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ELSEVIER

Spectral Properties of Aza-15-crown-5 Containing Styryl Dyes

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ABSTRACT

The spectral properties of a series of styryl dyes containing the aza-15-crown-5 macrocycle are investigated. Using absorption UV-Vis spectroscopy the protonation and aggregation processes are studied and the corresponding pK_a values and dimerization constants K_D determined. Oligomer formation occurs in the presence of $HClO_4$ or ClO_4^{2-}, and a scheme describing these processes is suggested.

1 INTRODUCTION

The formation of aggregated dye molecules in solution is well documented.[1-8] Studies on this process are of interest because most of the spectroscopic and photophysical characteristics of dyes are significantly influenced by self-association.[8-11] In the course of our research on the synthesis and coordination properties of dyes containing a phenylaza-15-crown-5 macrocyclic moiety[12-16] a series of new styryl dyes were obtained.[12] As a part of these investigations the protonation and aggregation ability of these dyes were studied and the results obtained are reported in this paper.

2 EXPERIMENTAL

The synthesis of dyes 1–5 was described previously[12] and their absorption spectra were recorded on a Perkin-Elmer Lambda 17 UV-Vis spectrophotometer using spectral grade solvents. The spectral data acquisition was processed by means of original computer-based programmes described elsewhere.[8]
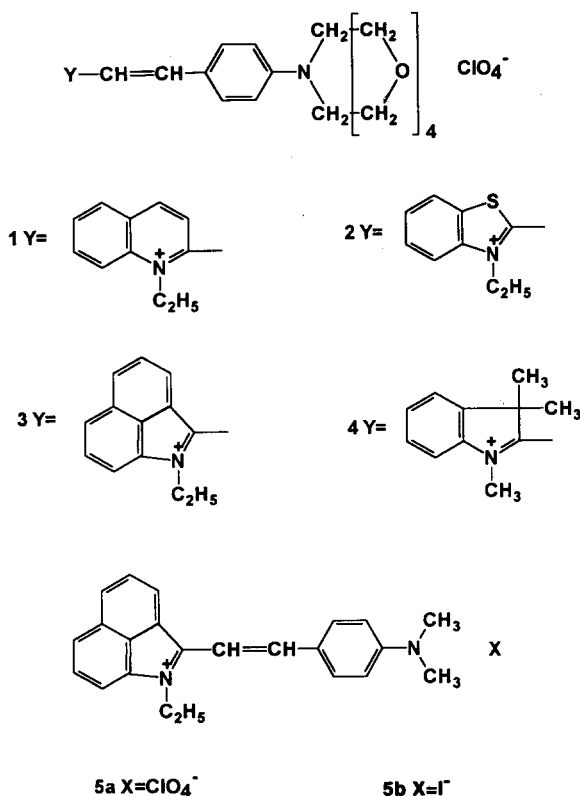
Scheme 1

3 RESULTS AND DISCUSSION

Protonation of the dyes

In acid medium dyes **1–5** undergo a hypsochromic colour change due to the protonation of the macrocyclic nitrogen atom (in dyes **1–4**) or of the N,N-dimethylamino group (in dye **5**). In such cases, the intramolecular charge transfer (CT) between the macrocyclic (or N,N-dimethylamino) donor nitrogen and the heterocyclic acceptor nitrogen atoms does not occur, and the long-wavelength CT band disappears. A new shortwavelength band is observed, which could be assigned to a localized $\pi–\pi^*$ transition.

The pK_a values were obtained using the standard procedure;[14] the pK_a values and spectral characteristics of the neutral and protonated forms of dyes **1–4**, are collected in Table 1. Evidently the protonation proceeds at the macrocyclic N-atom in dyes **1–4** and its basicity decreases in the order **1** >**2** >**3** >**4**, similarly to the corresponding stability constants of Ca^{2+}, Sr^{2+} and Ba^{2+} with these dyes.[15–17]

TABLE 1
The pK_a Values and Spectral Characteristics of the Neutral and Protonated Forms.

Dye	pK_a	Neutral form[a]		Protonated form	
		λ_{max} (nm)	ϵ_{max}	λ_{max} (nm)	ϵ_{max}
1	2·23	495	44 310	348	16 320
2	1·40	499	50 730	354	22 800
3	0·99	628	66 340	414	29 700
4	0·89	523	53 000	371	22 860

[a]In diluted solution.

