Determination of Average Aggregation Number of Solochrome Mordant Dyes by Spectrophotometric Method

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The average aggregation number of four solochrome mordant dyes have been determined spectrophotometrically. Solochrome black WDFA is found to be highly aggregated whereas solochrome yellow 2GS is least aggregated and other two possess intermediate values. The stability of the aggregated species is substantiated by the changes in thermodynamic parameters, viz. ΔS, ΔH and ΔF.

THE aggregation of dyes in solution depends on several factors, viz. structure of the dyes, its concentration, pH, presence of foreign ions, degree of dissociation, etc. Rushbrook[1] considered the phenomenon as involving weak interactions to bring about smaller degree of aggregation, which in turn affects the thermodynamics functions such as ΔS, ΔH and ΔF appreciably. Of the various physico-chemical methods available to study this phenomenon, the spectrophotometric method based on the deviation from Beer's law is the most convenient one[2]. In this paper we report our results on the aggregation of four solochrome dyes, viz. solochrome yellow 2GS (I), solochrome red ERS (II), solochrome black PVS (III) and solochrome black WDFA (IV). The thermodynamic parameters have been evaluated to throw light on the nature of micellization and the results have been compared with those obtained using the polarographic method[3].
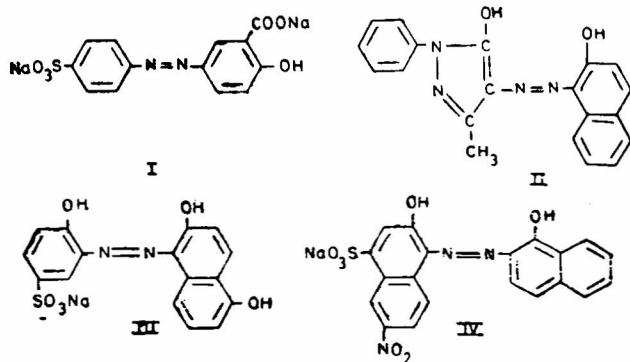
Experimental Procedure

The dye samples (ICI, India) were purified by recrystallization twice from 50% aq. ethanol and desiccated over silica gel and tested for purity by chromatography[4]. The solutions (10 mM) of these dyes were prepared in doubly distilled water. All other reagents used were of Analar grade.

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Bausch and Lomb's spectronic-100 was employed for spectrophotometric measurements at $25° \pm 0.1°$ using cell width of 1·0, 5·0 and 10·0 mm.

pH measurements were done on ELICO pH meter using a glass electrode. Thermodynamic parameters were determined at 30°, 35°, 40° and $45° \pm 0.1°$.

Procedure — Solutions of desired concentrations were obtained by adding a fixed amount 8 ml of the Britton-Robinson buffer (pH 5·80) to the varying amounts (0·08 to 0·8 ml) of 10 mM dye. KCl was added to keep the ionic strength constant (0·15M). The final volume was made up to 10 ml by adding requisite amount of water. The solutions were left overnight in dark before spectrophotometric measurements.

Calculation of aggregation number by spectrophotometry — Giles *et al.*[2] suggested expression (1)

$$(1-\alpha) = Aa/\Delta A \qquad \ldots(1)$$

for calculating average aggregation number of dyes by spectrophotometric method. In this expression A is the absorbance; ΔA, the deviation of absorbance from linear Beer's law, a denotes the probability of the photon being absorbed by the monomer and α is the fraction of N-monomers in the combined state. So that $M = M_0/(1-\alpha)$ would give average molecular weight of the aggregates. The average aggregation numbers so determined are given in Table 1.

