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Aggregation of *o*,*o*′-dihydroxyazo dyes–1. Concentration, temperature, and solvent effect

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Abstract

The aggregation behavior and tautomerism of three *o*,*o*′-dihydroxy and one o-hydroxy-o′-methoxy azo dyes were studied by UV-visible spectroscopy. Concentration dependent spectroscopic changes with the formation of isosbestic points were observed indicating dimer–monomer equilibria. Combining all obtained data, the conclusion was reached that the spectroscopic changes were due to a shift of the monomer–dimer equilibrium of the hydrazo form caused by the inversion of the intermolecular hydrogen bonding to intermolecular hydrogen bonding. The $k_{aggregation}$ for the dye selected as an example was evaluated statistically and was found [$(1.82 \pm 0.30) \times 10^4$ liter mol^{-1}]. The effect of temperature (10–60°C) on the monomer–dimer ratio and the effect of solvents upon stabilization of one form over the other, supported the conclusion that the driving forces for the dimerization were the hydrophobic effect and the high degree of entropy in solution.

Keywords: Azodyes; Aggreation; Tautomerism; UV-visible

1. Introduction

The aggregation of dyes in aqueous solution is of extreme importance in biological, colloid, surface, textile, photographic and analytical chemistry [1]. In order to determine the mode of aggregation, the aggregation constant in equilibrium and the aggregation number, the aggregation of dyes has been investigated by a variety of methods, viz. polarography [2,3], conductometry [4], UV-vis [5–12], NMR [13,14], light scattering [15] and electrolyte effects [16] measurements. The tautomerism of *o*,*o*′-dihydroxy azo compounds [17–19], is not fully rationalized due to the existence of different species in equilibrium (azoenol–hydrazoketone and monomer–dimer), which are highly affected by the nature of the solvent [20–27]. X-ray and ^{13}C NMR have shown that fast phenoxy proton intramolecular switching between nitrogen and oxygen atoms at a rate of about 2.10^{-3} s^{-1} exists in solution, as well as solid state [28]. The effect of sulfonate groups on the aggregation of some dyes has also been investigated [3,11]. The aggregation number (estimated as two) [2,3,11] was not affected by changing the degree of sulfonation. However, increasing the number of sulfonate groups was found to increase the k aggregation value at all temperatures investigated.

In this paper, the effect of concentration on the UV-vis spectra of an aqueous solution of three mono-sulfonated aryl azo pyrazolone and one aryl

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azo naphthol dyes was studied. The effect of temperature on the absorption pattern, and consequently on the different existing forms, was investigated. The UV-vis spectra of these dyes in solvents, were compared with that in aqueous solution, and the different existing species are discussed. The study has been undertaken in an effort to give a new approach for the dye aggregation through hydrogen bond inversion.

2. Experimental

The dyes I–IV (given by the abbreviations HNAP, HCAP, MNAP and HCAN, respectively) have the structures shown in Scheme 1. They were prepared by normal diazotization of the relevant amine-containing component and coupling with the appropriate coupler in alkaline medium at 0°C [29]. The dyes were precipitated from neutral solution by NaCl, dissolved in hot DMSO, filtered and then precipitated by acetone [30]. TLC analysis of each dye showed no visible impurities.

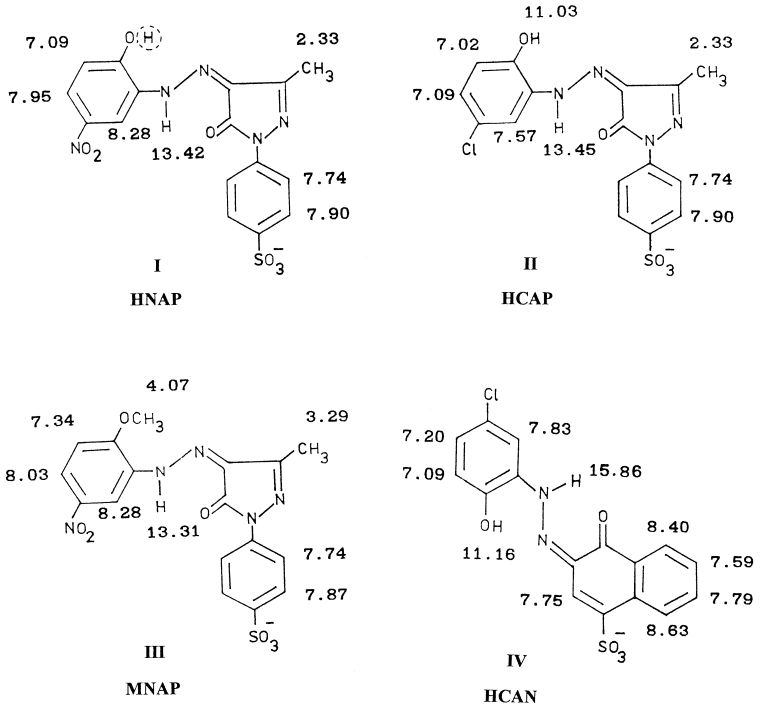
A stock solution 10^{-3} mol liter^{-1} of the dyes were prepared in double-distilled water and investigated spectrophotometrically, and were found to be stable for months.