Self-association

Another important characteristic of ionic dyes is the possible self-association in water.[8-11] In the concentration range 10^{-6} to 10^{-3} M, suitable for UV-Vis spetroscopy, the monomer (M)–dimer (D) equilibrium is mainly observed:[4-8]

$$2M \rightleftharpoons D$$
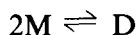
The main relationships describing this equilibrium are as shown in eqns 1–3.

$$\text{mass balance: } c_M^i + 2c_D^i = c_o^i \tag{1}$$

$$\text{dimerization constant } K_D = \frac{c_D^i}{(c_M^i)^2} \tag{2}$$

$$\text{additivity principle: } A^i = c_M^i \epsilon_M l^i + c_D^i \epsilon_D l^i, \tag{3}$$

where c_M^i and c_D^i are the equilibrium concentrations of the monomer and the dimer, respectively, in i^{th} solution with total concentration c_o^i; A^i is the measured absorbance; ϵ_M and ϵ_D are the molar absorptivities of the monomer and dimer,respectively; l^i is the path length, so that $l^i c_o^i = $ const. Expressing the molar part of the monomer by x_M^i the relationships in eqns 2 and 3 are transposed to eqns 4 and 5:

$$K_D = \frac{1 - x_M^i}{2c_o^i(x_M^i)^2} \tag{4}$$

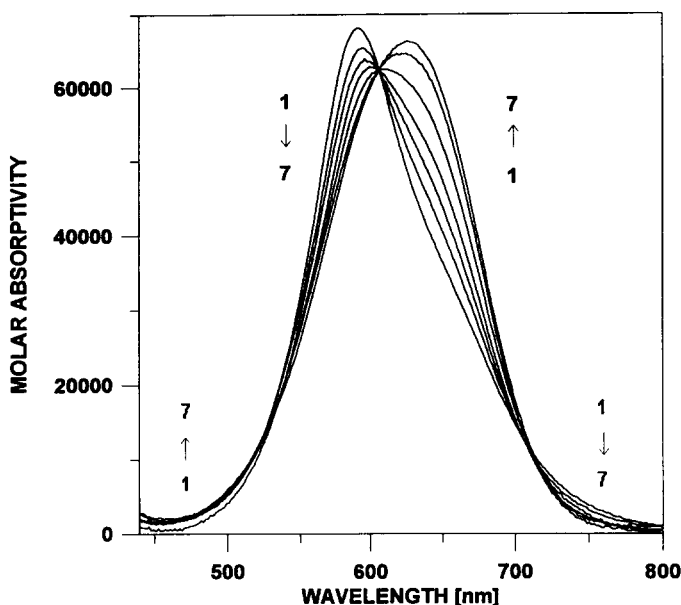$$\epsilon^i = x_M^i \epsilon_M + \frac{1 - x_M^i}{2} \epsilon_D. \tag{5}$$

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MOLAR ABSORPTIVITY

WAVELENGTH [nm]

Fig. 1. Absorption spectra of dye **3** in water (c_0^i; $i = $: 1 – 8·3 × 10^{-5}, 2 – 4·15 × 10^{-5}, 3 – 2·77 × 10^{-5}, 4 – 1·66 × 10^{-5}, 5 – 8·3 × 10^{-6}, 6 – 2·77 × 10^{-6}, 7 – 1·66 × 10^{-6}, $l^i c_0^i$ =8·3 × 10^{-6}).

Thus the dimerization constant could be easily obtained if the spectral characteristics of the monomer (ϵ_M) and dimer (ϵ_D) are known.The dimer spectrum cannot usually be obtained experimentally, but on the other hand, the monomer spectrum could be evaluated only in strongly diluted solutions, but it is connected with significant imprecision.[18] Therefore, the quantitative analysis of monomer–dimer equilibrium is in fact a quantitative analysis of a two-component mixture with unknown spectra of both individual components. The problem is generally insoluble. For this reason, in the case of dyes **1-5** a quantitative analysis using an approach for analysis of two-component mixture based on the nonlinear curve fitting procedure was performed.[8]

The absorption spectra of dye **3** in water are shown in Fig. 1. Increase of dye concentration leads to a decreasing intensity of the monomer band at ~ 630 nm and an increasing intensity of the dimer band at ~ 590 nm. The spectra depicted in Fig. 1 were analysed using the method described previously[8] and the results obtained are presented in Table 2, together with the data for the other dyes. It should be pointed out that in the concentration range investigated there is no evidence for aggregation of dye **4**. A possible reason for this could be steric hindrance originating at the methyl group in the heterocyclic ring. The calculated monomer and dimer spectra of dye **3** are shown in Fig. 2. According to the exciton theory[1,19] the dimer spectrum consists of two bands — the first one (H-band) shifted hypsochromically

TABLE 2
Dimerization Constants and Spectral Characteristics of the Monomer and Dimer Forms

