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Solvent Characteristics in the Spectral Behaviour of Eriochrome Black T

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ABSTRACT

The visible electronic spectral behaviour of Eriochrome Black T, in a number of organic solvents of different characteristics has been examined. It was concluded that the dye exists in solution in basic solvents (based on their autoprotolysis constant, pK_s*) in an azo* $\rightleftharpoons$ *hydrazone tautomeric equilibrium, while in acetone, acetonitrile and DMSO it exists mainly in the azo form. In DMF and other basic solvent solutions, the dye exhibits an acid–base equilibrium of the type* $H_2In^- \rightleftharpoons HIn^{2-} + H^+$*. The proportional concentration of the base form* (HIn^{2-})*, as well as the relative tautomerisation, are largely dependent upon the concentration of Erio T, the basicity of the solvent and the tendency of the base and/or the hydrazone form to be stabilized by H-bonding interaction with the solvent molecules. The compound was found to aggregate in water and hydroxylic solvents. The bands displayed by the differents forms of the compound have been assigned to an electronic transition involving the whole molecule with an appreciable charge transfer character.*

INTRODUCTION

Eriochrome Black T (2-hydroxy-1-(1-hydroxynaphthyl-2-azo)-6-nitronaphthalene-4-sulfonate), is one of a very important family of azo dyes containing the hydroxy naphthalene moiety. It has acid–base properties and responds as a pH as well as a pM indicator. It is known as triprotic acid (H_3In), giving up its sulfonic group proton in acidic

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medium, so that the dye can be represented as H_2In^-, which possesses the following equilibria:[1]

$$\underset{\text{red}}{H_2In^-} \underset{pH\,=\,6{\cdot}3}{\rightleftharpoons} H^+ + \underset{\text{blue}}{HIn^{2-}} \underset{pH\,=\,11{\cdot}6}{\rightleftharpoons} H^+ + \underset{\text{yellowish orange}}{In^{3-}}$$

Much interest has been devoted to the applications of Erio T as an analytical reagent[1,2] and also as a reagent in pharmaceutical analysis.[3] Pilipenko *et al.*[4] studied the electronic spectra of Erio T in aqueous solutions at different pH values and in DMF.

However, the current literature is limited with respect to a detailed study of the spectral behaviour of this indicator in different solvents. In continuation of our interest in studying the spectral behaviour of hydroxyazo compounds,[5–8] this paper presents a study of the role of solvent characteristics in the spectral behaviour of Erio T; solvents used were ethanol, methanol, acetone, DMSO, DMF and acetonitrile.

EXPERIMENTAL

Eriochrome Black T (AR grade) was purchased from Aldrich Chemicals Co. and was used without further purification. All solvents used were of spectral grade (BDH or Merck). Stock solutions (10^{-2} mol. dm^{-3}) of the compound in each solvent were prepared and more dilute solutions then obtained by appropriate dilution.

The electronic spectra of freshly prepared solutions at room temperature (~25°C) were recorded on a CECIL CE 599 using 1 cm matched silica cells.

RESULTS AND DISCUSSION

Effect of Erio T concentration

The visible electronic spectra of different concentrations of Eriochrome Black T (H_2In^-) in various organic solvents, viz. methanol, ethanol, dimethyl formamide (DMF), dimethylsulfoxide (DMSO), acetone, acetonitrile and water were recorded. Representative spectra are shown in Figs 1–3. Examination of the results indicates that the visible electronic spectra of Erio T largely depend on both the nature of the solvent and the concentration of the solute, with a somewhat more complicated behaviour in DMF, in which composite bands are observed.