Infrared spectra were taken in KBr discs and also in Nujol using a Perkin–Elmer 684 SP combined with P.E. data station. ^{1}H NMR and H,H-COSY spectra were measured in DMSO-d_6 at 400.13 MHz on a Bruker AM 400 (Belgium). UV-vis measurements were performed on a PU 8800 SP (UK) combined with a cell temperature controller and a Best compact 386 SX PC unit. Quartez cuvettes with thickness 0.1 mm till 4.0 cm were used for measurements.

3. Results and discussion

3.1. Structure

The dyes in both the solid state and in concentrated solution exist exclusively in the hydrazo structure. Infrared spectra (KBr) display vibration bands corresponding to the νC=O and νC=N



Scheme 1. Structure and ^{1}H NMR chemical shifts.

groups at 1655 and 1500 cm^{-1}, respectively. No vibration bands were observed at the position corresponding to νN=N around 1420 cm^{-1}. ^1H NMR and H,H-COSY spectra in DMSO-d_6 gave the ^1H chemical shifts, which correspond to the hydrazo forms, as shown in Scheme 1.

The selected azo dyes were chosen to have a comparable structure. Change both in the auxochrome ($^-NO_2$, ^-OH, $^-OCH_3$ and ^-Cl) and in the coupler (methyl phenyl pyrazolone and Neville–Winther's acid) were performed. These changes could elucidate the chromophore characters, and result in some comparative correlation. Some of the results obtained from the ^1H NMR and H,H-COSY chemical shifts are as follows:

(a) The hydroxyl proton of HNAP was non-detectable, though that of HCAP dye displays a signal at 11.03 ppm. This is due to the strong cross conjugation of the nitro group in the p-position to the hydroxyl group. The effect of the nitro group (−R and −I effect) and the possibility of fast exchange of this proton with the proton of water traces which might exist in DMSO. Both effects cause complete desheilding of this proton. However, for the HCAP dye, the chloro substituent has a lower effect on the p-hydroxyl group, due to its relatively small negative inductive effect (−I).

(b) The ^1H NMR spectral pattern of both the HNAP and MNAP dyes are almost the same in δ values and multiplicity, with only one difference. The chemical shift of the proton in the o-position to the hydroxy group was 7.09, but the same o-position to the methoxy group was 7.34. The downfield shift of the latter is due to the higher electronegative inductive effect of the methoxy group compared to the hydroxyl group.

(c) The δ values for the o-hydroxy-p-chloro proton of HCAN and that of the HCAP dye are approximately the same for all protons. This means that the environment around this part is the same, regardless of the second coupler type. Hence, the HCAN might be compared directly with the HCAP dye in the case of the hydroxyl proton ionization and the inter- or intramolecular hydrogen bonding which occurs with this proton.

3.2. Effect of dye concentration on association in water

Figs. 1–4 show the electronic absorption spectra of solutions of different concentrations of the dyes, HNAP, MNAP, HCAP and HCAN, respectively, in water in the range 5.0×10^{-6}–10^{-3} mol liters^{-1} and at 22±0.1°C. HNAP Fig. 1, at concentration 5.0×10^{-4} mol liter^{-1}, displays two absorption peaks. The first is of low intensity at 328 nm and the second band is of higher intensity and of a broad nature between 400 and 500 nm. Since the azo group absorbs at shorter wavelength than the hydrazo group and the dye is confirmed to exist mainly in the hydrazo form, the 328 nm band is concluded to be the azo form absorption, whereas the 400–500 nm band is due to the hydrazo form. The latter band is argued to represent equilibrium between two species (monomer–dimer) of the hydrazo form.

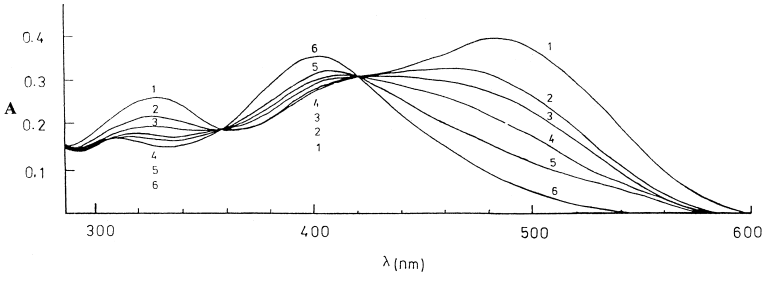


Fig. 1. The EAS of HNAP in water pH 4.9, at 22±1.0°C (c×d=2.0×10^{-5} mol liter^{-1}). Curves 1–6 represent: 5.0×10^{-6}, 1.0×10^{-5}, 2.0×10^{-5}, 5.0×10^{-5}, 2.0×10^{-4}, and 1.0×10^{-3} mol liter^{-1} dye measured in a 4.0, 2.0, 1.0, 0.4, 0.1 and 0.02 cm cuvette, respectively.

