

Secondly, the extinction coefficients at all the C_0 values measured are determined using the ϵ_D , ϵ_{D_2} and K_{Agg} values obtained above, and the end product is designated ϵ_{Calc} . The equations utilized for this calculation are derived as follows

Dyes and Pigments **19** (1992) 161–168



New Procedure to Calculate the Aggregation Constants of Dyes

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(Received 20 January 1992; accepted 2 March 1992)

ABSTRACT

A new procedure to calculate the aggregation constants of dyes is proposed. This procedure can determine not only the aggregation constants but also the extinction coefficients of dye monomers. It is therefore of particular value in the case of dyes which form aggregates even at low concentration. The aggregation constants for the dyes studied were calculated using the present procedure and compared with the previous values. From the results, factors pertinent to the estimation of the aggregation constants are discussed.

1 INTRODUCTION

The authors have previously investigated the aggregation behaviour of azo dyes, most of which contained fluorine substituents, by means of visible absorption spectra and ^{19}F nuclear magnetic resonance measurements.^{1–6} Through these studies it became apparent that the determination of the extinction coefficients for dye monomers is difficult, because in the case of dyes having large aggregation constants, the dye aggregates exist even at the limited dilute concentration where spectroscopic measurements are possible. Thus, it is difficult to calculate the extinction coefficients of dye monomers spectroscopically.

In this context, a new procedure to calculate simultaneously the

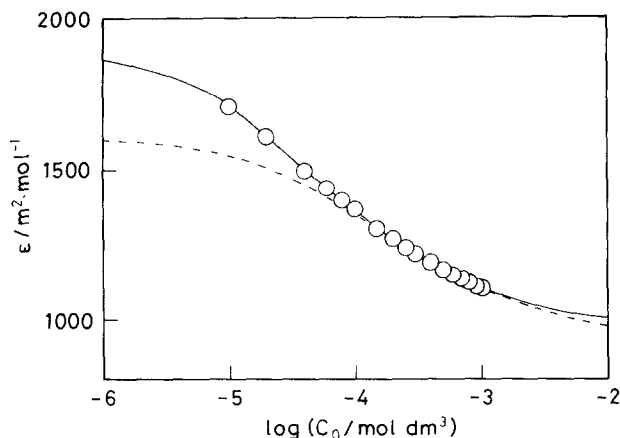


Fig. 1. Relationship between ϵ at 540 nm and the dye concentration for **R-1** at 298 K.

of the dye monomers. Furthermore, the wavelength (540 nm for both **R-1** and **R-2**) where the change of the extinction coefficients with increasing dye concentration is largest was used in order to obtain the most accurate values, although the same values were given at all the wavelengths measured because of the existence of isosbestic points.

Figure 1 shows the plot of the observed extinction coefficients, ϵ , against the logarithm of the dye concentrations for **R-1** at 298 K, where the solid line

TABLE 1
The ϵ and ϵ_{Calcd} values for **R-1** at 298 K

Dye concentration (mol dm ⁻³)	ϵ (m ² mol ⁻¹)	ϵ_{Calcd} (m ² mol ⁻¹)	$ \epsilon - \epsilon_{\text{Calcd}} $ (m ² mol ⁻¹)
1.00×10^{-5}	1710	1707	3 (0.18%)
2.00×10^{-5}	1610	1612	2 (0.12%)
4.00×10^{-5}	1498	1503	5 (0.33%)
6.00×10^{-5}	1437	1438	1 (0.07%)
8.00×10^{-5}	1396	1393	3 (0.21%)
1.00×10^{-4}	1364	1359	5 (0.37%)
1.50×10^{-4}	1299	1302	3 (0.23%)
2.00×10^{-4}	1267	1264	3 (0.24%)
2.50×10^{-4}	1236	1237	1 (0.08%)
3.00×10^{-4}	1219	1216	3 (0.25%)
4.00×10^{-4}	1188	1185	3 (0.25%)
5.00×10^{-4}	1165	1164	1 (0.09%)
6.00×10^{-4}	1147	1147	0 (0.00%)
7.00×10^{-4}	1133	1134	1 (0.09%)
8.00×10^{-4}	1121	1123	2 (0.18%)
9.00×10^{-4}	1110	1114	4 (0.36%)
1.00×10^{-3}	1105	1106	1 (0.09%)

TABLE 2
The Aggregation Constants, K_{Agg} ($\text{dm}^3 \text{mol}^{-1}$)

	288 K	298 K	308 K	318 K
<i>In the absence of urea</i>				
R-1	$21\,400 \pm 300$	$14\,700 \pm 200$	$9\,100 \pm 200$	$5\,810 \pm 120$
R-2	$8\,360 \pm 150$	$5\,100 \pm 80$	$2\,840 \pm 60$	$1\,390 \pm 40$
<i>In the presence of urea</i>				
R-1	$15\,100 \pm 300$	$9\,600 \pm 200$	$6\,010 \pm 100$	$4\,250 \pm 100$
R-2	$5\,570 \pm 90$	$3\,320 \pm 80$	$1\,800 \pm 40$	$1\,060 \pm 40$

expresses the fitting curve determined by means of the present procedure and the broken line is the fitting curve calculated using ε_D of the authors' previous paper.⁶ As the value at $5 \times 10^{-6} \text{mol dm}^{-3}$ was considered in the previous study,⁶ the ε_D value was estimated as a much lower value than the real one. The data point at $5 \times 10^{-6} \text{mol dm}^{-3}$ has a large error ($\pm 80 \text{m}^2 \text{mol}^{-3}$) because of the smaller value of the absorbance (about 0.1), so that it is neglected in the present study. The observed extinction coefficients, ε , the calculated extinction coefficients, $\varepsilon_{\text{Calc}}$ and the difference between the above two values for **R-1** at 298 K are given in Table 1. This table suggests that the present procedure is more reasonable for determining the aggregation constants. The method which the authors had previously utilized places emphasis on the linearity of the plot of $(\Delta\varepsilon/C_0)^{1/2}$ against $\Delta\varepsilon$ in only a high concentration region, but the present method demonstrates that analysis in all the concentration regions is necessary.