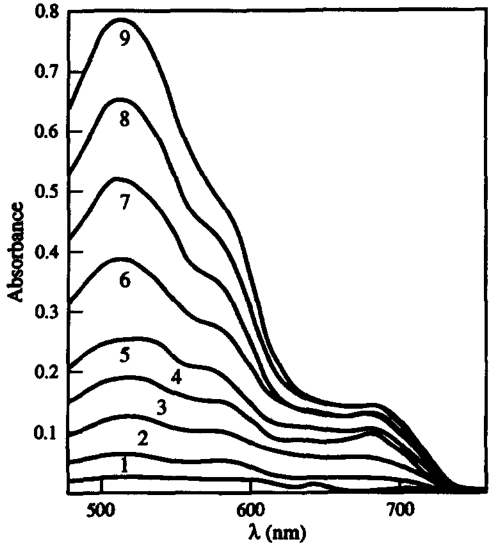


Fig. 1. Electronic absorption spectra of Erio T in ethanol; (1) 4·0 × 10^{-6} M, (2) 1 × 10^{-5} M, (3) 2 × 10^{-5} M, (4) 3 × 10^{-5} M, (5) 4 × 10^{-5} M, (6) 6 × 10^{-5} M, (7) 8 × 10^{-5} M, (9) 1·2 × 10^{-4} M.

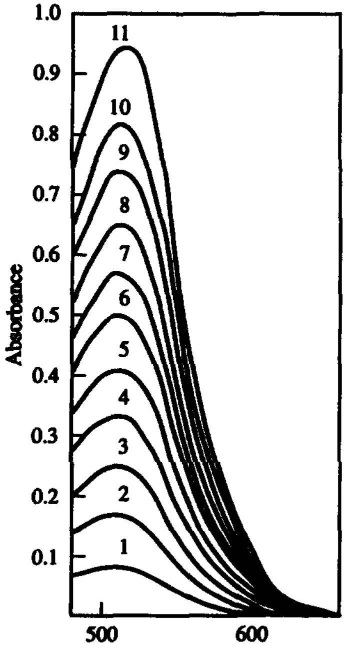


Fig. 2. Electronic absorption spectra of Erio T in acetone; (1) 2·0 × 10^{-5} M, (2) 4·0 × 10^{-5} M, (3) 6·0 × 10^{-5} M, (4) 8·0 × 10^{-5} M, (5) 1·0 × 10^{-4} M, (6) 1·2 × 10^{-4} M, (7) 1·4 × 10^{-4} M, (8) 1·6 × 10^{-4} M, (9) 1·8 × 10^{-4} M, (10) 2·0 × 10^{-4} M, (11) 2·3 × 10^{-4} M.

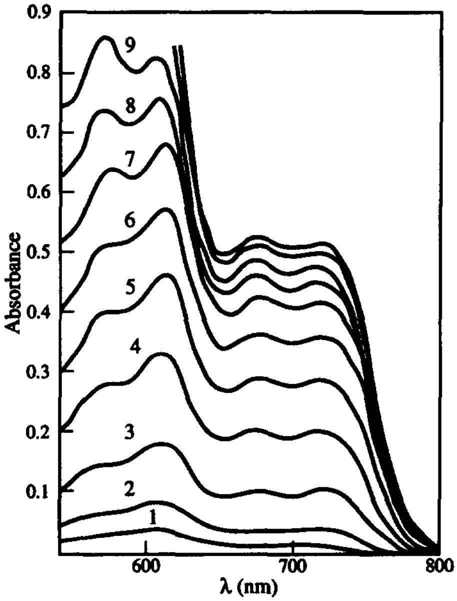
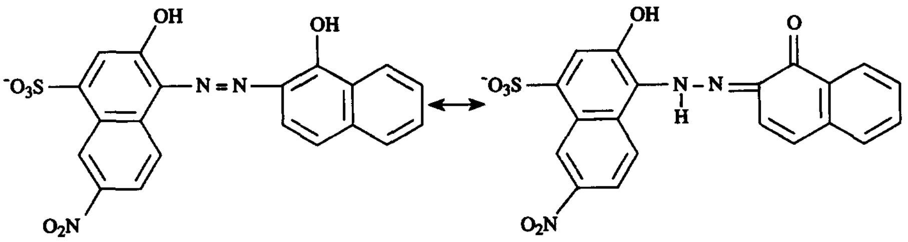


Fig. 3. Electronic absorption spectra of Erio T in DMF; (1) 8·0 × 10^{-6} M, (2) 2·0 × 10^{-5} M, (3) 4·0 × 10^{-5} M, (4) 8·0 × 10^{-5} M, (5) 1·2 × 10^{-4} M, (6) 1·6 × 10^{-4} M, (7) 2·0 × 10^{-4} M, (8) 2·4 × 10^{-4} M, (9) 2·8 × 10^{-4} M, (10) 3·2 × 10^{-4} M, (10) 3·6 × 10^{-4} M.