Calculation of thermodynamic parameters — Suppose SD is the dye which does not obey Beer's law in view of its undergoing aggregation. Further we denote the M band to monomer form and D band to dimer form so that for the equilibrium between monomer and dimer, we have

$$K = [SD]^2/[(SD)_2]$$

where K is the dissociation constant of the dimer. The observed extinction coefficient ϵ_0 would be

$$\epsilon_0 = \epsilon_M x + \tfrac{1}{2}\epsilon_D(1-x) \qquad \ldots(2)$$

where ϵ_M and ϵ_D are molar extinction coefficients of the monomer and dimer respectively and x is the fraction of the dye in the monomer form. K and x are also correlated by Eq. (3)

$$K = 2Cx^2/(1-x) \qquad \ldots(3)$$

TABLE 1 — AGGREGATION NUMBER OF DYES FROM SPECTROPHOTOMETRIC DATA

$[\text{Dye}] \times 10^4$	$a_{\text{abs}} \times 10^{-6}$	A	ΔA	$(1-\alpha)$	$M = M_0/(1-\alpha)$	$\bar{N} = M/M_0$
		SOLOCHROME YELLOW 2GS, $M_0 = 345 \cdot 2$				
80·0	0·144	1·01	0·15	1·00	345·2	1·00
1·0	0·144	1·30	0·26	0·72	478·8	1·39
5·0	0·144	1·72	0·50	0·50	790·4	2·00
7·0	144	1·88	0·75	0·34	1015·0	3·00
		SOLOCHROME RED ERS, $M_0 = 344 \cdot 1$				
80·0	0·150	0·70	0·01	1·00	344·1	1·00
8·0	0·150	1·71	0·27	0·60	573·3	1·66
9 0	0·150	2·00	0·60	0·50	688·2	2·00
9·5	0·150	2·20	0·99	0·33	1032·3	3·00
		SOLOCHROME BLACK PVS, $M_0 = 385 \cdot 3$				
7·9	0·122	1·20	0·28	0·50	770·6	2·00
8·4	0·122	1·63	0·65	0·33	1156·0	3·00
9·0	0·122	2·40	1·45	0·20	1926·6	5·00
		SOLOCHROME BLACK WDFA, $M_0 = 461 \cdot 4$				
2·0	0·138	1·00	0·34	0·40	1153·5	2·50
4·0	0·138	1·60	0·66	0·33	1394·2	3·00
5·0	0·138	2·24	1·54	0·20	2307·0	5·00

where C is the total concentration of the dye. ϵ_M and ϵ_D are obtained by extrapolating the experimental values of ϵ_0 to $C = 0$ and α respectively. We may calculate x from Eq. (2) and K from Eq. (3).

Since the increase in temperature influences the absorption spectrum, this fact is made use of for calculating free energy of the dimerization (ΔF) employing Eq. (4)

$$\Delta F = -RT \ln K \qquad \ldots(4)$$

Heat of dimerization or enthalpy, (ΔH), is calculated using Eq. (5)

$$\log K = \log A - \Delta H/2 \cdot 3RT \qquad \ldots(5)$$

The entropy of dimerization, (ΔS), is calculated employing Eq. (6)

$$\Delta S = (\Delta H - \Delta F)/T \qquad \ldots(6)$$

Similarly, these parameters have been calculated for trimers and higher polymers.

Results and Discussion

Solochrome yellow 2GS (I) — It does not undergo aggregation in the concentration range $1 \cdot 0 \times 10^{-5}M$ to $9 \cdot 0 \times 10^{-5}M$, since no deviation from Beer's law is observed. Beyond this concentration deviations are observed. At a concentration of $5 \cdot 0 \times 10^{-4}M$, the values of absorbance A representing conformity to Beer's law is $1 \cdot 72$ (by extrapolation of the linear plot), while the actual experimental value is $1 \cdot 22$. Thus $\Delta A' = 0 \cdot 50$ (Table 1) and the probability of photon being absorbed by a monomer is $0 \cdot 144$.

From Eq. (1), the value of $(1-\alpha)$ is

$$(1-\alpha) = 1 \cdot 72 \times 0 \cdot 144/0 \cdot 48 = 0 \cdot 50$$

The average molecular weight of the dye is given by

$$M = M_0/(1-\alpha) = 345 \cdot 2/0 \cdot 50 = 790 \cdot 4$$

so that $\bar{N} = M/M_0 = 2$.

On similar consideration the value of $\bar{N}$ for conc. $7 \cdot 0 \times 10^{-4}M$ was found to be 3.

Solochrome red ERS (II) — This dye remains completely unassociated below $8 \cdot 0 \times 10^{-4}M$ but beyond this it begins to aggregate and the deviation from Beer's law starts. The values of $\bar{N}$ calculated by the method given above are 2 and 3 at [dye] $9 \cdot 0 \times 10^{-4}M$ and $9 \cdot 5 \times 10^{-4}M$ respectively.

