore the action of solvent molecules on the absorbing dye molecules may be at the minimum. Hexane was chosen as a representative of this group of solvents. It was only natural to use water as another solvent. Because these solvents are not miscible a third liquid was needed which was soluble in both hexane and water. Ethanol was suitable for this purpose. A series of solvent mixtures could be made from nonpolar hexane to the highly polar water by using these solvents.
B. Solvents. The anhydrous alcohol was prepared from 95% alcohol of ALKO using the magnesium alcoholate method. Hexane was a product of British Drug Houses Ltd. and boiled at 67–69°C.

C. Dyes. In connection with another problem, several azo dyes were prepared. Some of them were used in this investigation. These are listed below. Only the compound V was a commercial preparation. Before measurements the dyes were purified by two recrystallizations from ethanol. The used azo dyes were: I, 4-monomethylamino-4′-hydroxyazobenzene; II, 4-dimethylamino-4′-hydroxyazobenzene; III, 4-diethylamino-4′-hydroxyazobenzene; IV, 4-dimethylamino-4′-nitroazobenzene, and V, 4-dimethylamino-2′-carboxyazobenzene.

D. Preparation of solutions. A weighed amount of each dye was dissolved in pure ethanol. A series of hexane-ethanol and ethanol-water mixtures having about the same concentrations of dye were made using these stock solutions. The solvent components were measured volumetrically before mixing because the volumes are not completely additive. This quality of the solvents was taken into account when the concentrations of dyes were calculated. Also saturated hexane solutions were used as stock solutions. The concentrations in hexane were estimated spectrophotometrically using the same solvent mixture made from the two stock solutions. The binary solvent mixtures varied by 20% from each other. The absorption spectra in pure water could not be measured since the solubilities of the dyes were very small.

E. Measurement of the absorption spectra. The absorption spectra were determined by means of Beckman DU quartz spectrophotometer, using fused quartz absorption cells. The lengths of the cells were about 1 cm. In the reference cell there was the same solvent mixture as was used in the dye solutions. The absorbance of pure solvent was taken in

---

Fig. 1. Absorption spectra of 4-diethylamino-4′-hydroxyazobenzene (dye III) in hexane-ethanol mixtures: 0% ethanol (———), C = 1.482 × 10⁻⁴; 20% ethanol (— — —), C = 2.015 × 10⁻⁴; 100% ethanol (— — —), C = 2.015 × 10⁻⁴. The concentrations reported are without the volume corrections.

Fig. 2. Absorption spectra of 4-diethylamino-4′-hydroxyazobenzene (dye III) in ethanol-water mixtures: 100% ethanol (———), C = 2.015 × 10⁻⁴; 60% ethanol (— — —), C = 2.015 × 10⁻⁴; 40% ethanol (— — —), C = 4.030 × 10⁻⁴.
account when absorption spectra (a) were calculated according to Lambert-Beer's law. The absorbance values are independent of time.

RESULTS

(a) Aminohydroxy compounds. The spectra of dye III in hexane, ethanol, and in the mixture which includes 20 % ethanol in hexane are shown in Fig. 1. The principal change in the spectrum involves a decrease of the main band observed in hexane at about 400 mμ accompanied by the appearance of a shoulder in the longer wavelengths when ethanol was added. The spectra for the same compound in ethanol-water mixtures containing 100, 60, and 40 % ethanol is shown in Fig. 2. The addition of water also brings about a decrease of the main band accompanied by an increase of a band in the longer wavelengths. A shift towards the longer wavelengths in the spectrum is also possible. Similar effects were observed when the dyes I and II were measured.

(b) Nitroamino compound. The spectrum of dye IV measured in different solvent mixtures is shown in Fig. 3. The main absorption band was observed at 445 mμ in hexane. The addition of ethanol causes a shift in the wavelength of the absorption band. A similar effect can be observed when water is added in ethanol. No sign of the appearance of a new band was observed.