In the basic amphiprotic (MeOH and EtOH) and dipolar aprotic (DMF) solvents, the visible spectra of the indicator are characterised by two main bands. The shorter wavelength band appears as a broad structured band at low Erio T concentrations (≤3 × 10^{-5} M in MeOH, ≤4 × 10^{-5} M in EtOH and ≤2·0 × 10^{-4} M in DMF). On increasing the Erio T concentrations beyond these limits, two distinct maxima were apparent (at 530, 570 nm in MeOH; 515, 575 nm in EtOH; and 570, 610 nm in DMF), the absorbance of the higher wavelength maximum decreasing with increasing Erio T concentration, until it became a shoulder at higher concentrations. The absorbance of the shorter wavelength maximum increased gradually during this process.

This behaviour can be interpreted on the basis that Erio T exists in an azo-hydrazone tautomeric equilibrium:



Thus, the shorter wavelength maximum of the principal visible band corresponds to absorption by the azo form, and the longer wavelength maximum corresponds to absorption by the hydrazone form. This assignment is based on the fact that the ground state of the quinone–hydrazone form is less stable, and consequently of higher energy than the azo form, and in turn little energy is required for excitation in the former case. On the other hand, the basicity of the solvent plays an important role in stabilising one of these two tautomeric forms, and hence the less basic hydrazone form is more stabilised as the basicity of the medium is increased and therefore the contribution of the hydrazone form increases in the more basic solvents (c.f. Fig. 3).

Confirmation for the existence of Erio T in a tautomeric equilibrium in basic solvents is evident from the fact that the spectra of the dye comprise only one symmetrical visible band in the less basic solvents (CH_3CN, $(CH_3)_2CO$, DMSO).

This band, the λ_{max} of which lies in the range of the shorter wavelength maximum occuring in basic solvents, indicates that the compound exists, in the less basic solvents, mainly in the azo configuration.

The second visible band appearing at a longer wavelength (λ_{max} 670 nm, in water) (Fig. 4), can be ascribed to aggregation of the monoionised form of Erio T. This assignment is based on the fact that the relation between the absorbance of this band and the concentration of the compound is non-linear. This is also in accord with the previously reported tendency of this class of dyes to aggregate in aqueous solutions.[1,9,10] This aggregation seems to be associated with ionisation, since aggregation is reported to result in a considerable lowering in pK_a; the reported *a* value of the dimer of a related dye was ~3·0.[10] Ionisation of the aggregates in water is quite reasonable, in view of its considerable basicity ($pK_s = 14{\cdot}0$).

The visible spectrum of Erio T in basic organic solvents MeOH, EtOH and DMF (pK_s = 16·7, 18·90 and 18·0 respectively[11]) is characterised by a broad band appearing at longer wavelengths (λ_{max} 675–680 nm). On increasing the Erio T concentration, the absorbance of this band attains a more or less constant value. On the other hand, the absorbance of the shorter wavelength visible band increases with increasing Erio T concentration (Fig. 3). This behaviour can be interpreted on the basis that, in dilute solutions ($<2 \times 10^{-4}$ M), Erio T is able to exist in the doubly ionised form (HIn^{2-}) under the effect of the high basicity of these solvents

$$H_2In^- + S = HIn^{--} + H\ S^+ \ (S = \text{solvent}) \tag{1}$$

Accordingly, the longer wavelength visible band appearing in dilute solutions (blue coloured) of this compound in basic solvents can be ascribed to the di-anionic species. Evidence for the presence of Erio T, in