The species absorbing at low energy (480 nm) (hydrazo monomer) predominates in the case of samples of low concentrations. On going to more concentrated samples, the equilibrium is shifted towards the hydrazo dimer which absorbs at higher energy (400 nm). The percentage of hydrazo monomer in solution, and consequently the coexisting azo species decreases, due to the dimer formation. This is indicated by a hypochromic shift of the absorption band at 480 and 320 nm, and assigned to the hydrazo and the azo species, respectively. In the case of concentrations over 10^{-4} mol liter^{-1}, the high intense band at 400 nm prevails. Two clear isosbestic points are observed at 356 and 420 nm.

HCAP, (Fig. 2) at the lowest concentration, 5.0×10^{-6} mol liter^{-1} gives an intense band at 440 nm. Going to more concentrated solutions, this band is hypsochromically shifted. The most concentrated solution, (10^{-3} mol liter^{-1}, displays a band at 412 nm.

MNAP, (Fig. 3) at the lowest concentration, (5.0×10^{-6} mol liter^{-1}) displays absorption with two maxima at 412 and 310 nm. On increasing the concentration to 1.0×10^{-3}mol liter^{-1}, the main band at 412 nm is gradually hypochromically and hypsochromiclly shifted to 395 nm, while the band at 310 nm is only shifted hypercromically. The isosbestic point observed at 332 nm indicates that a simple equilibrium occurs between the pre-mentioned different species.

HCAN (Fig. 4) at low concentration (5×10^{-6} mol liter^{-1}) gives two bands at 300 and a nonsymetric band at λ_{max} 527 nm. In more concentrated solutions, the former band is gradually hypochromically shifted, and the 527 nm band is shifted hypsochromically with simultaneous hypochromic shift. At the highest concentration (1.0×10^{-3} mol liter^{-1}) the dye displays two bands. The first appears at 300 nm while the second appears at 495 nm with a shoulder at 527 nm.

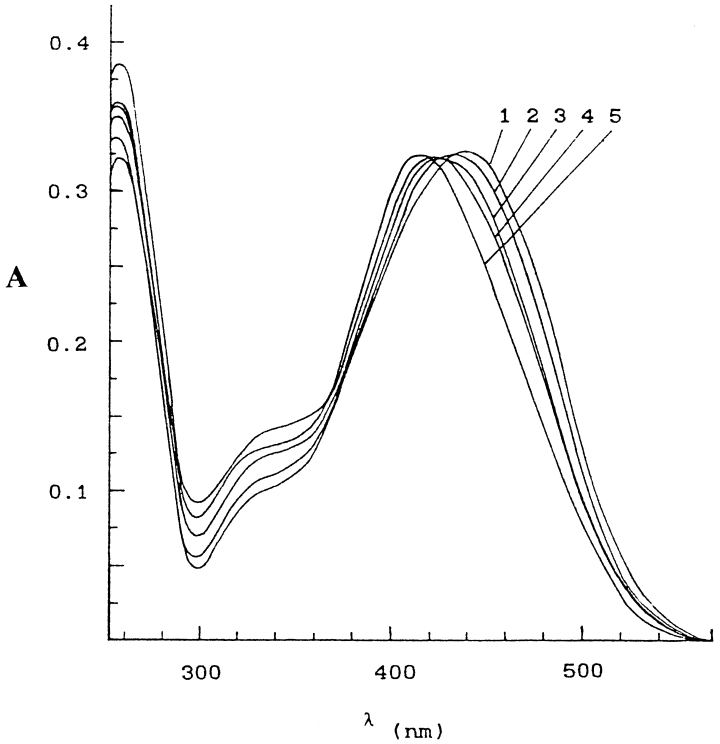


Fig. 2. Effect of concentration on EAS of HCAP dye in water (pH 5.9) at 22 ± 1.0°C (c×d = 2.0×10^{-5} mol liter^{-1}). Curves 1–5 represent: 5.0×10^{-6}, 1.0×10^{-5}, 2.0×10^{-5},1.0×10^{-4}, and 1.0×10^{-3} mol liter^{-1} dye measured in 4.0, 2.0, 1.0, 0.2 and 0.02 cm cuvette, respectively.

