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Spectroscopic studies of Solophenyl red 3BL polyazo dye tautomerism in different solvents using UV–visible, ^{1}H NMR and steady-state fluorescence techniques

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Abstract

Azo–hydrazone tautomerism of Solophenyl red 3BL (C.I. Direct 80) polyazo dye in dimethylsulfoxide, methanol, propionic acid, formamide, dimethylformamide and water was investigated using UV–visible, ^{1}H NMR and steady-state fluorescence techniques. The results showed that 3BL dye molecules exist as an equilibrium mixture of azo and hydrazone tautomer in all solvents, but azo form was dominant. In the UV–visible absorption spectra a broad intense band at 570 nm appeared which is related to azo (at 520 nm) and hydrazone (at 560 nm) tautomer bands and UV–visible band contour analyses further confirmed this statement. UV–visible absorption spectra of the two tautomric forms were completely distinguished in DMSO and DMF solvents while in water and propionic acid they were slightly distinguished. Furthermore, in methanol only azo tautomer was dominant. By increasing solvent polarity from water (1.82 D) to DMSO (3.96 D), the splitting of azo and hydrazone tautomers was increased. ^{1}H NMR studies also confirmed the azo and hydrazone tautomerization in D_2O and DMSO–d_6 solvents. Finally, steady-state fluorescence spectroscopy results showed that 3BL dye molecules did not exhibit any appreciable light emission in acidic, neutral and basic aqueous solutions or in other solvents.

Keywords: Azo–hydrazone tautomerism; Solophenyl red 3BL (C.I. Direct 80); UV–visible; ^{1}H NMR; Steady-state fluorescence spectroscopy

1. Introduction

Azo dyes are a versatile class of coloured organic compounds and depending on the number of azo linkages (–N=N–), these compounds can be further classified into subgroups, such as monoazo, bisazo, trisazo and polyazo. These classes of organic compounds have extensively been used in both industry for applications such as textiles, papers, leathers, gasoline, additives, foodstuffs, cosmetics and theoretical point of view [1–3]. In addition to other applications, azo compounds are used as photosensitive species in photographic or electrophotographic systems and are the dominant organic photoconductive materials in commercial copiers [4]. Photodynamic therapy (PDT) is a new type of treatment for tumors and certain diseases. This modality involves giving the patient a photosensitizing drug that accumulates in or is selectively retained by the diseased tissue. Subsequent illumination, typically with a laser, results in photo-damage or destruction of the diseased tissue with relatively little effect on the surrounding normal tissues. Indocyanine green (a tricarbocyanine dye) and other cyanine dyes, Procion blue HB (an amino anthraquinone derivative), Sudan black (a diazo dye) and some of other

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mono, di and polyazo dyes have also been suggested as possible photothermal sensitizers and show selective thermal damage of some forms of cancer and other diseases on illumination with a pulsed laser ([5] and references therein). The applications of these dyes strongly depended on their photophysical properties. For instance, some of the azo dyes can exhibit interamolecular proton transfers which in consequence can form tautomerism of azo and hydrazone. Proton tautomerism plays an important role in many fields of chemistry and especially biochemistry [6–16]. The hydrazone form that absorbs light at longer wavelengths was found to render higher photoconductivity to dual-layered photoreceptors [4]. It is well known that the proton transfer can occur in ground and/or excited state, but only during the last decade the excited state proton transfer has been the subject of substantial interest. Molecules giving rise to excited state tautomers by interamolecular proton transfer are often used as laser dyes, in higher energy radiation detectors and molecular memory storage devices, as fluorescence probes and polymer protectors [6]. Alarcon et al. have reported fluorescence and absorption data for substituted hydroxybenzaldehydes and have found that emission comes only from the hydrazone form ([6] and references therein). In colourant industry, colour constancy is strongly depended on *cis–trans* isomerism of dyes [16]. The shift of tautomeric equilibrium was observed in different azo compounds by adding acids or alkalis into solvents, or by changing temperature. Moreover, in some cases, the changes caused by heating remained even for several months [4]. It was also found that the type of solvent exerts a profound influence on the tautomerism. Generally, a more polar solvent favors the hydrazone form whereas less polar solvents favor the azo form [15,17]. Several authors have written papers [4–6, 12–15,17–19] or reviews (references therein [14]) on the subject of azo–hydrazone tautomerism. Despite the extensive studies on the tautomerism, some essential problems are still open to debate. Thus the electronic, NMR, IR and Raman spectroscopy of tautomers in azo–hydrazone tautomerism have been investigated in diverse solvents. The existence of more than one tautomer has been spectroscopically confirmed [14]. Solophenyl red 3BL (C.I. Direct 80) was used in this work as a polyazo dye which for its several tautomers can theoretically exist and can exhibit interesting properties and was extensively used in textile industry. To the best of our knowledge from literature relatively less attention has been paid to study of tautomerism of polyazo dyes, therefore in the present study UV–visible, ^{1}H NMR and steady-state fluorescence spectroscopy were used in study of 3BL dye tautomeric behavior in different solvents.