Solochrome black PVS (III) — This dye undergoes greater aggregation than the above mentioned two dyes of corresponding concentrations. Thus a value as high as $\bar{N} = 5$ is observed at [dye] $9 \cdot 0 \times 10^{-4}M$ as against 2 in the case of solochrome yellow 2GS and solochrome red ERS.

Solochrome black WDFA (IV) — Amongst the dyes investigated in the present study, this dye undergoes the largest aggregation. Here the aggregation number is 3 at [dye] as low as $4 \cdot 0 \times 10^{-4}M$ and is $\bar{N} = 5$ at $5 \cdot 0 \times 10^{-4}M$ (Table 1). In the concentration range $1 \cdot 0 \times 10^{-5}$ to $4 \cdot 0 \times 10^{-5}M$ the dye remains unaggregated.

Polarographic measurements — To support the above data, we carried out the measurements polarographically[3] in the presence of Robinson-Britton buffer of pH $5 \cdot 8$ and found that the value of aggregation number obtained by both these methods are comparable.

Thermodynamic parameters — The values of ΔS, ΔH and ΔF for different aggregated species at different temperatures are summarized in Table 2. For dimer formation, for example, the entropy values for different dyes do not differ largely but are approximately same at 45°. Similarly enthalpy varies between $4 \cdot 0$ and $4 \cdot 36$ for all these dyes. The magnitude of decrease in free energy is also not appreciable.

However, the onset of trimer formation brings about a large variation in the values of ΔS, ΔH

TABLE 2 — THERMODYNAMIC PARAMETERS OF SOLOCHROME MORDANT DYES FROM SPECTROPHOTOMETRIC DATA

Temp. °C	Solochrome yellow 2GS				Solochrome red ERS				Solochrome black WDFA			
	$K(10^{-4})$	$-\Delta F$ cal/mole	ΔH cal/mole	ΔS e.u.	$K(10^{-4})$	$-\Delta F$ cal/mole	ΔH cal/mole	ΔS e.u.	$K(10^{-4})$	$-\Delta F$ cal/mole	ΔH cal/mole	ΔS e.u.
FOR DIMER												
45	3·309	2·973		3·20	4·62	3·882		3·79	4·27	3.62		3·66
40	3·158	2·850		3·68	4·51	3·770		3·94	4·19	3·51		3·85
35	3·074	2·765	4·0	4·00	4·42	3·660	4·36	412	4·07	3·40	4·19	4·03
30	2·823	2·513		4·09	4·29	3·522		4·28	3·98	3·28		4·18
FOR TRIMER												
45	1·318	0·721		33·8	1·382	0·806		34·2	1·35	0·752		33·5
40	1·287	0·652	11·5	34·5	1·314	0·777	12·2	34·9	1·30	0·746	11·8	33·9
35	1·263	0·616		35·0	1·277	0·742		35·6	1·24	0·739		34·6
30	1·251	0·601		35·4	1·235	0·728		36·0	1·20	0·726		35·0
FOR PENTAMER												
45									0·726	0·319		49·2
40									0·638	0·306		50·3
35									0·610	0·282	16·6	51·0
30									0·559	0·269		51·7

and ΔF (Table 2). Enthalpy has been found to increase to 12 (on an average) compared to 4·2 (for dimer formation). The magnitude of increase in entropy was considerable whereas ΔF decreased significantly. Such a behaviour confirms the view of Rushbrook[1] that the dyes undergo aggregation and not polymerization. This trend in the values of ΔF, ΔH and ΔS is observed for the formation of pentamer in the case of solochrome black WDFA.

It is difficult to explain the increase in entropy. However, we held the view that it can be attributed to the breaking of the iceberg structures around the polar molecules when they leave the aqueous environment in order to undergo aggregation[5]. It is also established that in contrast to dimerization of carboxylic acids, the micellization of dye stuff does not stop at the dimeric stage but proceeds to form trimer and higher aggregates also, probably through London-van der Waal's forces[6]. Therefore, our results are in line with the observations of the other authors and are comparable with the results obtained with the other techniques.

Acknowledgement

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