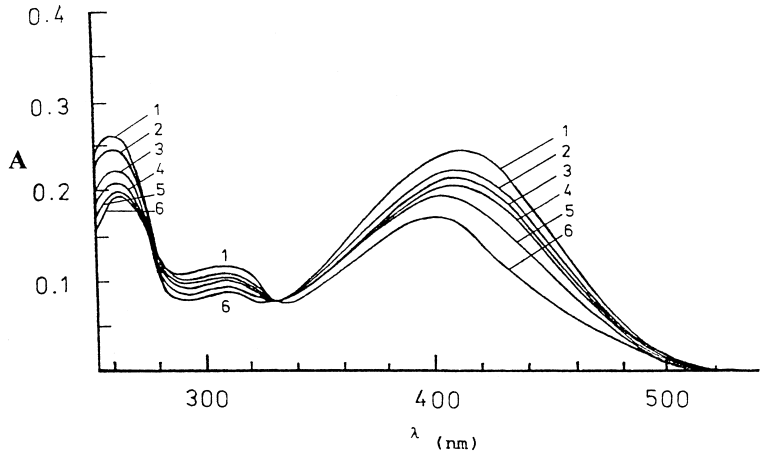


Fig. 3. Effect of concentration on the EAS of MNAP in water (pH 5.9) at 22±1.0°C ($c \times d = 2.0 \times 10^{-5}$ mol liter^{-1}). Curves 1–6 represent: 5.0×10^{-6}, 1.0×10^{-5}, 2.0×10^{-5}, 5.0×10^{-5}, 2.0×10^{-4}, and 1.0×10^{-3} mol liter^{-1} dye measured in 4.0, 2.0, 1.0, 0.2, 0.1 and 0.02 cm cuvette, respectively.

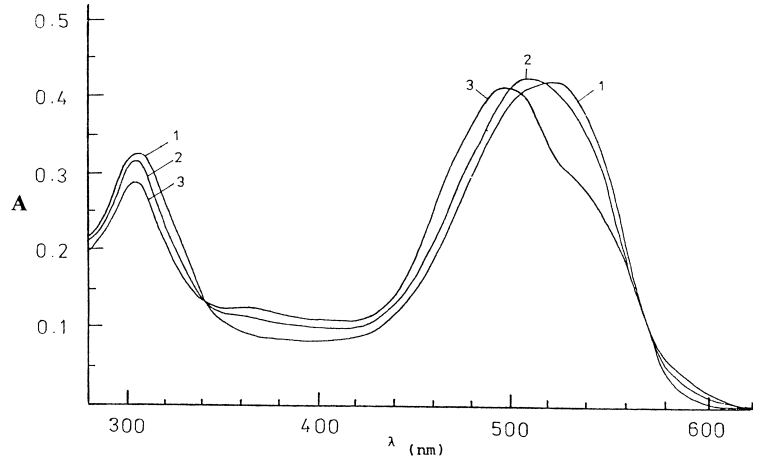
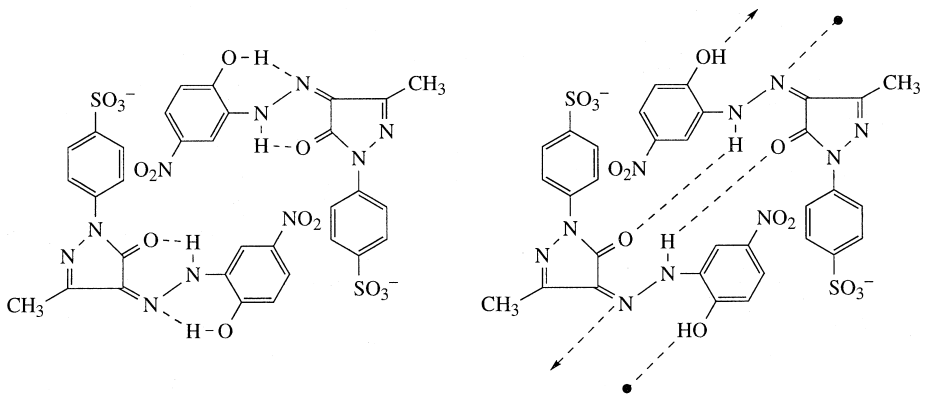


Fig. 4. Effect of concentration on the EAS of HCAN in water (pH 5.7) at 22±1.0°C ($c \times d = 2.0 \times 10^{-5}$ mol liter^{-1}). Curves 1–3 represent: 5.0×10^{-6}, 5.0×10^{-5} and 1.0×10^{-3} mol liter^{-1} dye measured in 4.0, 0.4 and 0.02 cm cuvettes, respectively.