2. Experimental

2.1. Material

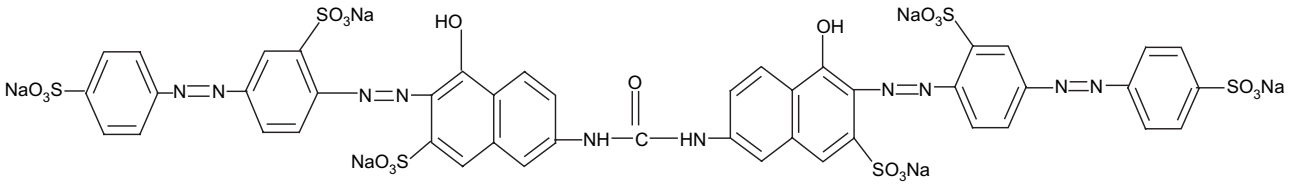
Chemical structure of commercial Solophenyl red 3BL (C.I. Direct 80) polyazo dye presented in Scheme 1, was obtained from Ciba-Geigy and was used as received without further purifications. Dimethylsulfoxide (DMSO), methanol, propionic acid (PA), formamide (FA), dimethylformamide (DMF) and pyrene were obtained from Merck. The pH value of solutions was adjusted with H_2SO_4 and KOH solutions and water for dye solution preparation was doubly distilled.

2.2. Absorption and emission spectroscopy

A double beam Varian Cary 500 Scan UV–visible spectrophotometer was used to record the absorption spectra over a wavelength range 200–800 nm which combined with a cell temperature controller with accuracy of ± 0.1 °C. Quartz cuvettes were used for measurements in solution via $l = 1$ cm. Photoluminescence of dye solutions was studied with a Shimadzu RF-5000. Samples were illuminated with a 450 W xenon UV source at an excitation wavelength of 534 nm (monomer maximum absorption wavelength) and 633 nm (dimer maximum absorption wavelength). Emission spectra were recorded over a wavelength range 200–1000 nm with excitation slit width 3 nm and emission slit width 3 nm.

2.3. NMR spectroscopy

^{1}H NMR spectra were recorded at 298 K on a Bruker AM 500 advanced instruments operating on ^{1}H: 500.135 MHz; ^{13}C: 125.033 MHz. Chemical shifts are expressed in ppm downfield from tetramethylsilane. In all experiments D_2O and DMSO–d_6 were used as



Scheme 1. Chemical structure of commercial Solophenyl red 3BL (C.I. Direct 80) polyazo dye.

solvent and tetramethylsilane was as the internal standard.

3. Results and discussion

3.1. UV–visible spectroscopic studies in aqueous solution

Fig. 1 shows the electronic absorption spectra of Solophenyl red 3BL in water with various dye concentrations (pH = 7.32). The UV–visible spectrum of 3BL dye consists of many absorption bands. It is observed that the absorption spectrum of 3BL is characterized by two bands in the visible region, with their maxima located at ca. 570 and ca. 380 nm, and by two bands in the ultraviolet region located at ca. 230 and ca. 280 nm (trace b). The absorbance bands at 230 and 280 nm are due to the benzene and naphthalene rings of 3BL, respectively, and are assigned to a $\pi \rightarrow \pi^*$ transition. The two bands in the visible region are due to the chromophore-containing azo linkage. It seems that the less intense band centered at ca. 380 nm is due to the partly forbidden $n \rightarrow \pi^*$ transition. On the other hand, the more intense broad band is attributed to the presence of two forms of the dye molecules (viz. azo at ca. 520 nm and hydrazone tautomers at ca. 570 nm) in solution and stems from an allowed $\pi \rightarrow \pi^*$ transition. 3BL is subjected to intramolecular hydrogen bonding tautomeric interactions between the hydrogen of hydroxyl group on the naphthyl group and the corresponding azo linkage. The hydrazone form is bathochromic compared to the azo form and has usually a higher tinctorial strength. Therefore, the band at higher wavelength corresponds to the hydrazone form, whereas the band at lower wavelength is linked to the azo form of 3BL dye. The shape analysis of this broad band at ca. 570 nm shows that, the ratio of azo form to the hydrazone form in aqueous solutions is much higher because the azo form is favored by water due to intramolecular hydrogen bonding. Furthermore, as can be seen from Fig. 1 by increasing dye concentration from 4×10^{-6} to 4×10^{-4} mol dm^{-3} (b–d), a new band in relation to aggregation of dye molecules was not observed and just the intensity of characteristic bands was increased. Therefore, it seems that this polyazo dye remained mostly in non-aggregated form by concentration variation in neutral aqueous solution and in mentioned concentration range. It should be noted that the higher concentrations of 3BL dye (4×10^{-3} mol dm^{-3}) was not detected by our spectrophotometer with quartz cuvettes via $l = 1$ cm as shown in the inset of Fig. 1 (case a). The absorption band at ca. 570 nm is broad and asymmetric, in order to analyse band shape we used the UV–visible band contour analysis method in the next stages.

