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Aggregation of o, o′-dihydroxyazo dyes II. Interaction of 2-hydroxy-4-nitrophenylazoresorcinol in DMSO and DMF

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Abstract

The aggregation behavior and tautomerism of several concentrations (10^{-4}–10^{-5} mol liter^{-1}) of 2-hydroxy-4-nitrophenylazoresorcinol in DMSO and DMF was investigated by UV-visible spectroscopy. The electronic absorption spectra were recorded immediately after dissolving the dye sample in the solvent. The absorption spectra of the solutions were then measured on intervals through 36 days (868 h) at 22°C. The lowest concentration (1×10^{-5} mol liter^{-1}) gave an intense electronic absorption band at λ 404 nm that was assigned to the azo monomer form. This absorption pattern was slightly bathochromic shifted with time. Concentrations above 6×10^{-5} mol liter^{-1} gave two absorption bands at ca. λ 420 and ca. λ 520 nm. The former band was assigned to the dimeric form of the dye and the latter one to the hydrazo monomeric form. The time dependence of the electronic absorption spectra of all solutions above 6×10^{-5} mol liter^{-1} reflected a linear exchange from the absorption band at λ 520 nm (hypochromically shifted) to the absorption band at λ 420 nm (hyperchromically shifted). Equilibrium between the different species was reached in about 450 h after mixing. Then, both bands were stable for ca. 100 h. After this time both bands started to reflect a hypochromic shift, indicating degradation of the absorbing species. In DMF the time dependence of the absorption spectra of 6.4×10^{-5} mol liter^{-1} of the dye reflected the same behavior of the dye in DMSO. However, the above mentioned bands assigned to the dimer and the hydrazo monomer forms appeared at ca. λ 470 nm and ca. λ 550 nm, respectively. It was concluded that this concentration time dependent interaction is most probably due to the shifting of the hydrazo-azo equilibrium, caused by the shifting of the dimer-monomer equilibrium. This reaction was followed kinetically using the initial rate method. The observed kinetic profile resembles that of auto-catalyzed reactions. A mechanism was proposed to account for the observed kinetics.

Keywords: Azodyes; Tautomerism; Aggregation; UV-visible spectroscopy; Solvent effect; Kinetics

1. Introduction

The tautomeric behavior of a number of hydroxy azo dyes has been recognized in different solutions [1–6]. This tautomerization, which resulted from the intramolecular proton transfers between nitrogen and oxygen atoms, have been studied by various techniques, including UV-visible [7,8] and NMR spectroscopy [9,10]. These techniques provided a quantitative determination of the relative concentration of the azo and hydrazo forms. Hydroxy azo dyes capable of

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undergoing azo-hydrazone tautomerism are those in which the hydroxy group is conjugated to the azo group, i.e. o-hydroxy and p-hydroxy azodyes [6]. Whether such tautomerism is actually observed depends on several factors but principally on the relative thermodynamic stability of the azo and the hydrazo tautomer [2]. It was also found that the type of solvent exerts a profound influence on the tautomerism [11–13]. Generally, a more polar solvent favors the hydrazone form whereas less polar solvents favor the azo form. This has been extensively studied by the effect of solvents with different polarities, as well as aqueous solvents, on the UV-visible spectra of a series of hydroxyazo dyes [14–16]. The solvent effect on the azo-hydrazo tautomerism, or on the monomer–dimer equilibrium was found not to correlate with any of the physical parameters of the solvents (polarity, dielectric constant, and refractive index); it depends on the solvent structure and the microscopic environment of the dye in the solvent matrix [17]. Temperature, also, was found to affect the azo-hydrazone tautomeric equilibrium. Electronic spectra at different temperatures, and HOMO quantum calculations showed that the proton transfer takes place after dimerization of the molecule [18,19].

On the other hand, the aggregation behavior of some o-hydroxy and o,o′-dihydroxy azo dyes in water and in solvents was recently studied by spectroscopic methods [20–23]. Aggregation occurring at relatively high dye concentration was found to have a remarkable effect on the azo-hydrazone tautomers in solution, through the existence of monomer–dimer equilibrium.

In this paper, the effect of changing concentrations of 2-hydroxy-4-nitrophenyl azoresorcinol on the different tautomeric forms was investigated in dimethylsulfoxide (DMSO) and dimethylformamide (DMF). It is noteworthy to mention that in this work, the effect of time on the monomer dimer equilibrium was investigated and their kinetics was also analyzed. This very important factor was ignored in several previous analytical works, which may give rise to misleading results concerning the quantitative determination of the azo-hydrazo forms.

2. Experimental

2.1. Material

2-Hydroxy-4-nitrophenylazoresorcinol, as free acid, was prepared, purified and characterized as described in previous work [24]. All solvents used were of spectrophotometric analytical grade. Dimethylsulfoxide and dimethylformamide were obtained from Merck and were kept free of moisture by the use of molecular sieves.

