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Effects of Hydrating Water Molecules on the Aggregation Behavior of Azo Dyes in Aqueous Solutions

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ABSTRACT

The aggregation behavior of three sulfonated monoazo dyes (C.I. Acid Red 88, C.I. Acid Red 13 and C.I. Acid Red 27) was investigated by means of visible absorption spectroscopy to elucidate the effects of the sulfonate groups. The aggregation numbers of the three dyes were estimated as two. The aggregation constant K_{Agg} *of the dye containing two sulfonate groups was the largest. This result is inconsistent with that expected from the electrostatic repulsion between the sulfonate groups in the dyes, suggesting that the other effects are dominant. The thermodynamic parameters determined from the temperature dependence of* K_{Agg} *indicates that hydrophobic interaction is involved in the aggregation reaction. From this, it is concluded that the hydrating water molecules around the dyes play an important role in the aggregation process. Furthermore, the effects of urea were investigated to clarify the influence of cosolutes on the aggregation behavior.*

1 INTRODUCTION

It is well known that the aggregation behavior of small molecules plays an important role in various research fields such as biological, colloid, surface, textile and photographic chemistry.[1] Particularly, the aggregation behavior of dyes has been a pertinent example.[2–4]

We have studied the aggregation of azo dyes containing fluorine atoms by means of visible absorption spectra and ^{19}F nuclear magnetic resonance measurements.[5–9] These results indicate that the introduction of fluorine

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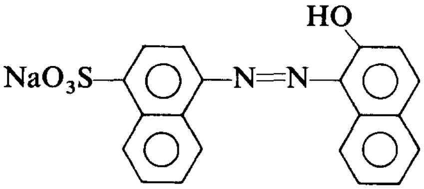
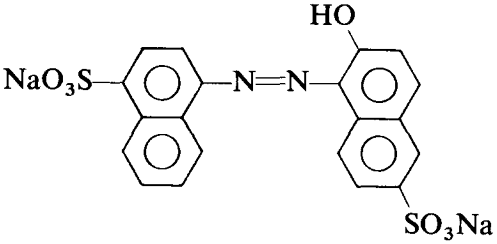
atoms into the dye molecules influences their aggregation behavior. Furthermore, it was found that the number of sulfonate groups contained in the dye molecules affects not only the aggregation constants but also the structure of the aggregates.[6] Thus, the sulfonate groups are the key in elucidating the aggregation processes. Duff *et al.* studied the effects of increasing the degree of sulfonation using polarography.[10] However, thermodynamic treatments for the effects of sulfonate groups have not been widely reported.

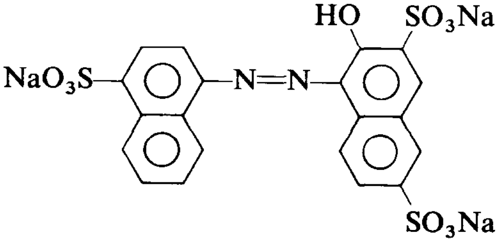
In this present study, the aggregation behavior of three azo dyes containing a different number of sulfonate groups (C.I. Acid Red 88 (R-1), C.I. Acid Red 13 (R-2), C.I. Acid Red 27 (R-3)) in aqueous solutions is investigated using visible absorption spectroscopy. The structural formulae of the dyes are:



R-1



R-2



R-3

The aggregation constants were determined from the dependence of the extinction coefficients upon the dye concentration, and the thermodynamic parameters were estimated from their temperature dependence. In addition, measurements in the presence of urea were carried out to elucidate the effects of cosolutes. Through the effects of sulfonate groups and cosolutes, the role of the hydrating water molecules around the dyes is discussed.

2 EXPERIMENTAL

R-1 and R-3 were commercially purchased from Tokyo Kasei Kogyo Co., and used after repeated salting-out with NaCl and reprecipitating the aqueous solutions with acetone. R-2 was prepared by coupling diazotized 4-amino-1-naphthalene-sulfonic acid with sodium 2-hydroxy-6-naphthalenesulfonate under alkaline conditions and it was purified in the same manner as R-1 and R-3. All three dyes gave satisfactory purity as confirmed by elemental analysis (R-1: Found: C, 57·05; H, 3·56; N, 6·62%; calcd (containing 5·2% H_2O): C, 56·88; H, 3·68; N, 6·63%; R-2: Found: C, 45·53; H, 2·97; N, 4·90%; calcd (containing 5·6% H_2O): C, 45·13; H, 2·90; N, 5·27%; R-3: Found: C, 35·20; H, 2·68; N, 4·07%; calcd (containing 11·8% H_2O): C, 35·05; H, 2·94; N, 4·09%).

The visible absorption spectra of the aqueous solutions of the dyes were recorded using a Shimadzu UV-240 spectrophotometer at 292, 300, 310 and 319 K in the absence and presence of urea (1 mol dm^{-3}).

3 RESULTS AND DISCUSSION

3.1 Effects of sulfonate groups on dye aggregation

The visible absorption spectra of R-1 are shown in Fig. 1. The maximum absorption wavelength shifted to lower wavelength (blue shift) and the extinction coefficient at that wavelength decreased with increasing dye concentration. Furthermore, a distinct isosbestic point was observed around 568 nm. A similar spectral change was also observed for R-2 and R-3. It is convenient to use the extinction coefficients, ε, at a specific wavelength to

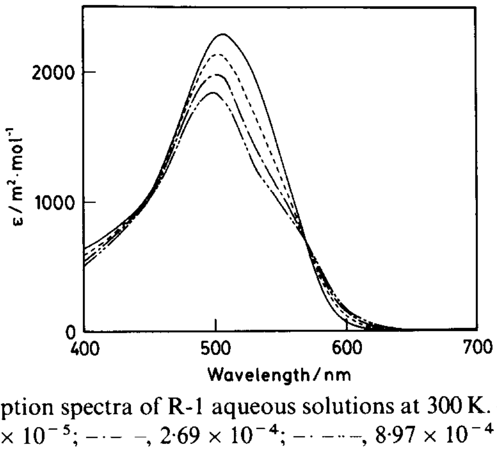


Fig. 1. Visible absorption spectra of R-1 aqueous solutions at 300 K. ———, 8·97 × 10^{-6}; – – – –, 7·17 × 10^{-5}; —·— —, 2·69 × 10^{-4}; —·· ——, 8·97 × 10^{-4} mol dm^{-3}.