3.2. UV–visible spectroscopic studies in different solvents

Fig. 2 shows the electronic absorption spectra of Solophenyl red 3BL in various solvents. As shown in this figure, a broad and doublet band corresponding to the lowest transition which is centered at ca. 570 nm has different shapes in various solvents with exception of methanol in which we observed only one single electronic band. The splitting of in question broad band into two distinct bands via different peak positions in various solvents with exception of methanol is pronounced, especially peaks resolving is more pronounced in DMF and DMSO solvents. From these findings, it is clear that the splitting level is also dependent on the

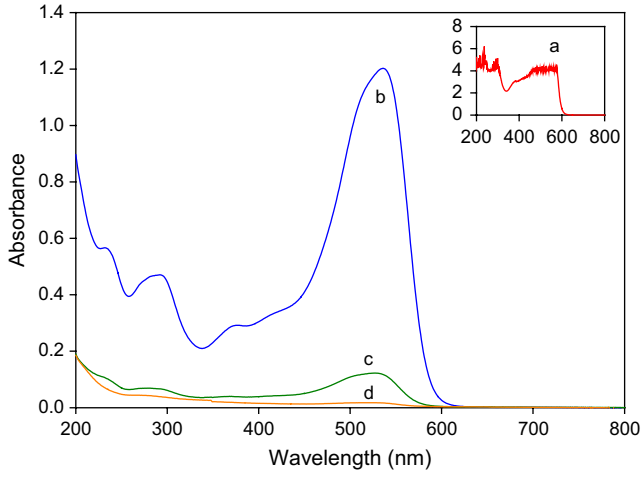


Fig. 1. UV–visible absorption spectra of Solophenyl red 3BL in water at different dye concentrations. (a) 4×10^{-3}, (b) 4×10^{-4}, (c) 4×10^{-5} and (d) 4×10^{-6} mol dm^{-3}.

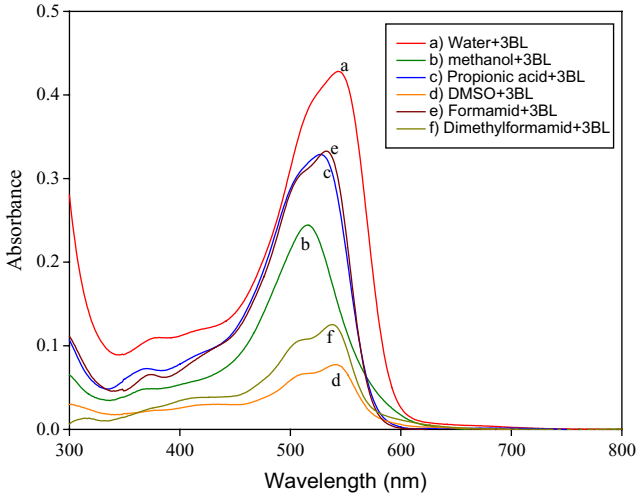
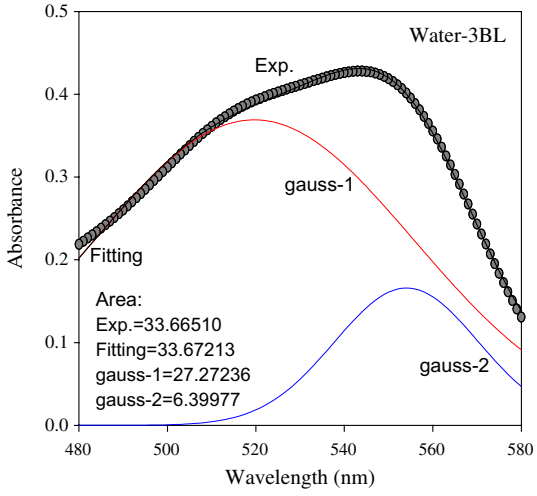
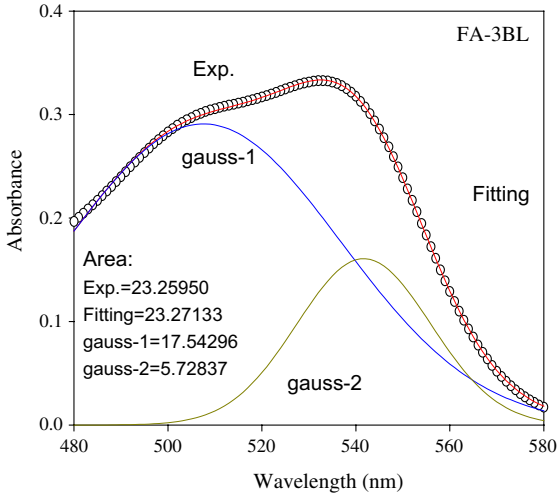
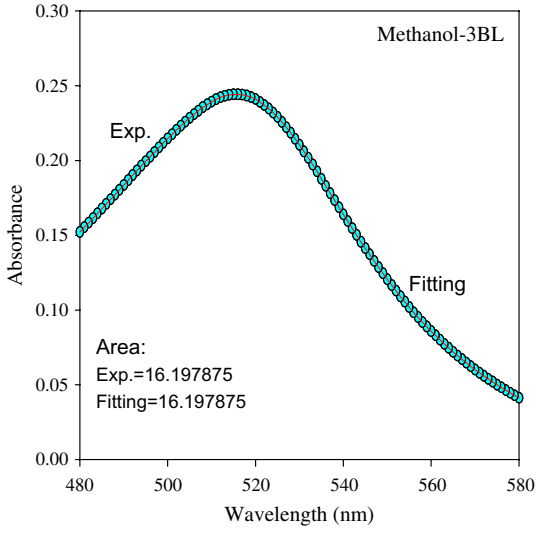