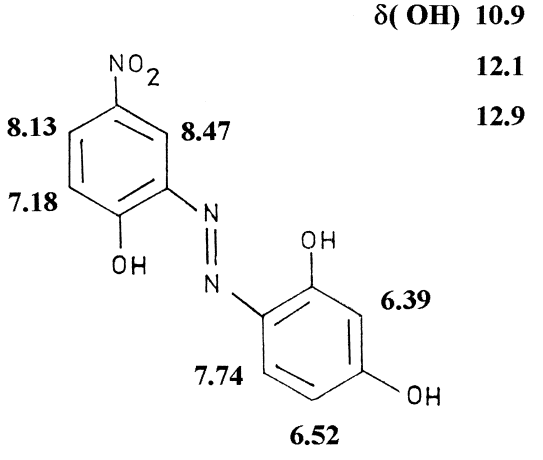
2.2. Instrumentation

^{1}H NMR spectra were recorded on a Bruker AM 400 instrument (Belgium); a Perkin–Elmer 684 Spectrophotometer combined with a P.E data station was used to measure the IR spectra. The UV-visible spectra were recorded on Pye Unicam 8800 (Cambridge, UK) and Perkin–Elmer Lambda 5 spectrophotometers, both combined with a cell temperature controller, with accuracy of ± 0.1°C. Quartz cuvettes with different thickness (0.1−10 cm) were used during the measurements.

2.3. Measurements

2.3.1. IR

IR spectra were taken once in KBr discs and again mulled in Nujol at the range 4000–500 cm^{-1}.



Scheme 1. Structure and H^1 chemical shifts of 2-hydroxy-4-nitro phenyl azoresorcinol.

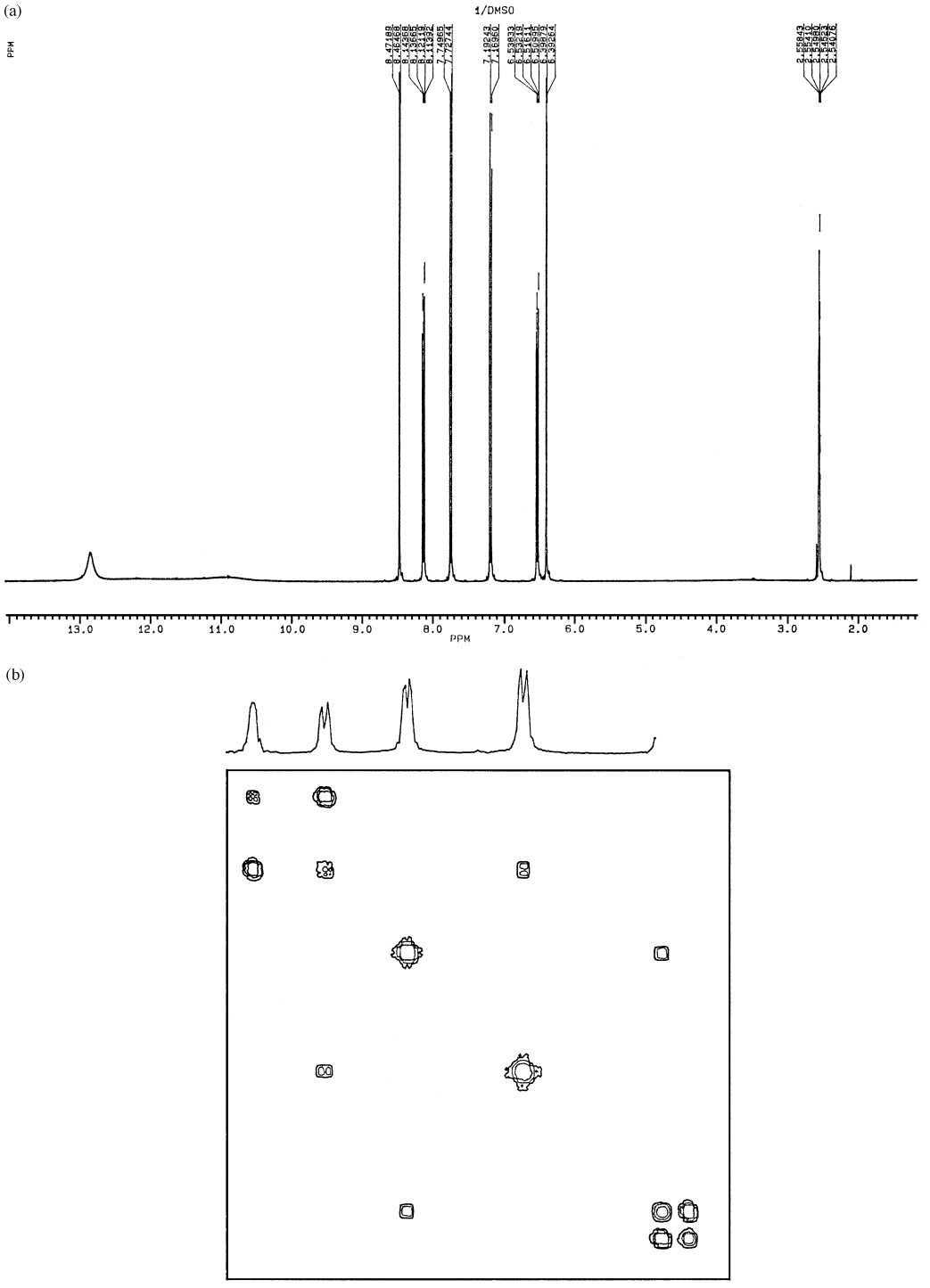


Fig. 1. (a) One dimensional and (b) two dimensional ^{1}H NMR spectra of 2-hydroxy-4-nitrophenylazoresorcinol in d_6-DMSO (on a Bruker 400 instrument measured at 400.13 MHz).

