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THERMODYNAMICS OF THE DIMERIZATION AND TRIMERIZATION OF HALOFLUORESCEIN DYES

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ABSTRACT

The changes of free energy, enthalpy and entropy produced by the dimerization and trimerization of the fluorescein dianion and its halogenated derivatives eosin and erythrosin are determined. The nature of the association forces is discussed, justifying the previously described geometric structures of the aggregates.

INTRODUCTION

When the concentration of fluorescein dianion solutions and solutions of its halogenated derivatives eosin and erythrosin are increased, variations in their optical properties (absorption and emission) are produced. This behaviour is attributed to dimerization [1–8], which changes their characteristics as photosensitizers [9] and quantum counters [10] and also weakens the output powers of their lasers [11,12], among other side effects.

The fluorescein dimer has been considered to be due to hydrogen bonding [1,5]. Recently, a smaller contribution of van der Waals forces has been indicated [5,6]. In the halofluorescein dimers, the participation of hydrophobic interactions has been suggested [1].

In this work, changes of free energy, enthalpy and entropy produced not only by the dimer formation but also by the trimer formation of fluorescein, eosin and erythrosin are determined. On the basis of the molecular structures of dyes and aggregates, the nature of the intermolecular forces is discussed. The previously reported [5,7] geometric parameters that characterize the disposition of monomers in the aggregates are justified.

EXPERIMENTAL

The dyes used, fluorescein, eosin and erythrosin, were obtained from Fluka (for microscopy). They were twice recrystallized from ethanol and

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dried in a vacuum oven. Other chemicals were Suprapur grade from Merck. Spectra were recorded in aqueous solutions at pH 12 (NH_4OH) containing 0.01 M KCl. The temperature range was from 20 to 50°C at 10°C intervals and the concentrations ranged from 5×10^{-6} to 3×10^{-1} M for fluorescein and 10^{-1} M for the other dyes.

The absorption spectra were recorded on a Perkin-Elmer spectrophotometer model EPS-3T. For concentrated solutions, an RIIC cell model BT-10 of variable optical path and with a special device for thermostatting was used. Due to technical problems, it was not possible to record changes in the electronic absorption with temperature at concentrations greater than 3×10^{-2} M.

The corrected fluorescence spectra were registered on a Perkin-Elmer spectrofluorimeter model MPF-3. The cell used was rectangular of 1 mm optical path. The angles between the normal to the cell and the excitation and emission (photomultiplier) directions were 30 and 60°, respectively. The spectra were corrected for the influence of re-absorption and re-emission phenomena [13].

RESULTS AND DISCUSSION

In previous work [5,7], the aggregation of the fluorescein dianion and its halogenated derivatives eosin and erythrosin was studied at 20°C. The molecular structures of the dyes are given in Fig. 1. The formation constants and absorption spectra of their dimers and trimers were determined. The splittings observed in the spectra were due to the interaction between the dipolar moments of the chromophore part of the monomers, i.e. depending on the relative disposition of their planal xanthene groups. The interpretation of absorption splittings by means of the exciton theory indicated that these groups are placed in parallel planes at a distance of R Å forming their dipolar moment angles of θ degrees. The geometric parameters obtained for

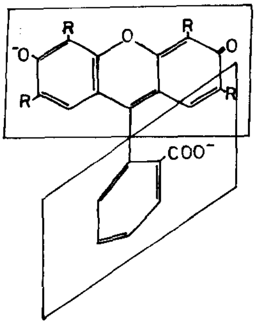

Fig. 1. Molecular structure (quinonoid) of the dianionic form of fluorescein (Fl, R = H), eosin ($FlBr_4$, R = Br) and erythrosin (FlI_4, R = I).

TABLE 1

Monomer transition moments ($|\vec{M}|^2$) and formation constants (K, standard concentration = 1 M), excitonic interactions (U), angles between the xanthene groups of the monomers (θ) and the distance between them (R) for the dimer (d) and trimer (t) of fluorescein (Fl), eosin ($FlBr_4$) and erythrosin (FlI_4) dianions [5,7]

	$\|\vec{M}\|^2$ (e.s.u.^{2} cm^2)	K_d	K_t	U (cm^{-1})	θ (deg)	R (Å)
Fl	58.7	5.0±0.5	10± 3	717	76	4.6
$FlBr_4$	66.3	115 ±3	155±20	743	71	5.3
FlI_4	69.6	127 ±3	150±20	752	69	5.5
Estimated error	±1			±40	±1	±0.4

the dimers also explain the trimer spectra, indicating non-appreciable changes in the relative disposition of the monomeric units in both aggregates.

In Table 1, the results obtained for the monomer transition moments are given together with those for the formation constants, excitonic interactions, θ and R for the fluorescein, eosin and erythrosin aggregates. Molecular models show that the angle θ formed by the planar xanthene groups is due to the steric effects between the benzoic groups, which are constrained to be roughly perpendicular to the chromophore rings. The thermodynamics of these molecular associations are now studied and the forces that take part in them are discussed.

The formation enthalpies of the dimers (ΔH_d^0) have been evaluated from the van't Hoff equation and from the dimerization constants at different temperatures obtained from the respective absorption spectra [5].

Though it was not possible to record the variation with temperature of the absorption spectra of very concentrated solutions ($> 3 \times 10^{-2}$ M), the trimerization enthalpies (ΔH_t^0) have been calculated from the variations produced by the temperature on the emission of those solutions. In the evaluation, it is assumed that the rate constants of the fluorescence quenching produced by the trimers do not depend on the temperature. This assumption, obtained for the quenching produced by the dimers, has been extended to the quenching caused by the trimers because both are produced by the same mechanism [6,8]. A detailed description of the calculation method has been given previously [6].