Azopyrazolones and the dyes under investigation exist predominantly in the hydrazo-keto form. Hence, this tautomeric form should exist in aqueous solution. Regarding the aggregation of sulfonated azo dyes in water through hydrogen bonding forming aggregates at relatively high concentrations, mainly to the dimer form by charge interaction between the hydrazo groups partial dipoles, the spectral change observed is explained on the basis of a hydrazo-monomer hydrazo-dimer equilibrium Scheme 2. The higher energy electronic absorption band is attributed to the hydrazo-dimer that prevails at high concentration, to lower both the system entropy and the hydrophobic interaction between the major organic part of the dye molecules and water. The dimerization between each of the two hydrazo molecules occurs through intermolecular hydrogen bonding orienting the water solubilizing groups and hydrophilic groups (e.g. $-SO^{-}_{3}$ and OH groups) in contact with water and the hydrophobic organic part is in the dimer, thus minimizing contact with



Hydrazo-monomer $\underset{\text{Dimerization}}{\overset{\text{Monomerization}}{\rightleftharpoons}}$ Hydrazo-dimer

Scheme 2. Hydrazo-monomer hydrazo-dimer equilibrium.

water. On dilution, intermolecular hydrogen bonding undergoes gradual stretching, and further dilution causes monomerization by rupture of this intermolecular hydrogen bonding, and its conversion to intramolecular hydrogen bonding inside the monomer.

	$^{\lambda}$max monomer (nm)	$^{\lambda}$max dimer (nm)	
HNAP	480	400	δλ 80
HCAP	440	412	δλ 28
MNAP	412	395	δλ 17
HCAN	527	495	δλ 32

The concentration equilibrium constant (K_c) for the dimerization of HNAP was calculated based on absorbance measurements at N_λ wavelength $\lambda_i(i=1,2, \ldots N_\lambda)$ in the region of the two forms existence for a series of N_s solutions with different total concentration t_j ($j=1,2, \ldots N_s$) of the dye. The best estimation of the concentration equilibrium constant (K_c) and molar absorption coefficient values for the monomer and dimer ($^{\epsilon}i$, 1 and $^{\epsilon}i$, 2, respectively) can be obtained by minimization of the criterion function (U) having the form of the weighed sum of squared deviations [16].

$$U(K_c, \epsilon_{i,1} \ldots \epsilon_{N,2}) = \Sigma_{i=1}^{N\lambda} \Sigma_{j=1}^{Ns} W_{i,j}[\epsilon_{i,1} C_{1,j} + \epsilon_{i,2} C_{2,j} - {}^{1} A_{i,j}^{\text{obs}}]^2$$

where C_1, j and C_2, j are the concentration of monomer and dimer in the jth solution, respectively; $^{W}i,j$ are weight coefficients; $^{A}i,j^{\text{obs}}$ are experimental absorbance values. The K_c values for HNAP were calculated through the above equation using a non-linear regression computer program. The K_c values obtained were relatively comparable in the wavelength range 420–520 nm, giving an average $K_c = (1.82 \pm 0.30) \times 10^{-4}$ liter mol^{-1}. However, outside this wavelength range, irregular K_c values are obtained.

3.3. Effect of temperature on the hydrazo monomer–dimer equilibrium

The change of the HNAP absorption spectral pattern at two concentrations (1.0×10^{-5} and 1.0×10^{-4} mol liter^{-1}) was studied at different temperatures. The 10^{-5} mol liter^{-1} solution exists in a mixture of hydrazo monomer and dimer at low temperature. Raising the temperature from 10°C ± 1.0 to 60°C ± 1.0 propagates the monomer formation. This is indicated from the dimension of

the dimer band at 410 nm, accompanied by a hyperchromic shift of the monomer band at 480 nm. An isosbestic point appears at 420 nm (Fig. 5).

The 10^{-4} mol liter^{-1} dye solution (Fig. 6) at relatively low temperature exists predominantly in the dimer form, as shown by the band at 400 nm. Raising the temperature from 10°C ± 1.0 to 60°C ± 1.0 results in significant hyperchromic shift at the wavelength range corresponding to the monomer form at 480 nm. This is accompanied by a slight hypochromic shift of the dimer band at 400 nm. Again an isosbestic point is observed at 420 nm, i.e. the same position as it appears in Fig. 1. The shift of equilibrium by heating was reversible for the 10^{-4} mol liter^{-1} solution, but was irreversible by cooling the 10^{-5} mol liter^{-1} solution from 70 to 10°C.

The most probable explanation is that at low temperature the charge delocalization through the molecule is partially restricted, and the hydrogen bond length (intermolecular hydrogen bonding) is relatively shorter and more stable. Also the high degree of entropy in the concentrated solution assists dimerization. Raising the temperature of the 10^{-4} mol liter^{-1} solution increases the molecule energy, charge delocalization, weakens the intermolecular hydrogen bonding, and consequently assists dimer dissociation (monomerization). The effect of heating on the monomer/dimer ratio in this case is small, due to high entropy caused by high concentration that restricts the formation of monomer. On loosing this heat energy (cooling) the formed monomer species aggregate to the lower entropy and lower energetic dimer form through a reversible equilibrium. Meanwhile, the monomer amount, on heating the