Sharp spectra were obtained in both matrices supporting the purity and structure of the azo compound.

2.3.2. *^{1}H NMR*

The ^{1}H NMR spectrum of the dye sample was measured at 400.13 MHz in d_6-DMSO, H^1 chemical shifts being referred to the solvent signal ($\delta = 2.55$). Two-dimensional proton spectra was also measured and analyzed (Fig. 1). The H^1 chemical shift values for the different protons are given in Scheme 1.

2.3.3. *UV-visible*

The working solutions (1.0×10^{-4}–1.0×10^{-5} mol liter^{-1}) were prepared by diluting the stock solution of 2-hydroxy-4-nitrophenyl azoresorcinol (1.0×10^{-3} mol liter^{-1}) using DMSO. The spectrum of each solution was recorded in the wavelength range 240–700 nm immediately after mixing. The solutions then were incubated in the dark at room temperature (22° ± 1.0°C). During the incubation, the spectra for each solution were measured intervally through 36 days (868 h). Only one concentration (6.4×10^{-5} mol liter^{-1}) of the

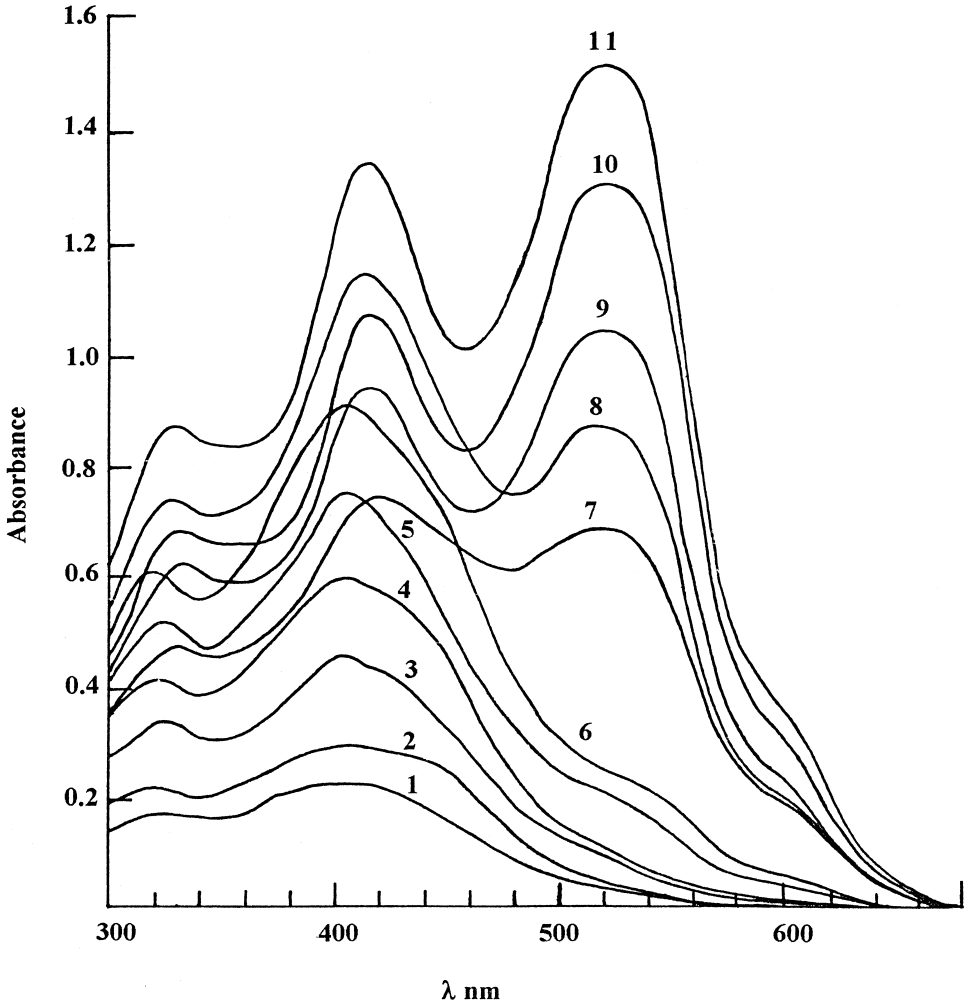


Fig. 2. UV-visible absorption spectra for different concentrations of 2-hydroxy-4-nitrophenylazoresorcinol in DMSO at 22°C. Plots 1–11 are 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 6.5, 7.0, 8.0, 9.0, 10.0 (10^{-5} mol liter^{-1}), respectively; the spectra were measured immediately after preparation.