Table 2 shows the aggregation constants, K_{Agg} for **R-1** and **R-2** in the absence and presence of urea. Some of the K_{Agg} values given in Table 2 are

TABLE 3
The ε_D and ε_{D_2} Values ($\text{m}^2 \text{mol}^{-1}$) at 540 nm

	288 K	298 K	308 K	318 K
ε_D				
R-1 (absence of urea)	1 879	1 888	1 871	1 848
R-1 (presence of urea)	1 964	1 934	1 895	1 871
R-2 (absence of urea)	1 967	1 963	1 933	1 893
R-2 (presence of urea)	2 014	1 990	1 939	1 903
ε_{D_2}				
R-1 (absence of urea)	927	949	973	980
R-1 (presence of urea)	946	961	978	1 000
R-2 (absence of urea)	1 062	1 080	1 081	1 052
R-2 (presence of urea)	1 101	1 097	1 101	1 108

TABLE 4
The Enthalpy Change, ΔH_{Agg} , and the Entropy Change,
 ΔS_{Agg}

	ΔH_{Agg} (kJ mol^{-1})	ΔS_{Agg} ($\text{J mol}^{-1} \text{K}^{-1}$)
In the absence of urea		
R-1	-33.4 ± 1.7	-33 ± 6
R-2	-45 ± 4	-82 ± 11
In the presence of urea		
R-1	-32.6 ± 1.0	-33 ± 3
R-2	-42.6 ± 1.4	-76 ± 5

much larger than those shown in the previous paper⁶ and others are a little smaller. This is clearly due to the more accurate values of ϵ_D . The ϵ_D values determined using the present procedure are given in Table 3 together with the ϵ_{D_2} values. From this table, it is apparent that the ϵ_D values change with temperature and the existence of the cosolute. In the previous paper,⁶ this change was not considered, so that inexact results were obtained. The dependence of ϵ_D on both temperature and the existence of the cosolute is probably attributable to variation of the hydration around the dyes.

From the temperature dependence of K_{Agg} , the enthalpy change, ΔH_{Agg} , and the entropy change, ΔS_{Agg} , were calculated (Table 4). These thermodynamic parameters showed the opposite behaviour to those given in the authors' previous paper:⁶ the present results suggest that the aggregation of **R-1** is less enthalpic and more entropic than that of **R-2**.

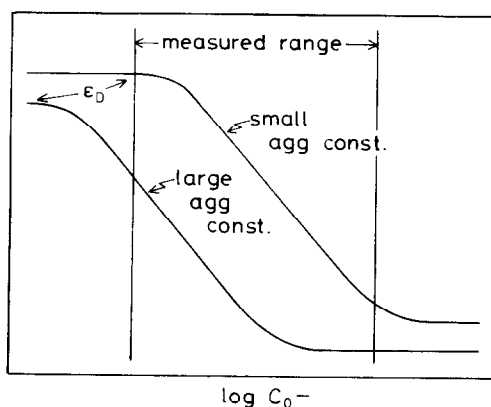
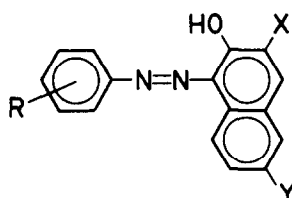


Fig. 2. Schematic curves of ϵ against dye concentration with low and high aggregation constant.

TABLE 5
The Aggregation Constants, K_{Agg} ($\text{dm}^3 \text{mol}^{-1}$), at 298 K
for Other Dyes Studied

	<i>Present study</i>	<i>Previous study</i>
AS	870 ± 50	590 ± 30 (Ref. 4)
FAS	$1\,460 \pm 50$	$1\,180 \pm 50$ (Ref. 4)
<i>m</i> -FTS	$1\,500 \pm 80$	510 ± 50 (Ref. 1)
AR	310 ± 20	300 ± 20 (Ref. 4)
FAR	200 ± 30	$70 \sim 140$ (Ref. 4)
<i>m</i> -FTR	203 ± 11	260 ± 20 (Ref. 2)



X = H,	Y = SO ₃ Na,	R = H:	AS
X = H,	Y = SO ₃ Na,	R = <i>penta</i> -F:	FAS
X = H,	Y = SO ₃ Na,	R = <i>meta</i> -CF ₃ :	<i>m</i> -FTS
X = SO ₃ Na,	Y = SO ₃ Na,	R = H:	AR
X = SO ₃ Na,	Y = SO ₃ Na,	R = <i>penta</i> -F:	FAR
X = SO ₃ Na,	Y = SO ₃ Na,	R = <i>meta</i> -CF ₃ :	<i>m</i> -FTR

Thus, it must be concluded that in the previous paper,⁶ the use of inexact ϵ_D values led to misleading results.

The aggregation constants, K_{Agg} , for other dyes were determined using the present procedure (Table 5). In the case of dyes with smaller K_{Agg} values, differences between the present and previous results are not evident. However, with large K_{Agg} values, the results show a large discrepancy. This may be explained by means of a schematic figure (Fig. 2). In the case of the dyes having smaller K_{Agg} values, ϵ_D can be determined experimentally, while for the dyes whose K_{Agg} values are larger, ϵ_D must be calculated by extrapolation; this extrapolation includes the main error factor.

The present procedure has high accuracy in extrapolation, and therefore it is believed that the method is able to determine more accurate values of K_{Agg} and ϵ_D .

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