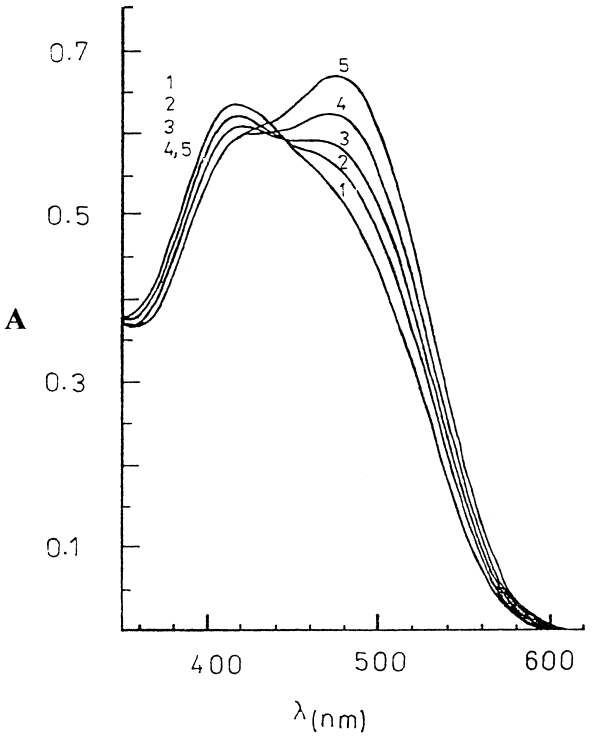


Fig. 5. Effect of increase of temperature on the EAS of 1.0×10^{-5} mol liter^{-1} HNAP dye in water in 4.0 cm cuvette. Curves 1–5: 10, 30, 40, 50, 60 ± 1.0°C.

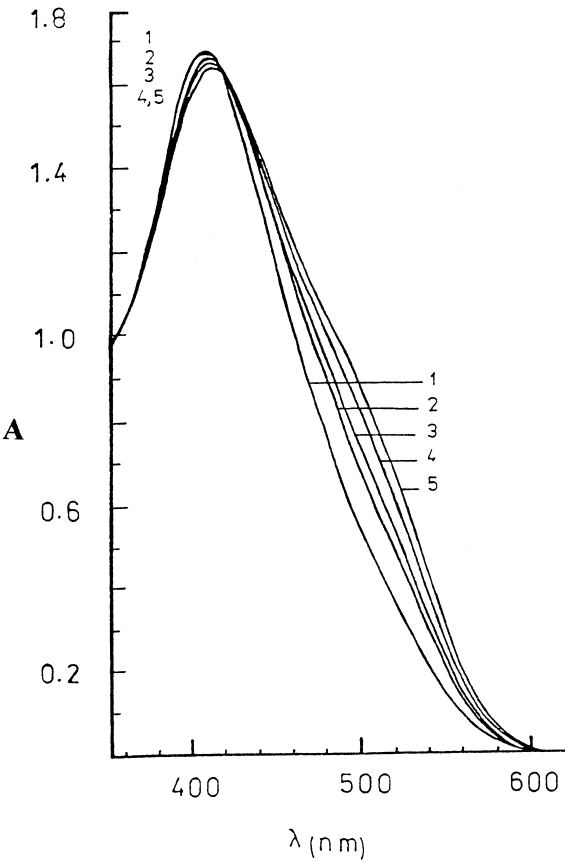


Fig. 6. Effect of increase of temperature on the EAS of 1.0×10^{-4} mol liter^{-1} HNAP dye in water. Curves 1–5: 10, 30, 40, 50, 60 ± 1.0°C.

10^{-5} mol liter^{-1} solution, increases significantly. Two factors, heat and dilution, work in parallel to perform significant monomerization. Cooling this diluted solution from 70 to 10°C does not affect the dimer/monomer ratio (irreversible temperature effect). This is due to the stabilization of the already formed monomer, at high temperature, by dilution.

3.4. *Effect of solvent*

The electronic absorption spectra at 3.8×10^{-5} mol liter^{-1} of selected HNAP and HCAP dyes (Figs. 7 and 8) in DMSO, DMF, n-butanol and water, respectively, were recorded over the wavelength range 300–620 nm at 22 ± 1.0°C. HNAP (Fig. 7) in DMSO, DMF, n-butanol and water shows a completely different absorption pattern. In DMSO a band occurs at 415 nm, and corresponds to the hydrazo–dimer. DMF stabilizes both the hydrazo-dimer and the hydrazo-monomer forms absorbing at 430 and 532 nm, respectively, The latter form is predominant. In butanol, both the hydrazo–dimer and the hydrazo–monomer forms exist in a slow equilibrium, as indicated by the slightly overlapped band at 420 and 500 nm. In water, as in butanol, the two bands observed at 420 and 470 nm are due to the absorption of the hydrazo-dimer and hydrazo-monomer forms. However, these two bands almost nearly overlap as one broad band, which might be explained as a result of a fast equilibrium between the dimer and monomer forms. HCAP (Fig. 8) displays an intense band at 440 nm in DMF, whereas in other solvents, this band occurs at 418 nm regardless of the solvent type. In the case of DMF, the hydrazo-monomer is more stabilized. DMF probably