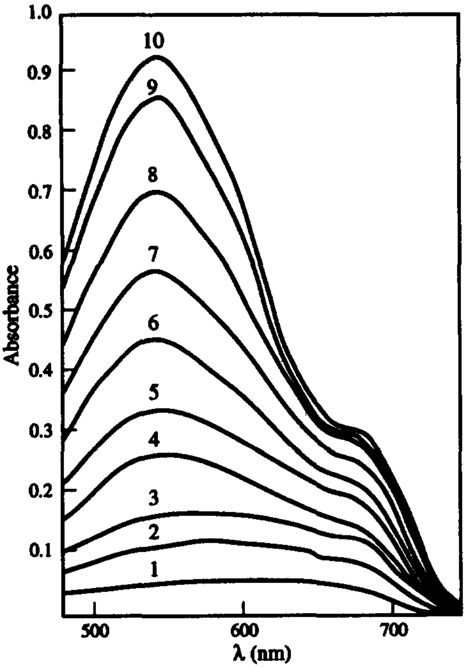


Fig. 4. Electronic absorption spectra of Erio T in water; (1) 2·0 × 10^{-5} M, (2) 4·0 × 10^{-5} M, (3) 6·0 × 10^{-5} M, (4) 1·0 × 10^{-4} M, (5) 1·2 × 10^{-4} M, (6) 1·6 × 10^{-4} M, (7) 2·0 × 10^{-4} M, (8) 2·4 × 10^{-4} M, (9) 2·8 × 10^{-4} M, (10) 3·0 × 10^{-4} M.

an acid–base equilibria of the type described in eqn (1), is evident from the visible spectra of alkaline methanolic solutions of Erio T, where a band at the same wavelength (680 nm, cf. Fig. 5) develops, but with high intensity denoting a large extent of ionisation in the alkaline medium relative to that in organic solvents. Also, alkaline solutions of the less basic solvents (acetone and acetonitrile, pK_s = 32·5 and ≥33·3, respectively at 25°C)[12,13] are characterised by an additional absorption band occuring at almost the same wavelength, and the solutions also have the same colour (blue). This interpretation is considered reasonable, recalling that the reported value for pK_{a_2} (formation of HIn^-) of Erio T is 6·3. In addition to the basicity of DMF, its pronounced character as a strong H-bond acceptor facilitates the deprotonation of H_2In^- form of Erio T. This behaviour reflects the role of these basic organic solvents as ionising media, and is in accord with recent postulations by Mahmoud *et al.*[14–16] concerning such a property of basic solvents. Since the third ionisation constant of Erio T is high (pK_a = 11·6), it is expected that this could not be attainable in organic solvents alone.

The visible spectra of Erio T in weakly basic solvents (acetone, acetonitrile and DMSO) show a main, almost symmetrical band, with

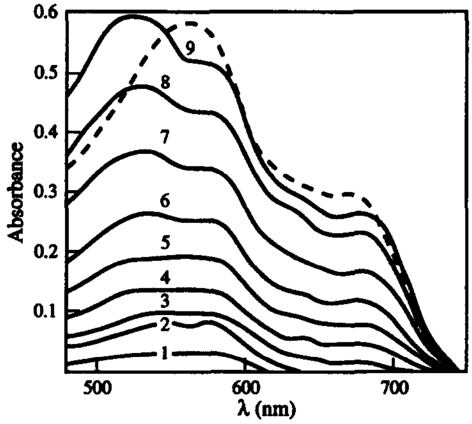


Fig. 5. Electronic absorption spectra of Erio T in methanol; (1) 4·0 × 10^{-6} M, (2) 1·0 × 10^{-5} M, (3) 1·5 × 10^{-5} M, (4) 2·0 × 10^{-5} M, (5) 3·0 × 10^{-5} M, (6) 4·0 × 10^{-5} M, (7) 6·0 × 10^{-5} M, (8) 8·0 × 10^{-5} M, (9) 1·0 × 10^{-4} M, dotted line in alkaline methanol.

maximum absorption at 510–515 nm. The absence of the longer wavelength visible band, representing absorption by the doubly ionized species, even in very dilute solutions in these solvents, reveals a difficult formation of the HIn^{--} conjugate base. This behaviour is consistent with the low basicity of these solvents (pK_s 32·5 for acetone, ≥33·3 for CH_3CN and 33·5 for DMSO[17] at 20°C).