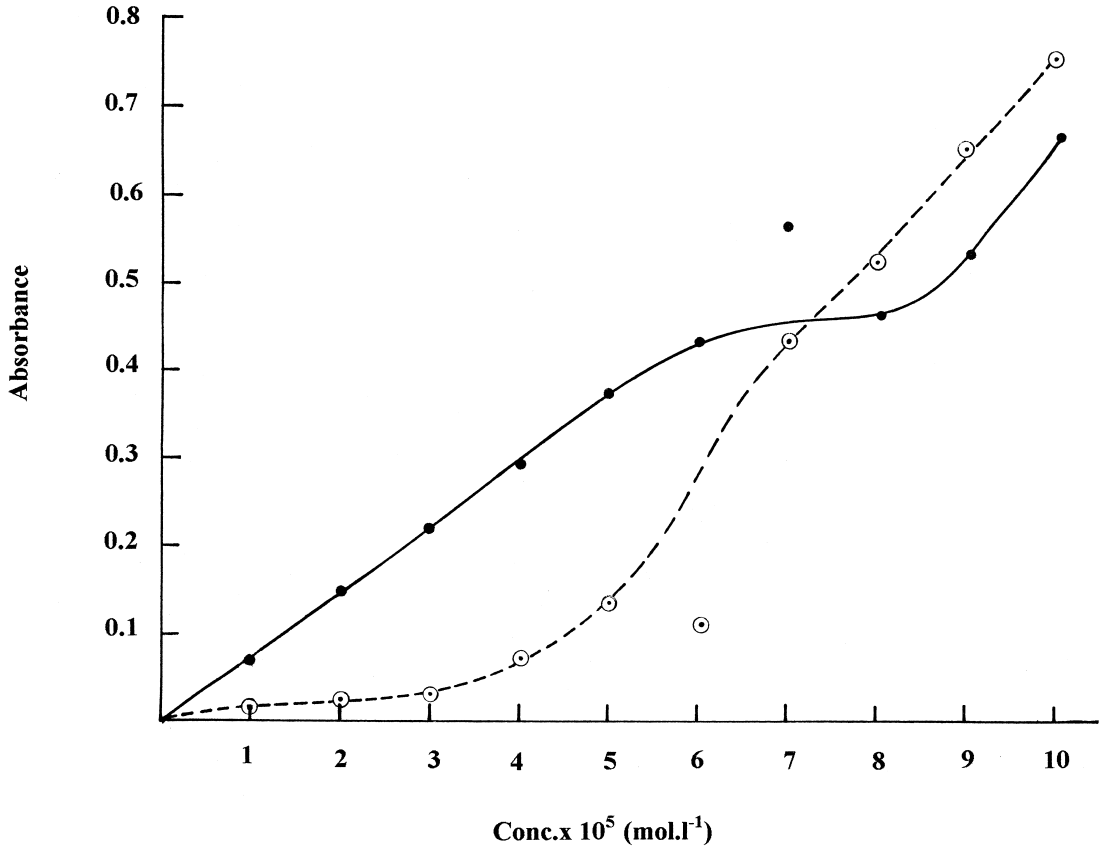


Fig. 3. Plot of absorbance vs concentration for 2-hydroxy-4-nitrophenylazoresorcinol in DMSO at 22°C at the position of the two absorption maxima: — 420 nm, - - - 520 nm).

dye was prepared in DMF and its spectrum was measured immediately. The solution incubated in the dark at room temperature was then subjected to time interval measurements during 49 days (1130 h). All the previously mentioned measurements were run under the same operating conditions where λ 240–700, scan speed 5 nm s^{-1}, grid scale 20 nm cm^{-1}, bandwidth 2 nm and sensitivity 2 s.