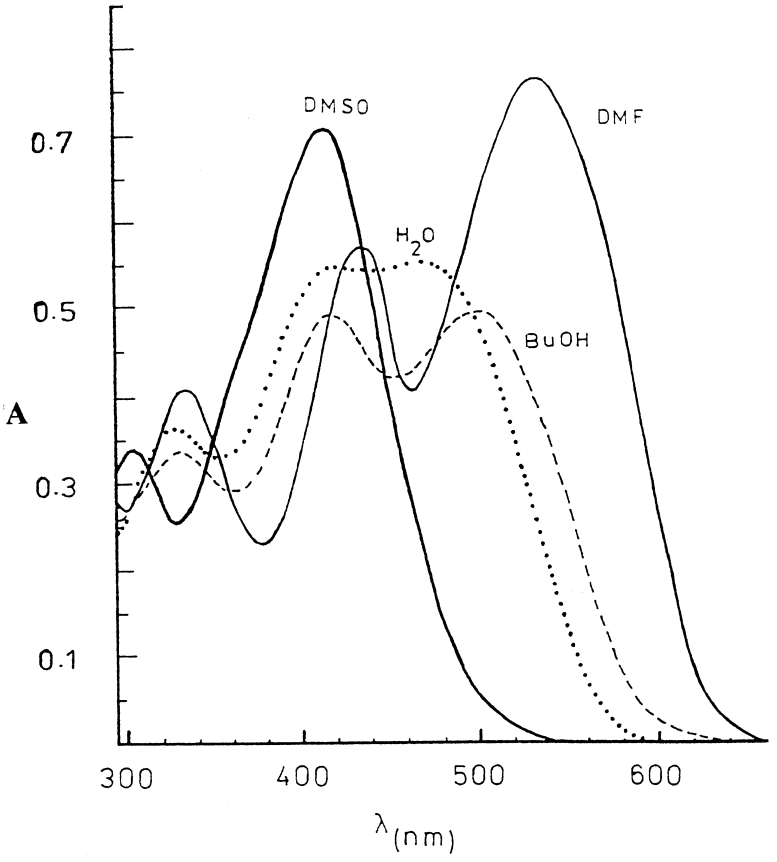


Fig. 7. The EAS of 3.8×10^{-5} mol liter^{-1} HNAP dye in DMF, DMSO, H_2O and butanol.

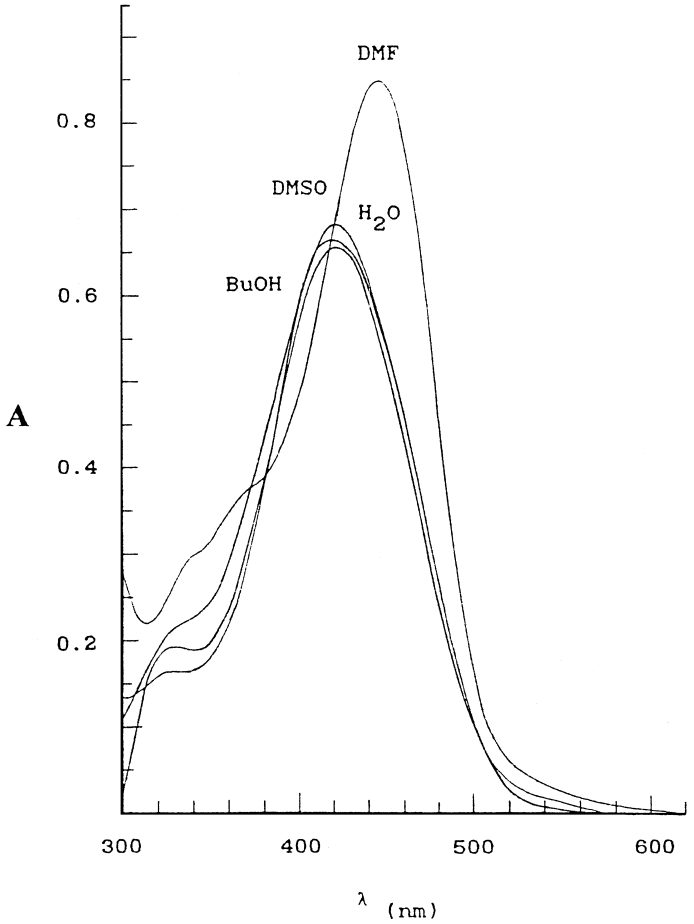


Fig. 8. The EAS of 3.9×10^{-5} mol liter^{-1} HCAP dye in DMF, DMSO, H_2O and butanol.

destabilizes the dimer form by decomposition of its intermolecular hydrogen bonding. DMSO, H_2O and butanol stabilize the intermolecular hydrogen bonding in the dimer more than the intramolecular one in the monomer form. Based on the above results, it is concluded that the main criterion, which changes the shape and position of the electronic absorption band in solvents is the hydrazo-monomer-dimer equilibrium. Changes in the spectra depend on the solvent's physical parameters (micro structure, hydrogen bonding, polarity, etc.), which affect this equilibrium through their effect on the inter- or intramolecular hydrogen bonding existing in the dimer or monomer forms, respectively. Therefore, the solvent role is to stabilize one form rather than the other, to enhance or slow or block the rate of achieving the equilibrium, and to accommodate one form of lower activation energy and steric factors than the other.