Examination of the data reported in Table 1 shows that although acetonitrile and methanol have comparable dielectric constants (36·0 and 32·6, respectively), the spectral behaviour of Erio T in these two solvents is quite different. The broad shoulder appearing at a longer wavelength in

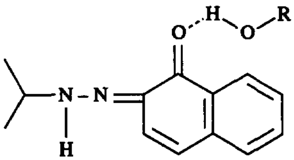
TABLE 1

λ_{max} (nm) Values of the Visible Absorption Bands of Erio T in Organic Solvents and in Water

Solvent	λ_{max} *(nm)*			
	Azo form	*Hydrazone form*	*Ionisation*	*Intermolecular CT*
Methanol	530	570	680	—
Ethanol	515	575	680	—
Acetone	510	—	—	—
Acetonitrile	510	—	—	—
DMSO	515	—	—	—
DMF	570	610	675	720
Water	540	575	670[a]	—

[a] of the aggregate.

methanol is absent in acetonitrile, while it appears in other hydroxylic solvents of different dielectric constants (H_2O, D = 78·5 and EtOH, D = 24·3). This behaviour indicates that specific solute–solvent interaction, such as H-bonding and basicity effects, and not electrostatic effects, play the major role in the tautomerisation and acid–base properties of Erio T in the presence of organic solvents. Therefore, the tendency of hydroxylic solvents to donate H-bonds seems to favour the formation of the hydrazone form through strong intermolecular H-bonding between the carbonyl group of the solute and the OH of the solvent, such as



Band assignment and solvent effect

Values of λ_{max} and ε_{max} of the visible absorption bands displayed by both the monoionic (H_2In^-) and di-ionic (HIn^{--}) forms of Erio T, in various organic solvents, are listed in Table 1. The two visible absorption bands responsible for the absorption by the mono- and doubly ionised form can be assigned to an electronic transition involving the whole molecule, associated with intramolecular charge transfer character. This charge transfer seems to originate from the OH group as a source to the nitro group as a sink.

It is expected that CT interaction occurs more easily within the di-ionic form (HIn^{--}) than in the mono-ionic one (H_2In^-). This reflects in a lower excitation energy for the CT band of HIn^{2-} relative to that of H_2In^- and this is the reason why the CT band of the di-ionic form appears at a longer wavelength than that of the mono-ionic form, as Table 1 shows. On the other hand, it is evident from Table 1 that the λ_{max} of the azo form of the compound acquires, in general, a red shift as the polarity of the solvent increases, confirming its CT nature.

The additional band, appearing only in DMF solutions at longer wavelength (λ_{max} 720 nm) can be ascribed to the formation of a hydrogen-bonded solvated complex between DMF and the dye molecules. Since the charge transfer forces play an important role in H-bonding,[18] one can assign this band to an intermolecular charge transfer transition. This involves an electron transfer from the lone pair of the oxygen atom of the DMF molecule (ψ_{01}) to the anti-bonding orbital of the acidic O–H group of Erio T. The location of this band, at a longer wavelength than that of the usual n–σ^* transition, is presumably due to the high stabilisation of the polar excited state of this transition by the polar solvent (DMF). The occurrence of such an intermolecular CT transition only in DMF as a solvent is quite reasonable in view of (i) the well known strong H-bond accepting character of DMF, and (ii) its low ionisation potential (9.12 eV)[19] relative to the other basic solvents used in this study (methanol and ethanol, ionisation potential = 10·84 and 10·49 eV, respectively).[19]

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