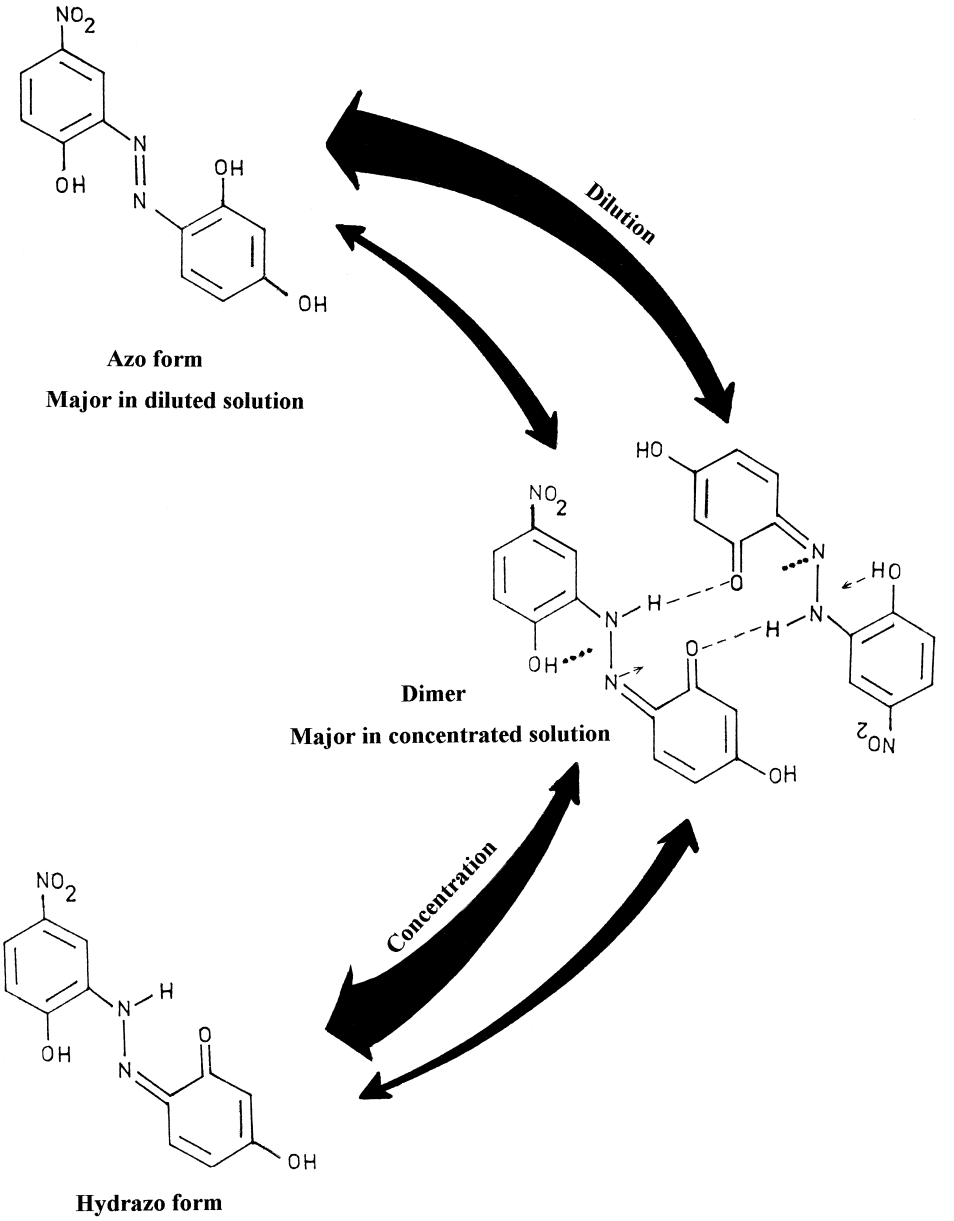
3. Results and discussion

3.1. Effect of concentration

The electronic absorption spectra of different concentrations of 2-hydroxy-4-nitrophenylazoresorcinol in DMSO are shown in Fig. 2. Inspection of this figure reveals that at very low concentrations only a major band appears at a wavelength of ca. 404 nm. On increasing concentration from 6.0×10^{-5}–1.0×10^{-4} mol liter^{-1}, a new band appears at ca. 520 nm with a simultaneous bathochromic shift of the band at 404–420 nm. In this concentration range, the intensity of this new band increases linearly with increasing concentration (Fig. 3). Due to the fact that, o,o′-dihydroxyazo dyes exist in the monomeric azo form rather than the hydrazo form at low concentration, the electronic absorption band at 404 nm can be attributed to the monomeric azo form of the indictor. With increasing concentration, more hydrazo form of the indicator will be generated. At a critical concentration, dimerization between the hydrazo species takes place. The dimerization of the azo form directly is impossible,

due to the lack of polarity in the molecule. The intermediate step, which includes the shift from the non-polar azo form to the polar hydrazo form, should proceed via the dimerization process, identified by the band at 420 nm assigned to the dimeric form. The presence of the hydrazo form is indicated by the band at 520 nm. The mechanism of the proposed inter-conversion is shown in Scheme 2.

The absorption–concentration relations (Fig. 3) plotted at the wavelengths 420 (dimer form) and 520 nm (hydrazo form) show abnormal



Scheme 2. The mechanism of inter-conversion between the different existing species of 2-hydroxy-4-nitrophenylazoresorcinol in DMSO.