Dye	lgK_D	Monomer		Dimer	
		λ_{max} (nm)	ϵ_{max}	λ_{max} (nm)	ϵ_{max}
1	1·47	491	46430	480	74600
				574	19300
2	2·06	498	51310	474	95730
				562	21320
3	4·09	626	66980	587	82050
				705	10600
5	4·17	631	31940	574	50550
				721	4730

with respect to the monomer band (M-band), and the second one (J-band) shifted bathochromically to the M-band. The occurrence and the relative intensity of H- and J-bands depends on the type of the dimer [1], which in this case is the 'sandwich' type.
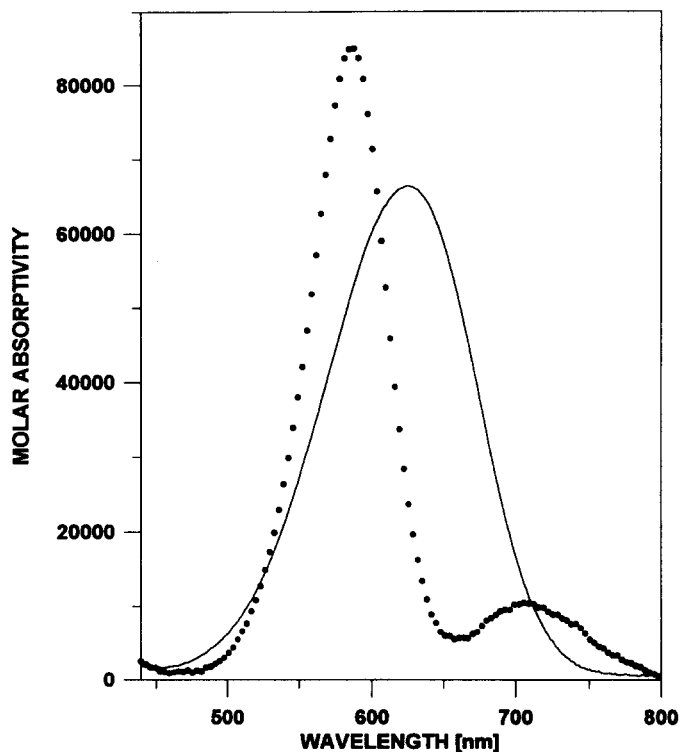

Fig. 2. Calculated spectra of the monomer (——) and dimer (• • •) forms of dye **3**.

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TABLE 3
Characteristics of the Monomer and Dimer Forms

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Dye	$lg(K_D)$	ν_M (cm^{-1})	$f_M{}^b$	ν_J (cm^{-1})	$f_J{}^b$	ν_H (cm^{-1})	$f_H{}^b$	R (Å)	α (°)
1	1·47	20 360	0·835	17 310	0·145	21 110	0·639	5·0	55
2	2·06	20 100	0·860	17 650	0·278	21 240	1·689	5·5	47
3	4·09	15 980	0·987	14 180	0·078	17 030	0·738	7·1	39
5^a	4·17	15 840	0·463	13 860	0·044	17 430	0·505	5·2	36

^{a}The results for **5a** and **5b** are the same.
^{b}Oscillator strength.

The calculated structural characteristics of the dimers — the separation distance R between the monomers and the angle α between the dipoles of the adjacent monomer molecules are presented in Table 3. The corresponding spectral characteristics of the monomer and dimer are represented in Table 2. For dyes **3** and **5**, which are structural analogs, comparison of the calculated $lg(K_D)$ values indicates that the macrocyclic moiety causes a steric hindrance on the dimerization process.

Spectral changes in the presence of perchlorates and perchloric acid in water

The addition of ClO_4^- (as salt) causes significant changes in the absorption spectrum of dye **3**. Initially the intensity of the monomer band at ~ 630 nm decreases, accompanied by an increase of the dimer band at ~ 590 nm, together with the appearance of a new band at ~ 530 nm. Most probably the latter band is due to higher aggregates. Further addition of perchlorate salt leads to precipitation of rose coloured crystals. After isolation, they were found to be readily soluble in water, and the spectrum obtained from them was identical to that of the pure dye.

The same effects were observed by addition of small amounts of perchloric acid up to pH = pK_a+2. The spectrum obtained in this case (Fig. 3) shows both dimeric (~ 590 nm) and oligomeric (~ 530 nm) bands. At pH<pK_a+2, protonation occurs.