(c) o-Methyl red. The spectra of dye V in hexane-ethanol mixtures including 100, 80, 40, and 0 % hexane are shown in Fig. 4. The absorption maximum was observed at 450 mμ in hexane. The shape of the absorption curves of this dye changes considerably as a result of the addition of ethanol in hexane. The change involves a decrease of absorption in the region of the main absorption band and an increase of a new absorption band at somewhat shorter wavelengths when ethanol has been added. The spectra of the same dye in ethanol-water mixtures including 0, 20, and 60 % of water are shown in Fig. 5. After

![Fig. 3. Absorption spectra of 4-dimethylamino-4'-nitroazobenzene (dye IV) in hexane-ethanol mixtures: 0 % ethanol (——), \( C = 3.445 \times 10^{-4} \); 20 % ethanol (---), \( C = 0.8732 \times 10^{-4} \). The same in ethanol-water mixtures: 100 % ethanol (--.--.--), \( C = 4.366 \times 10^{-4} \); 80 % ethanol (-----), \( C = 2.620 \times 10^{-4} \); 40 % ethanol (.....), \( C = 1.746 \times 10^{-4} \).](image)

Acta Chem. Scand. 16 (1962) No. 2
Fig. 4. Absorption spectra of 4-dimethylamino-2'-carboxyazobenzene (dye V) in hexane-
ethanol mixtures: 0 % ethanol (-----), \( C = 0.7530 \times 10^{-4} \); 20 % ethanol (---),
\( C = 0.2742 \times 10^{-4} \); 60 % ethanol (.-.-.-), \( C = 0.8226 \times 10^{-4} \); 100 % ethanol
(.-.-.-), \( C = 1.371 \times 10^{-4} \).

Adding 20 % of water only one absorption maximum is observed. This maximum may also shift toward longer wavelengths upon the addition of water.

DISCUSSION

The appearance of a shoulder on the long wavelength side of the principal absorption band which increases upon addition of ethanol to hexane with

Fig. 5. Absorption spectra of 4-dimethylamino-2'-carboxyazobenzene (dye V) in ethanol-
water mixtures: 100 % ethanol (-----), \( C = 1.371 \times 10^{-4} \); 80 % ethanol (--.--),
\( C = 0.8226 \times 10^{-4} \); 40 % ethanol (-.-.-), \( C = 0.5484 \times 10^{-4} \).

compounds I, II, and III (Fig. 1) suggests the formation of some new species A in the solution. When water was added to solutions of these dyes in ethanol similarly an increase of the absorption band was observed (Fig. 2). Therefore an additional species B may be suggested.

\[
\begin{align*}
R_1R_2N-C_6H_4-N=\equiv-N-C_6H_4-OH & \rightarrow A \\
R_1R_2N-C_6H_4-N=\equiv-N-C_6H_4-OH + H_2O & \rightarrow B
\end{align*}
\]

In the mixtures of ethanol and water both reactions are possible.

A similar effect was reported in aromaticazo compounds having + M groups in the para position. These + M groups, possessing an unshared electron pair and thus capable of entering into resonance with the azo group, bring this phenomenon better out but groups of this type are not necessary since also trans- and cis-azobenzene were found to give a similar change in the absorption spectrum.

The observed changes in the spectra of azobenzenes suggest an action of the solvent on the most reactive site in these molecules, the azo group. The trans \(\equiv\) cis isomerization cannot be the explanation since both forms of azobenzene show the same solvent effect.

The behavior of compound V (o-methyl red) seems to be quite different. Upon the addition of ethanol to hexane (Fig. 4) a new strong absorption band shows up but now on the shorter wavelength side of the original absorption maximum. In absolute ethanol solution both bands can be clearly observed. This effect again supports an assumption of a formation of a new species. Upon addition of water to ethanol the original band decreases rapidly (Fig. 5), until in 80 % of ethanol only one maximum can be observed, indicating that water also acts on the dye.