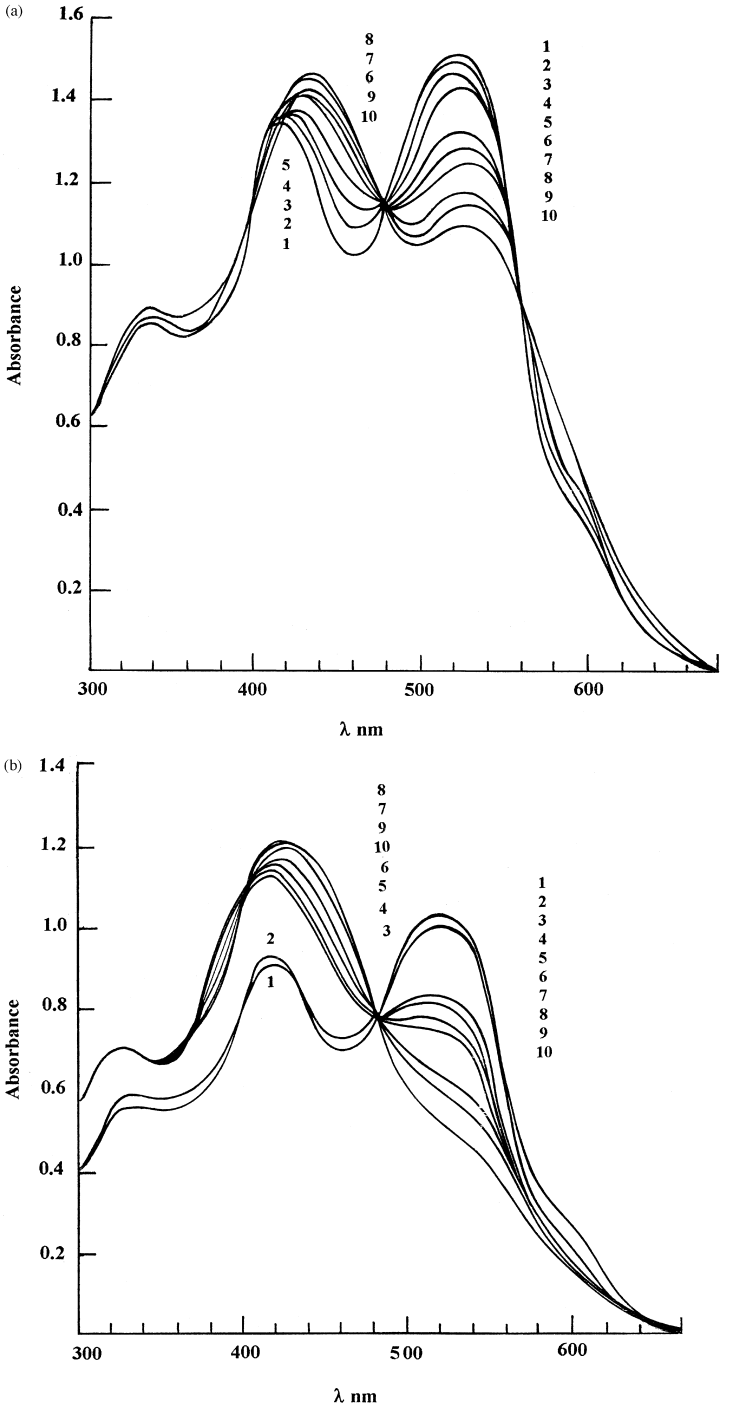


Fig. 4. (a) The effect of time on the UV-visible absorption spectra of 10.0×10^{-5} mol liter^{-1} of 2-hydroxy-4-nitrophenylazoresorcinol in DMSO at 22°C during 868h; plots 1–10 represent times equal to zero, 24, 48, 72, 148, 197, 221, 481, 558 and 868h respectively (b) The effect of time on the UV-visible absorption spectra of 7.0×10^{-5} mol liter^{-1} of 2-hydroxy-4-nitrophenylazoresorcinol in DMSO at 22°C during 868 h; plots 1–10 represent times equal to zero, 24, 48, 72, 148, 197, 221, 481, 558 and 868 h, respectively.

dependency in the concentration range of ca. 5×10^{-5}–8×10^{-5} mol liter^{-1}. In this concentration range, the absorption and hence, the ratio of different species in solution is remarkably affected by any slight change in concentration. It was also not surprising that the spectra in the range 5×10^{-5}–6×10^{-5} mol liter^{-1} were not reproducible. Consequently, this concentration might be considered as a Critical Dimer Concentration (CDC), below which only the monomer form exists in solution. Further evidence for this proposition will be presented in the kinetic section.

3.2. Effect of time

The effect of time on the electronic absorption spectra of 10 different concentrations (1.0×10^{-4}–1.0×10^{-5} mol liter^{-1}) was studied in the period of 868 h. Fig. 4a and b shows data obtained for the 1.0×10^{-4} and 7.0×10^{-5} mol liter^{-1} of the dye in DMSO incubated at $22^\circ \pm 1.0^\circ$C in the dark. It is observed that, the absorption band at 520 nm undergoes a hypochromic shift with time, while that at λ 420 nm undergoes a hyperchromic shift. An isosbestic point appears at λ 480 nm, and indicates the existence of equilibrium between the two existing absorbing forms of the dye (dimer and monomer). The absorption spectra of concentrations below 6×10^{-5} mol liter^{-1} reflect that a very small hypochromic shifts occurs around 520 nm. These spectral findings are most probably due to the shift of equilibrium from the formation of the hydrazo monomer (520 nm), immediately resultant by dissolving the dye in DMSO, to the dimeric form that absorbs at 420 nm. The shift of this equilibrium towards more favorable and less free energy system is very slow, and time dependent in this case. The time-absorbance dependence (Fig. 5a and b) reveals that in the period between 450 and 550 h, negligible change in the spectra was observed for the 520-nm band. After this period, all the electronic absorption bands of all concentrations showed a gradual hypochromic shift. This is probably due to the dye degradation.

The effect of time on the electronic absorption spectra of the dye in DMF for the period of 1130 h (Fig. 6), reflected the same behavior as that observed for the DMSO, whereas the band assigned to the monomer form appeared at 580 nm. A sharp isosbestic point appears at 450 nm, indicating the existence of a simple equilibrium. The effect of temperature on this equilibrium and other similar systems, including thermodynamic investigations of such interactions, has already gave preliminary promising results in our investigations [25].

3.3. Kinetics and mechanism of the interaction

From the above results, two types of reactions are resolved in this system. The first is a tautomerization between the azo and the hydrazo forms of the dye. Though this is a relatively very fast reaction in aqueous solution [6], it was slow, resolved and interrupted in the chosen solvent system. The second reaction is the dimerization of the hydrazo species of the dye. The formation of this dimer is evident from the observed hyperchromic shift of its absorption band at 420 nm. Both reactions are relatively slow in these solvent systems and are the driving factors for the observed time dependence spectral changes. In order to investigate the kinetics of these reactions, the absorbance at 520 nm was followed as a function of time at 22°C (Fig. 5a and b). The initial rate was evaluated from the curve obtained for each concentration (Table 1). Concentrations above 5.0×10^{-5} mol liter^{-1} showed a single step reaction. However, concentrations below 5.0×10^{-5} mol l^{-1} reflected two steps reaction with an individual initial rate constant for each (Table 1). At 2.0×10^{-5} mol liter^{-1} and 1.0×10^{-5} mol liter^{-1}, an inductive period was observed and the initial rate of the first step was very small to be evaluated (ca. zero) at this range. The plot of the initial rate vs concentration (Fig. 7), displays two distinguished types of dependence. Both are typical correlation of that observed for auto-catalyzed reactions [26,27] and display two individual steps with two individual rates. For concentrations below 5.0×10^{-5} mol liter^{-1}, the two steps are interpreted with the first step being much faster than the second, However, above 5.0×10^{-5} mol liter^{-1}, only the initial rate of the second step can be interpreted. The mechanism of reaction, based on the previous kinetic data, can be explained as follows:

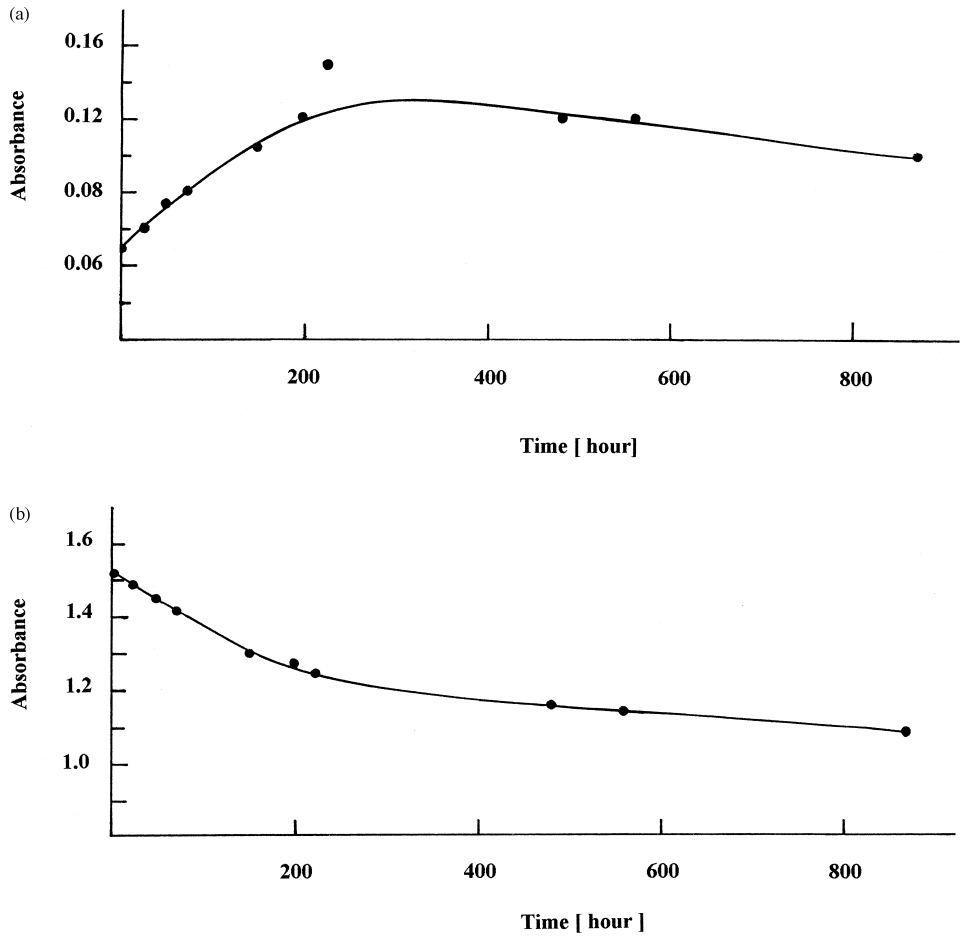


Fig. 5. (a) Plot of the absorbance vs time at wavelength 520 nm for low concentration, 3.0×10^{-5} mol liter^{-1}, of the dye in DMSO at 22°C. (b) Plot of the absorbance vs time at wavelength 520 nm for high concentration, 10.0×10^{-5} mol liter^{-1}, of the dye in DMSO at 22°C.

$$\text{Azo} \Longleftrightarrow \text{hydrazo} \quad \text{(via dimer, major at low concentration)} \tag{1}$$

$$\text{Hydrazo} \Longleftrightarrow \text{dimer} \quad \text{(at high concentration)} \tag{2}$$

$$\text{Rate (1)} = K_{obs}[\text{azo}][\text{dimer}]$$

$$\text{Rate (2)} = K'_{obs}[\text{hydrazo}][\text{dimer}]$$

The first step represents the initial rate of the hydrazo formation, due to the effect of the strong polar solvent on the azo form. This rate is relatively faster than the rate of the second step which is devoted to dimer formation. The hydrazo formation is catalyzed by the amount of dimer in solution. At low concentrations, below 5.0×10^{-5} mol liter^{-1}, the dimmer concentration is very small and the hydrazo formation is relatively slow, and its initial rate formation can be traced. Above 5.0×10^{-5} mol liter^{-1}, the dimer concentration is high, and consequently the rate of the hydrazo formation is very fast, and its initial rate is non-traceable.