4. Conclusion

The aggregation of *o*,*o*′-dihydroxyazo dyes in solution is strongly affected by the concentration of the dye, the temperature and the solvent in which the measurements are performed. Since the aggregation of these dyes increases dimer formation, these factors directly shift the dimer–monomer equilibrium in solution through their effect on the inter- or intramolecular hydrogen bonding, which exists in the dimer and monomer forms,

respectively. At high dilution, the less stable intermolecular hydrogen bonding in the dimer form is converted to the more stable intramolecular hydrogen bonding in the monomer form, which is not affected by more further dilution. Heating has the same effect as dilution, and stabilizes the monomerization. The role of solvent on the dimer monomer equilibrium is due to how far do the solvent parameters stabilize one form of hydrogen bonding (inter or intra) relative to the other (Scheme 1).

References

[1] Burdett BC. In: Why-Jones E, Gormally J, editors. Aggregation processes in solution, Amsterdam and New York: Elsevier, 1983.
[2] Iyer S, Singh G. JSDC 1973;89:128.
[3] Duff DG, Kirkwod DJ, Stevenson DM. JSDC 1977;93:303.
[4] Kendrick KL, Gilikerson WR. J Solution Chem 1987;16:257.
[5] Monahan AR, Blossey F. J Phys Chem 1970;74:4014.
[6] Momahan AR, Germano NJ, Blossey DF. J Phy Chem 1971;75:1227.
[7] Monahan AR, Deluca AF, Ward AT. J Org Chem 1971;36:3838.
[8] Tull AG. JSDC 1973;89:132.
[9] Ott R, Widmer U, Zolinger H. JSDC 1975;91:330.
[10] Hsieh BR, Desilets D, Kazmaier PM. Dyes and Pigments 1990;14:165.
[11] Hamada K, Nonogaki H, Fukushima Y, Munkhbat B, Mistsuishi M. Dyes and Pigments 1991;16:111.
[12] Hamada K, Nishizawa M, Kitsuishi M. Dyes and Pigments 1991;16:165.
[13] Hamada K, Take S, Lijima T. J Chem Soc, Faraday Trans 1986;82:3141.
[14] Asakura T, Ishida M. J Colloid Interface Sci 1989;130:184.
[15] Dalyner A, Flowers A, Pailithorpe M. J Colloid Interface Sci 1980;74:71.
[16] Liska M, Bartos L, Valasek J. Chem Papers 1989;43:303.
[17] Fabian J, Hartman H. Light absorption of organic colorants. New York: Springer–Verlag, 1980.
[18] Gordon PF, Georgy PF. Organic chemistry in colour. New York: Springer–Verlag, 1983.
[19] Pati S. The chemistry of the azo and azoxy groups, Part I. John Wiley, New York, 1975.
[20] Nepras M, Titz M, Necas M, Lunak S, Hardina R, Lycka A. Collect Czech Chem Commun 1988;53:213.
[21] Grasso D, Millefiori S, Fasone S. Spectrochimical Acta 1975;31:187.
[22] Saito I, Bansho Y, Kakuta A. Kogy Kagaku Azsshi 1968;70:1715. Chem Abs 1968;68:70149h.
[23] Skulski L, Kleps J. Plo J Chem 1981;55:1809. Chem Abs 1983;98:1998144.
[24] Reeves RL, Kaiser RS, Maggio MS, Sylvester EA, Lawton WH. Can J Chem 1973;51:628.
[25] Yamamoto K, Nakai K, Kawaguchi T. Dyes and Pigments 1989;11:137.
[26] Kishimoto S, Hirashima T, Manabe O. Kogyo Kagaku Zasshi 1967;70:1379. Chem Abs 1968;68:78769p.
[27] Saito I, Banso Y. Kogyo Kagaku Azsshi 1969;72:1149. Chem Abs 1970;72:80314.
[28] Olivieri AC, Wilson RB, Poul IC, Curtin DY. J Am Chem Soc 1989;111:5525.
[29] Fierz David HE, Blangey L. Fundamental processes of dye chemistry. New York: Inter Science, 1949.
[30] Venkatarman K. The analytical chemistry of synthetic dyes. New York: John Wiley & Sons, 1977.