It has been reported that in carbon tetrachloride solution o-methyl red shows no infrared band associated with the free OH stretching frequency because of an intramolecular hydrogen bond.

\[
\text{(CH}_3\text{)}_2\text{N} \text{-} \begin{array}{c}
\text{N} \\
\text{H} \\
\text{O-CO}
\end{array} \text{-}
\]

This ring structure is possible also in solutions of the aprotic hexane. The measured absorption band was at 450 \(\text{m}_{\mu}\) (Fig. 4).

A compound like o-methyl red having an acetyl group instead of carboxyl group and therefore no hydrogen bond to the azo group showed an absorption maximum at 405 \(\text{m}_{\mu}\) when the spectrum was measured in solution containing 95 % of ethanol in water. Also in indifferent solvent the maximum was at about the same wavelength. Thus the formation of a hydrogen bond with the azo group causes a change toward longer wavelengths in the absorption band from 405 \(\text{m}_{\mu}\) to 450 \(\text{m}_{\mu}\).

The dyes I, II, and III in pure hexane solution show an absorption band at about 400 \(\text{m}_{\mu}\). The new bands observed in solutions of ethanol or water appear at about 465 \(\text{m}_{\mu}\). Therefore the postulated mechanism of solvate formation through hydrogen bonds to the azo group seems to be verified for para substituted azobenzenes:

*Acta Chem. Scand. 16 (1962) No. 2*
ABSORPTION SPECTRA OF AZO DYES

\[ \text{Ar}_1-N=N-\text{Ar}_2 + \text{HOR} \rightleftharpoons \text{Ar}_1-N=N-\text{Ar}_2 \]

\[ \text{HOR} \]

\[ (R = \text{C}_6\text{H}_5 \text{ or H}) \]

In solutions of dye V in ethanol or water the situation is different. The most reactive place of the molecule is now the carboxy group and the action of solvent molecules on it seems to disturb the intramolecular hydrogen bond. A new species is formed showing an absorption maximum of only the azo group at 400 m\( \mu \).

In the dye IV the contribution of resonance structure C is large because the azo group has a minimum basicity \( ^6 \). Here the formation of the solvated

\[ (\text{CH}_3)_2\text{N}=\text{N}=\text{N}=\text{N}=\text{N}=\text{O} \]

species may be inhibited and there is only one species in different solvent mixtures (Fig. 3). The main absorption band of this dye is shifted to lower frequencies (or longer wavelengths) with an increase in the concentration of OH groups (or dipoles) in the solvent. A similar effect can be observed for azobenzenes \( ^7 \). In solutions of cis-azobenzene the shift is greater than in solutions of the trans-form. Since the former has a permanent dipole moment \( ^11 \) and the latter has not, this phenomenon may be due to the action of the dipolar field of the solvent on the dissolved dye molecules. The resonance structure C of dye IV is also highly polar producing a large shift in the absorption band from 445 m\( \mu \) in hexane to 505 m\( \mu \) in a solution of 40 % ethanol in water.

Similar, but smaller shifts can be observed in other series of the spectra (Figs. 1, 2, 4, 5). This effect also explains why the absorption band of the solvated dyes (I, II, III) measured in solutions of 40 % ethanol in water is at wavelengths about 15 m\( \mu \) longer than the band of o-methyl red measured in pure hexane solution.

It seems to be necessary to measure the spectra in both pure solvents and in their mixtures before these chemical and physical solvent effects can be observed and identified. Also a reference spectrum measured in any indifferent solvent is necessary; hexane is recommended for that purpose.

Acknowledgements. The writer gratefully acknowledges the courtesy of Dr. A. Meretoja and Mr. R. Linko for placing dye preparations at his disposal. The writer is also very much obliged to Professors A. Meretoja and H. B. Jonassen (Tulane University, U.S.A.) for interesting discussions.

REFERENCES

2. Sheppard, S. E. and Newsome, P. T. J. Am. Chem. Soc. 64 (1942) 2937.

Acta Chem. Scand. 16 (1962) No. 2
9. A work of this author which continues and will be published later.

Received August 27, 1961.