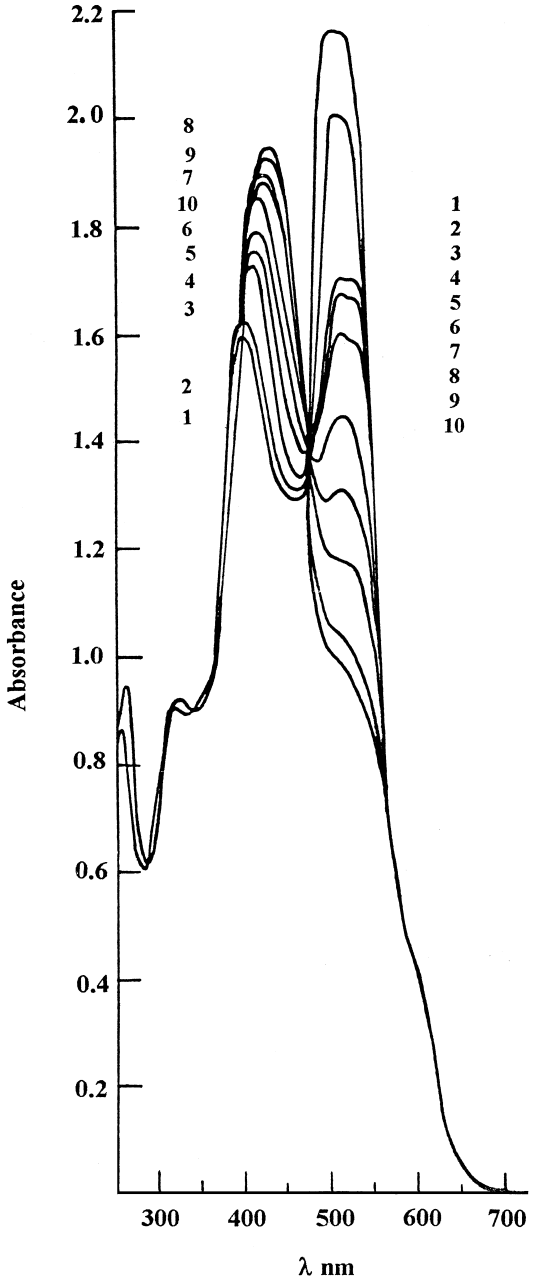


Fig. 6. The effect of time on the UV-visible absorption spectra of 6.4×10^{-5} mol liter^{-1} of 2-hydroxy-4-nitrophenylazoresorcinol in DMF at 22°C during 1130 h; plots 1–10 represent times equal to zero, 23, 145, 192, 284, 454, 644, 794, 960 and 1130 h, respectively.

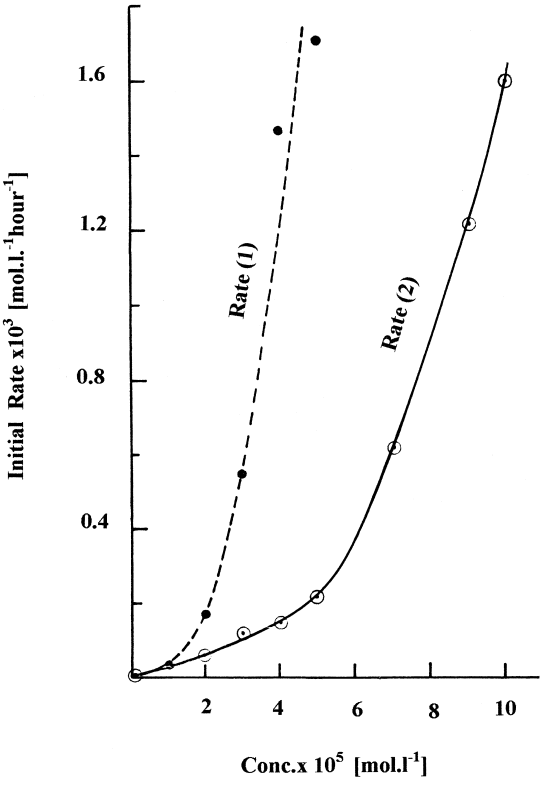


Fig. 7. Plot of the initial rate vs concentration for 2-hydroxy-4-nitrophenylazoresorcinol in DMSO at 22°C.

Table 1
The initial rate for the interaction of different concentrations of the dye in DMSO at 22° ± 1.0°C

Initial rate (10^3) mol liter^{-1} h^{-1}		Concentration (10^5) mol liter^{-1}
First step	Second step	
0.025	[a]	1.0
0.185	0.06	2.0
0.55	0.125	3.0
1.48	0.15	4.0
1.70	0.42	5.0
[b]	[b]	5.5
[b]	[b]	6.0
[a]	0.62	7.0
[a]	1.17	8.0
[a]	1.22	9.0
[a]	1.60	10.0

[a]Not observed.
[b]Data in this range are not reproducible.

4. Conclusion

The aggregation of o,o′-dihydroxy azo dyes in general, and the dye investigated in particular, is affected not only by the dye concentration, solvent and temperature [28] but also by the period of interaction between the dye and the solvent. The rate of aggregation is found to be highly temperature [25] and time dependent, and the reaction is argued to be auto-catalyzed by the formation of the dimer. The study of the temperature effect on the electronic absorption spectra of some azodyes, and the determination of the reaction kinetics, particularly at relatively high temperature, is very sensitive. Completely misleading results may be obtained if the period between preparing the solution and recording the spectra is not zero, or at worst very short and constant for all measurements. The behavior of the dye in both DMSO and DMF, and the direction of reaction, were almost the same. The azo form prevails at low dye concentrations. When the dye concentration reaches a critical concentration (ca. 5.0×10^{-5} mol liter^{-1}), the dye starts to dimerize. The formation of dimer highly catalyses the formation of the hydrazo species, and speeds the initial rate of the first reaction. The azo-dimmer–hydrazo equilibrium is affected by time, due to the dye tendency to aggregate where its species undergo favorable slow rearrangements to decrease the system free energy.

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