These oligomerization and protonation processes caused by $HClO_4$ could be represented by the following scheme:

$$\text{Oligomer} \rightleftharpoons D \rightleftharpoons 2M \rightleftharpoons 2MH^+$$
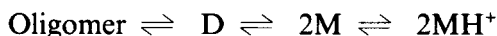
Evidently at pH>pK_a+2 the equilibrium is shifted towards oligomerization, while in strongly acid medium (pH<pK_a+2) the protonation process predominates. The influence of ClO_4^- (as salt) on the aggregation processes confirms the suggested scheme.
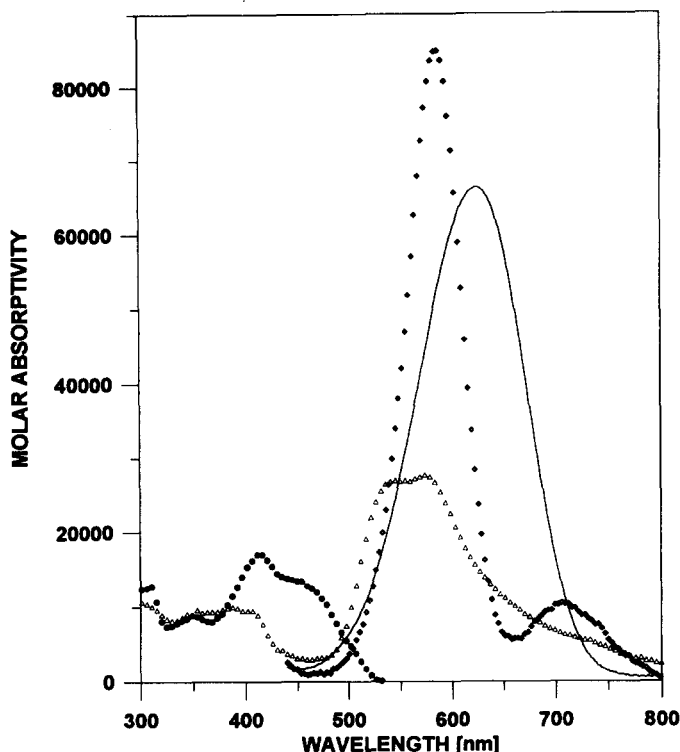
Fig. 3. Absorption spectra of the monomer (———), dimer (♦ ♦ ♦) and protonated form (● ● ●) of dye **3** in water. Absorption spectrum of dye **3** in water after initial addition $HClO_4$(ΔΔΔ).

It should be noted that these effects are observed only in the presence of perchloric acid and its salts. The cationic dye **3** is a perchlorate salt ($Dye^+ClO_4^-$) and the following equilibrium exists in aqueous solution:

$$Dye^+ClO_4^- \rightleftharpoons Dye^+ + ClO_4^-$$
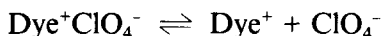
In aqueous solution, this process is shifted practically to the dissociated form, while the addition of ClO_4^- leads to an increase of undissociated form, favoring oligomer formation.

It was established that the spectral characteristics of the dyes studied depend on the nature of the solvent. In Table 4 the data observed for λ_{max} and ϵ_{max} of the longwavelength CT band of dye **3** are given. No clear relationship between the spectral characteristics and the dielectric constant of the solvents is observed, indicating a presence of specific solute–solvent interactions. It was found that this band consists of two subbands (long wavelength A and short wavelength B)[15,17] and their spectral characteristics (λ_{max} and oscillator strength f) obtained by curve resolution[20] are also collected.

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TABLE 4

Spectral Characteristics of Dye **3** in Different Solvents, Obtained by Resolving the Over-lapped Bands[20]

Solvent	D[c]	A-band		B-band		λ^{obs}_{max} (nm)	ϵ^{obs}_{max}
		λ_{max} (nm)	f	λ_{max} (nm)	f		
Chloroform	4·8	686	0·390	638	0·651	679	97 210
Dichlorethane	10·7	685	0·395	638	0·657	679	99 460
Isopropanol	18·3	672	0·264	623	0·355	663	54 230
Acetone	20·7	667	0·521	614	0·588	657	90 630
Methanol	32·7	662	0·474	611	0·591	654	86 940
Acetonitrile	37·5	661	0·605	611	0·753	652	86 640
DMSO	46·7	677	0·434	624	0·522	666	77 570
Water[a]	78·4	636	0·475	580	0·512	626	66 980
Formamide	110	664	0·450	611	0·567	654	80 720
Ca[2+][b]		517[d]	1·049[d]	619[e]	0·074[e]	548	35 500
Sr[2+][b]		526[d]	0·934[d]	610[e]	0·111[e]	536	41 730
Ba[2+][b]		530[d]	1·035[d]	608[e]	0·199[e]	522	42 640

[a]Characteristics of the monomer spectrum.
[b]Spectral characteristics of the complex formed in acetonitrile.
[c]Dielectric constant.
[d]Short wavelength subband.
[e]Long wavelength subband.

It is interesting to point out that the B-band exists in the resolved spectra of the complexes as a subband, while in the model compound **5** without a macrocyclic ring, only the A-band is present. This splitting of the CT-band could be associated with the nature of the macrocyclic ring, and further investigations will hopefully shed light on this phenomena.

ACKNOWLEDGEMENTS

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