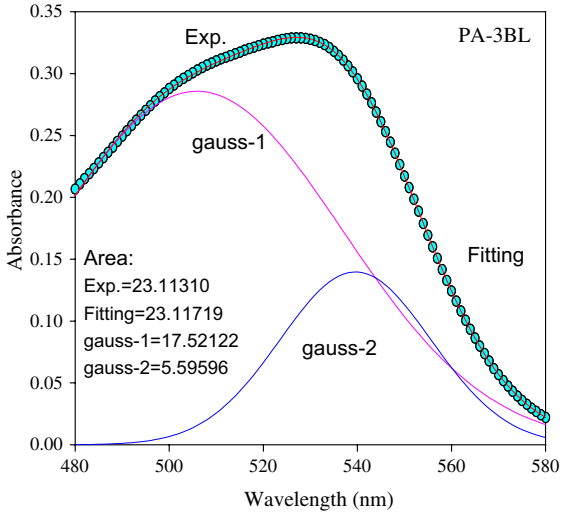
Fig. 2. UV–visible absorption spectra of Solophenyl red 3BL in different solvents.

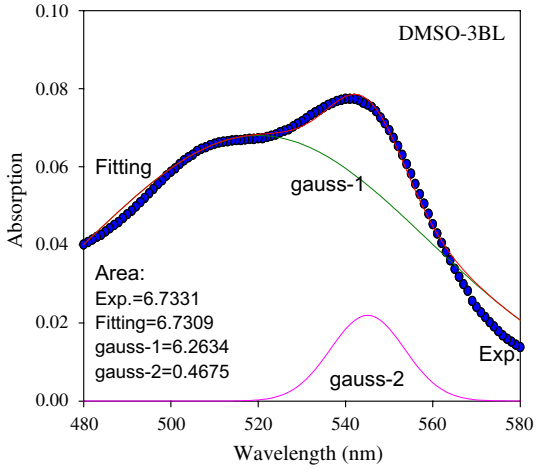
Table 1
Decomposed UV–visible absorption bands of Solophenyl red 3BL azo-hydrazone tautomers in different solvents

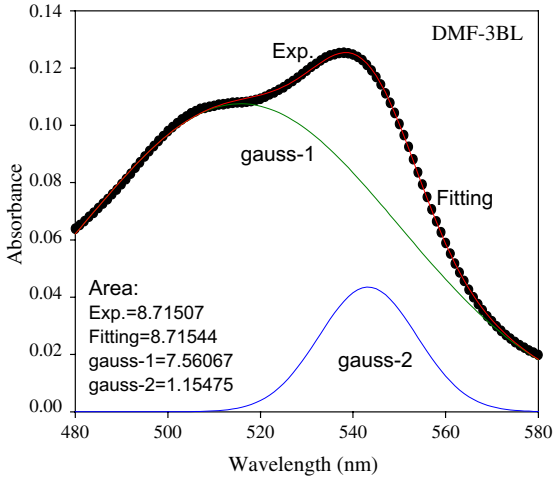












solvent polarity or structure and H-bonding process. We assigned these features to the existing azo–hydrazone tautomerism equilibrium. Similar trend for azo-functionalized dendrimers has been reported by Kap-Soo and his co-workers [12]. Since, azo form appeared in lower wavelength region and hydrazone form in higher wavelength, therefore in the case of 3BL dye the band in lower wavelength is related to azo tautomer and higher wavelength band to hydrazone tautomer. It is evident that in all solvents, the proportion of azo form is much higher than that of hydrazone form and the azo form is favored by all solvents but the proportion of hydrazone tautomers was changed significantly upon varying the solvent polarity. In methanol the proportion of azo tautomer reaches its maximum value and hydrazone tautomer apparently disappears or vanishes. By increasing the solvent polarity from water (1.82 D) to DMSO (3.96 D), the splitting of azo and hydrazone tautomers was increased. Further proportion of azo tautomer in methanol in comparison with the other solvents can be rationalized by the fact that the methanol could not make strong hydrogen bonding with 3BL molecules. It is clear that in all solvents the absorption bands of azo–hydrazone tautomers have overlapped, such that the resultant broad unresolved band cannot be quantified readily. Therefore, contour analysis should be used to resolve the overlapping bands into their individual components.