The enthalpies obtained at intermediate dye concentrations are not exactly the bond energies or the dissociation heats of the dimers because they also include the solution heats of monomers and aggregates. As the dyes have the same structure (Fig. 1), one may expect that the solutions heats are

TABLE 2

Free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) at 20°C of the dimerization (d) and trimerization (t) processes of fluorescein (Fl) [5], eosin ($FlBr_4$) and erythrosin (FlI_4) dianions

	Fl	$FlBr_4$	FlI_4	Estimated error
ΔG_d^0 (kJ mole^{-1})	-3.9	-11.5	-11.9	± 0.1
ΔH_d^0 (kJ mole^{-1})	-28	-21	-17	± 1
ΔS_d^0 (J mole^{-1} K^{-1})	-81	-34	-18	± 5
ΔG_t^0 (kJ mole^{-1})	-5.9	-12.6	-12.1	± 1
ΔH_t^0 (kJ mole^{-1})	-23	-17	-11	± 1
ΔS_t^0 (J mole^{-1} K^{-1})	-60	-14	$+2.9$	± 5

not very different. Then, the enthalpy changes may be used to draw some conclusions about the dimerization forces.

Changes in the standard free energy and entropy are evaluated from $\Delta G^0 = -RT \ln K$ and $\Delta S^0 = (\Delta H^0 - \Delta G^0)/T$, where K is the aggregation constant (Table 1). The results obtained at 20°C are given in Table 2.

This table shows that the halogenation * of fluorescein dianion supposes a decrement in the dimerization free energy change and an increment in the enthalpy and entropy variations produced by this association. This behaviour has been also reported by Rohatgi and Mukhopadhyay [1], though the results are different. Similar shifts are observed in the trimer formation functions, but while free energy changes are smaller than for the dimer, enthalpy and entropy variations are larger. Evidently, the halogenation and the number of the monomeric units imply changes in the nature of the association forces. The thermodynamic variations produced by the dimerizations are now discussed and then those produced by the trimerizations will be considered.

The enthalpy and entropy variations produced by the dimer formation of fluorescein are in the same range as the values found for hydrogen bonds [14]. For this reason, the fluorescein dimer is considered to be mainly due to this bond [1,5]. The separation between the parallel xanthene groups of the monomers (Table 1) is the necessary distance for a water molecule to form hydrogen bonds with the oxygens of these rings. The van der Waals additive forces also make some contribution in the formation of this association because the aggregation does not stop at the dimer stage [5,6].

The variations of enthalpy produced by the formation of eosin and erythrosin dimers (Table 2) are larger than for fluorescein. This indicates the

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* In this work, the term "halogenation" also indicates the increment in the atomic number of the substituted halogens in the fluorescein dianion.

participation of forces that do not depend on temperature to such an extent.

In order to interpret these thermodynamic results, the molecular structures of the dyes are considered (Fig. 1). The halogen atoms produce a more uniform distribution of the conjugated electronic system of the xanthene group, weakening the specific solvation of water on its oxygens. This supposes a decrease in hydrogen bond possibilities together with an increase in the dipolar induction of the chromophore rings. So, contribution of hydrogen bonds should be smaller in the halofluorescein dimers, but the participation of dispersion forces should be larger. The bigger dimerization enthalpies obtained for the eosin and erythrosin (Table 2) support this conclusion since the London forces do not depend on temperature [15].

The entropy changes produced by the formation of halofluorescein dimers (Table 2) also indicate the weakening of the solvent bridges in these aggregates because they are not negative enough to be due only to the dimerization process. Water is the only part of the system that is able to produce a positive change of entropy. The dimerization processes in the halogenated dyes should weaken the water solvation structure around the monomers, allowing a greater ordering of solvent molecules. This implies an increment in the entropy together with a decrease in the possibilities of hydrogen bond formation. Because of this consequence, the results have been interpreted as being due to hydrophobic interactions [1].

Apart from these forces, the contribution to the bond of the dipole–dipole interaction between the monomeric units should not differ too much in the aggregates of these dyes. The transition moments of the monomers and the geometric structures of the molecular associations are not very different (Table 1).

The thermodynamic variations produced by the trimerization processes (Table 2) imply changes in the intermolecular forces, not only with halogenation, but also with the number of monomeric units. The larger dipolar induction of the eosin and erythrosin xanthene groups also justifies the increment in the formation enthalpies and entropies of the halogenated trimers. In addition, the increase in trimerization enthalpies with respect to those for dimerization supposes a larger contribution of the London forces in the former associations. This is reasonable if one considers, on one hand, the parallel disposition of the chromophore groups of monomers in the trimers [5,7] and, on the other hand, the increase of these non-temperature-dependent forces in the halofluorescein dimers.

Finally, the larger formation free energy changes in the trimers are due to the positive excitonic interactions between the non-adjacent dianions [5,7].

Some aspects related with the geometric structures of the aggregates [5,7] (Table 1) can be explained now. The hydrogen bonds justify the small separation between the monomers in the fluorescein aggregates. The water molecules that take part in the bond decrease the electrostatic repulsion between the dianions, making the aggregation possible.

In the eosin and erythrosin aggregates, the weakening of the bridges formed by the solvent molecules allows a larger distance between their xanthene rings. The decrease produced by this separation in the steric effect of the benzoic groups and the participation of the London forces contribute to a better alignment of the monomeric units in these molecular associations.

Finally, the important aggregation of the halogenated dyes must be attributed to the bigger excitonic interactions, to the smaller repulsion (larger distance) between their dianions, and, mainly, to the dispersion forces that take part in their aggregates. This explains the decrease observed in the aggregation of these dyes when solutions of greater ionic strength are used. The added ions should tend to localize the charge of the chromophore rings, decreasing the dipolar induction and making easier the formation of hydrogen bonds.

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