3.3. UV–visible band contour analysis

The use of UV–visible spectroscopy for study of the tautomeric equilibrium between azo and hydrazone forms requires a knowledge of the molar extinction coefficients of the individual forms. To this end various semi-quantitative approaches are usually adopted [12,20–22]. In the present study, the absorption bands of the azo and hydrazone tautomers have been overlapped, such that the resultant broad unresolved bands cannot be quantified readily. Therefore, contour analysis was employed to resolve the overlapping bands into their individual components. Band contour analysis, a semi-quantitative method used to resolve complex bands in absorption IR and FT-IR, Raman and UV–visible spectra, was developed in the 1960s and has been used for other application such as fluorescence, DSC techniques and so on. It is an iterative least squares optimization involving four parameters: peak height, peak position, half-band width and baseline correction. Essentially, the method fits a given function (Lorentzian, Gaussian or some combination) to an experimentally observed band. The program used for band fitting in the present study was Igor-Pro 4.01, which has a non-linear least square band fitting procedure. This program was used in generating components bands. The most important quantity derived from this analysis is the band area of each component band which is directly related to the concentration of the corresponding tautomers and to oscillator strength. To resolve the spectra measured into sub-Gaussian bands, the corresponding individual peak positions must be known, this can be a quite difficult task especially in the case of azo dyes the spectra of which are lacking a detailed vibrational fine structure. Hence, we used the second derivative of UV–visible spectrum to obtain peak positions. The obtained resolved bands and quantitative results are presented in Tables 1 and 2. The results in Table 2 showed that by increasing solvent polarity the proportion of azo tautomer was increased whereas in contrast the proportion of hydrazone tautomer was decreased and these results show that intramolecular hydrogen bonding is favored for 3BL molecules than the intermolecular hydrogen bonding in all solvents.

3.4. Effect of aqueous solutions pH

It is well known that the aggregation of dye molecules has a remarkable effect on the azo–hydrazone tautomers in solution, through the existence of monomer–dimer equilibrium. Fig. 3 shows the absorption spectrum of Solophenyl red 3BL (4×10^{-4} mol dm^{-3}) in aqueous solution (pH = 1.14). A new broad band located at ca. 650 nm appeared which can be related to J-aggregation of dye molecules. It is worth to note that the colours of neutral, lowly acidic and basic aqueous dye solutions were red pinkish but in the case of highly acidic the colour of dye solution was changed to blue Fig. 4 (case b). Fig. 3 also shows the resolved Gaussian shape bands of monomer–dimer and azo–hydrazone tautomers of monomer of Solophenyl red 3BL. Also it is clear that there are two types of J-aggregates of dye molecules which may be due to two tautomers and/or is related to higher degree of monomer molecules aggregation such as trimer and so on. Table 3 shows their UV–visible absorption band

Table 2
UV–visible absorption band area ratio for azo–hydrazone tautomers (X_{Azo}) and ($X_{hydrazone}$) of Solophenyl red 3BL in different solvents

Solvent	Dipole moment (Debye)	X_{Azo} [a]	$X_{hydrazone}$ [b]
PA[c]	1.55	0.76	0.24
Methanol	1.66	≈1.00	≈0.00
Water	1.85	0.81	0.19
FA[d]	3.73	0.75	0.25
DMF	3.82	0.86	0.14
DMSO	3.96	0.93	0.07

[a] $X_{Azo} = \frac{\text{Area (Azo)}}{\text{Area}_{Exp}}$.

[b] $X_{hydrazone} = \frac{\text{Area (hydrazone)}}{\text{Area}_{Exp}}$.

[c] Propionic acid.

[d] Formamide.

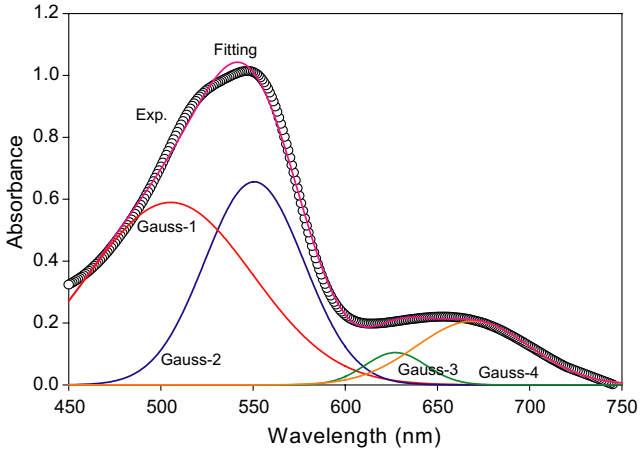


Fig. 3. The resolved Gaussian shape bands of monomer–dimer and azo–hydrazone tautomers of monomer of Solophenyl red 3BL (4×10^{-4} mol dm^{-3}) in aqueous solution (pH = 1.14).

positions and areas. As can be seen in Fig. 4 by decreasing solution pH, an absorption plateau appears and the total number of tautomers is converted to aggregated molecules.

3.5. Effect of temperature

Fig. 5 shows the thermal variation of aggregation phenomenon of Solophenyl red 3BL in aqueous solution at pH = 0.2 (curve (a) in Fig. 4). In order to obtain more insight into the temperature effect on the aggregation of dye molecules, we followed the dye solution absorptions at $\lambda = 534$ nm (for monomer molecules) and at $\lambda = 633$ nm (for dimer molecules) as a function of solution temperature. As shown in Fig. 5, from 25 to 90 °C the absorption values of monomer molecules decreased while those of the dimer molecules was increased. With considering azo and hydrazone

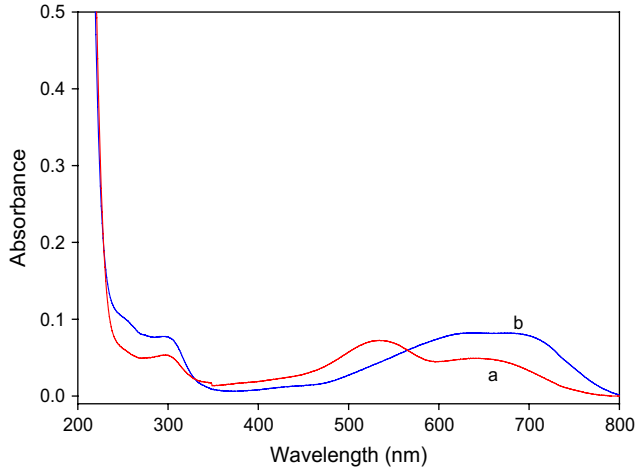


Fig. 4. Absorption spectra of aggregated Solophenyl red 3BL aqueous solution at different solution pH. (a) 0.2 and (b) less than 0.2.

Table 3
Decomposed UV–visible absorption band positions and area of monomer–dimer and azo–hydrazone tautomers of Solophenyl red 3BL (4×10^{-4} mol dm^{-3}) in aqueous solution (pH = 1.14)

Sub-bands	Gauss-1	Gauss-2	Gauss-3	Gauss-4	Gauss (1 + 2)	Gauss (3 + 4)
Peak position λ (nm)	506.00	551.00	627.00	669.00	543.00	665.00
Peak area	58.62	44.39	4.33	15.78	103.01	20.11

tautomers which cause two types of dimers, the decrease of monomer molecule absorption could be related to tautomer exchange and the increasing of dimer molecule absorption could be related to dimer exchange with temperature variation.

3.6. ^1H NMR studies

The basic structure requirement for azo–hydrazone tautomerism is the existence of labile proton in the molecule. This requirement is manifested in the case of azo dyes containing OH or NHR group conjugated with the azo group and these dyes exist as tautomeric azo–hydrazone mixture in solution and solid phase. It should be noted that only a statistical evaluation shows theoretical possibility for tautomerism in 92% of the monoazo dyes published in Colour Index [18,19]. Since, in the Solophenyl red 3BL two OH groups have conjugated with the two azo groups, therefore there are two possibilities for azo–hydrazone tautomerism. Whether such tautomerism is actually observed depends on several factors (such as solvent, temperature, concentration, aggregation of monomer molecules and so on) but principally on the relative thermodynamic stability of the azo and hydrazone tautomers. Fig. 6(a) and (b) shows the ^{1}H NMR spectra of 3BL azo dye in D_2O and DMSO, respectively. Owing to low solubility of dye in

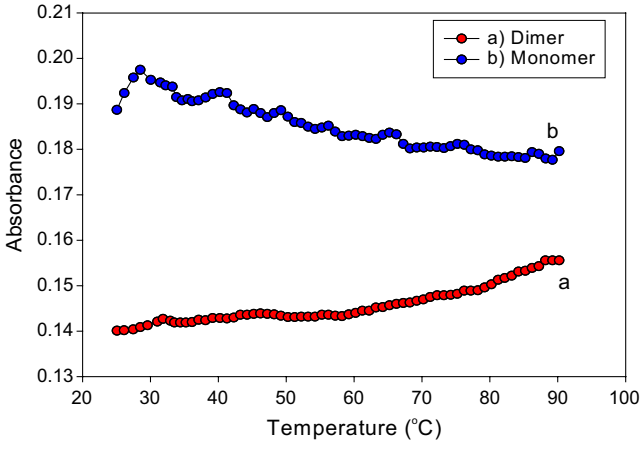


Fig. 5. Thermal analysis of Solophenyl red 3BL aggregation in aqueous solution at pH = 0.2. (a) Dimer at $\lambda = 633$ nm and (b) monomer at $\lambda = 534$ nm.

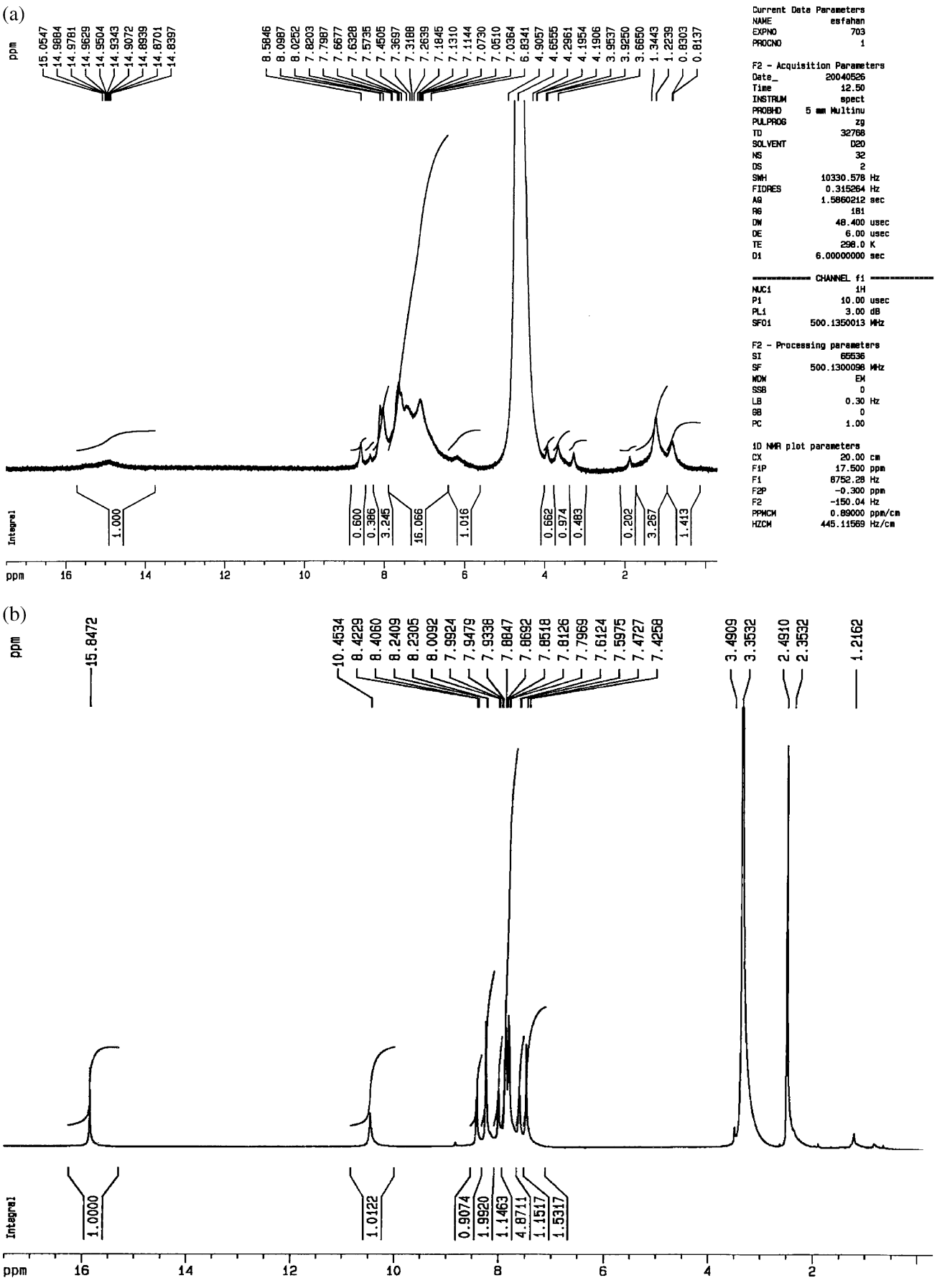


Fig. 6. (a) ^{1}H NMR spectrum of Solophenyl red 3BL polyazo dye in (a) D_2O and (b) DMSO–d_6.

D_2O the ^1H NMR lines of 3BL exhibit very weak intensity. In addition, due to dispersity of dye the concentration of ^{13}C nucleus in aqueous solution was very trace which in consequence we could not obtain the ^{13}C NMR spectrum of 3BL dye in D_2O. As it can be seen from Fig. 6(a) that there are a number of NMR lines between 0 and 4 ppm which are related to impurities protons of 3BL textile dye and NMR line ca. 5 ppm is due to D_2O and NMR lines between 6 and 9 ppm can be related to the aromatic rings protons. A relatively broad shoulder in the range from 14 to 16 ppm was also observed which can be assigned to the dynamic proton exchange between 3BL dye and solvent. Fig. 6(b) shows the ^1H NMR spectrum of 3BL dye in DMSO–d_6 solvent. As can be seen that there are a number of NMR lines between 0 and 2 ppm which are related to impurity protons of 3BL textile dye and NMR lines ca. 2.5 and 3.5 ppm are due to DMSO–d_6 and its water protons. The NMR lines between ca. 7 and 9 ppm can be related to the aromatic ring protons. This figure also showed up two additional peaks at 10.5 and 15.8 ppm corresponding to probably phenolic and –C=N–NH– or –CO–NH– protons, indicating that 3BL dye existed in an azo–hydrazone equilibrium mixture. As can be seen in an azo–hydrazone tautomeric mixture, the hydrazone form is stabilized by hydrogen bonding with polar solvents such as water. On the other hand, in the other solvents such as DMSO or DMF which the hydrogen bonding is not possible the azo form can be stabilized by intramolecular hydrogen bonding. Unexpectedly, as seen from the decomposed UV–visible absorption bands of Solophenyl red 3BL in Table 1 in all solvents azo tautomer is dominant; discrepancy can be rationalized by the fact that the intramolecularly hydrogen bonded six membered ring that is formed imparts a great deal of stability to the dyes. The energy of the intramolecular hydrogen bond formed in monoazo counterparts has been determined to have energy of 5–10 kcal/mol ([5] and references therein).

3.7. Fluorescence studies

Fluorescence which often occurs in cyclic, rigid molecules that contain π electrons is enhanced by the presence of electron-donating groups. Fluorescence of related *o*-hydroxy monoazo dyes as well as of some of the direct blue diazo dyes has been attributed to planarity induced by interamolecular hydrogen bonding ([5] and references there in). Fluorescence also decreased by electron-withdrawing groups as well as also depends on pH, solvent, temperature and so on. Non-rigid molecules, on the other hand, easily lose their absorbed energy by degradation and/or vibrational relaxation [23]. Since, the results of this study have vital importance in some applications, therefore light emission of 3BL dye

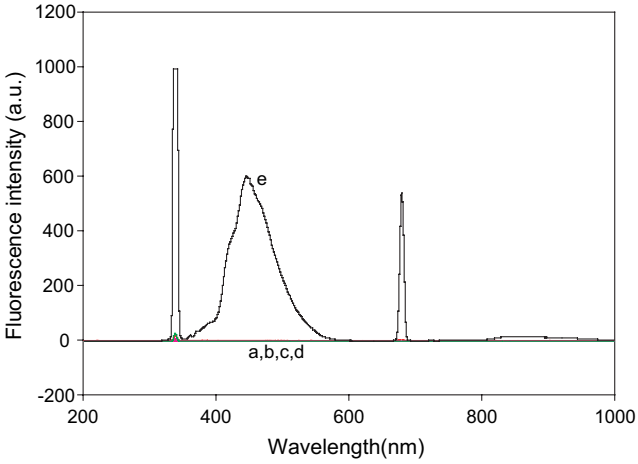


Fig. 7. Steady-state fluorescence spectra of 3BL in aqueous solvent with different solution pH. (a) Less than 1.14, (b) 1.14, (c) 7.32, (d) 11.90, and (e) fluorescence spectrum of pyrene as a reference fluorescent probe material.

was also studied. The steady-state fluorescence spectroscopy in aqueous solution at different pH showed that the 3BL dye does not have appreciable light emission properties (Fig. 7) and in other solvents (not shown here). This result could probably be related to the rotation of molecule segments around the N–C of amide functional group at the center of dye molecule single bond axis. Owing to this type of rotation, dye molecule does not have rigid structure. In consequence, dye molecule does not exhibit light emission behavior. In order to compare the fluorescence intensity of 3BL dye molecule and a well known fluorescence probe, the fluorescence spectrum of pyrene molecule which exhibits significant fluorescence emission is also shown in this figure. As can be seen the emission of 3BL dye in all solution pH in comparison with pyrene is negligible.

4. Conclusion

From our findings the following conclusions could be drawn:

- The results of ^1H NMR and UV–visible techniques show that the Solophenyl red 3BL polyazo dye has azo and hydrazone tautomer in all solvents with exception of methanol in which azo tautomer was dominant.
- Highly acidic condition of aqueous 3BL dye solution has a significant effect on the azo–hydrazone tautomeric equilibrium through the dimer formation.
- Fluorescence studies show that the 3BL dye molecule does not have any significant light emission property even in highly acidic condition of aqueous dye solutions and J-aggregation does not have any

significant effect on the light emission behavior of dye molecules.

Finally, this work is in progress in our laboratory in order to obtain more insight into the complexity of azo–hydrazone tautomeric behavior of polyazo dyes.

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