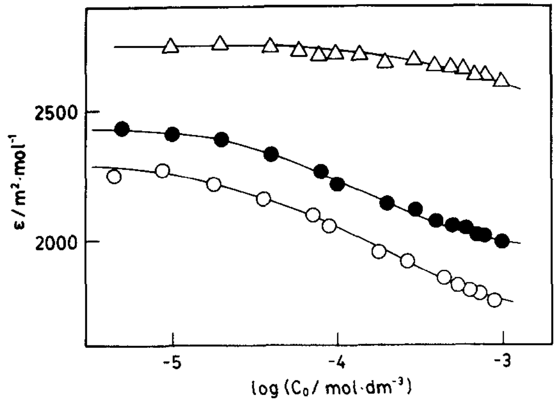


Fig. 2. Dependence of ε at 510 nm on the dye concentration at 300 K. ○, R-1; ●, R-2; △, R-3.

explain the spectral change. Figure 2 shows the dependence of ε at 510 nm (maximum absorption wavelength of the dilute solution) on the dye concentration, Co. For all three dyes, ε decreased with increasing dye concentration, but the manner of the change varied from dye to dye. As we have previously described[5,6] these changes are believed to be due to the interaction between the aromatic rings of the adjacent dye molecules, i.e. the stacking of the dyes.

Considering the existence of the isosbestic point, we assume the following single equilibrium:

$$n\mathrm{D} \rightleftharpoons \mathrm{D}_n \tag{1}$$

where D and D_n express the dye monomer and n-mer, respectively. From this assumption, eqn (2) is derived[6]

$$(\Delta\varepsilon/C_0^{n-1})^{1/n} = -(nK_{\mathrm{Agg}}/\Delta\varepsilon_{\mathrm{D}n}^{n-1})^{1/n}\Delta\varepsilon + (nK_{\mathrm{Agg}}\Delta\varepsilon_{\mathrm{D}n})^{1/n} \tag{2}$$

where K_{Agg} is the aggregation constant, $\Delta\varepsilon = |\varepsilon - \varepsilon_{\mathrm{D}}|$, $\Delta\varepsilon_{\mathrm{D}n} = |\varepsilon_{\mathrm{D}n} - \varepsilon_{\mathrm{D}}|$, ε is the molar extinction coefficient at a certain wavelength and ε_{D} and $\varepsilon_{\mathrm{D}n}$ are the molar extinction coefficients of monomer and n-mer, respectively. The ε values extrapolated to the extreme dilution in Fig. 2 were used as ε_{D}. The plots of $(\Delta\varepsilon/C_0^{n-1})^{1/n}$ against $\Delta\varepsilon$ with $n = 2$ gave the closest correlation coefficient to unity, so that the aggregation number of all the dyes

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

	292 K	*300 K*	*310 K*	*319 K*
R-1	4400 ± 300	2900 ± 200	1860 ± 170	1280 ± 80
R-2	4700 ± 200	3500 ± 300	2900 ± 300	2230 ± 190

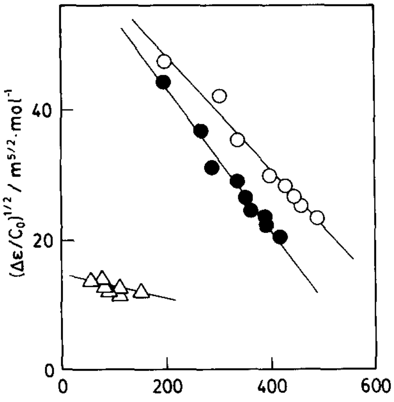


Fig. 3. Plots of $(\Delta\varepsilon/C_0)^{1/2}$ against Δε at 510 nm and 300 K. ○, R-1; ●, R-2; △, R-3.

investigated in the present study is concluded to be two, which is the same as the results given in our previous papers.[6,8,9]

The aggregation constants, K_{Agg}, were calculated from the slope and intercept of the linear plots shown in Fig. 3. As the large change of ε was not observed in the concentration region examined for R-3, no results having a high degree of accuracy were obtained. Although the K_{Agg} value for R-3 was estimated as 50–200 dm^3 mol^{-1}, it is very difficult to measure the temperature dependence of such a small aggregation constant, as described in our previous paper.[9] Therefore, the results for R-1 and R-2 only are discussed further.

The K_{Agg} values determined for R-1 and R-2 are given in Table 1. The K_{Agg} values for R-2 were larger than those for R-1 at every temperature. This suggests that the dye aggregation cannot be interpreted only by the electrostatic repulsion: this result is inconsistent with that presumed from the enhanced electrostatic repulsion with an increase in the number of sulfonate groups. To elucidate the reason for such a result, the thermodynamic parameters were determined from the temperature dependence of K_{Agg}. As shown in Fig. 4, van't Hoff plots (the plots of ln K_{Agg} against the reciprocal of temperature) gave good linearity, and the enthalpy change, ΔH_{Agg}, and the entropy change, ΔS_{Agg}, were therefore calculated from the slope and intercept of these plots, respectively (Table 2). The ΔH_{Agg} value for R-1 was

TABLE 2
The Enthalpy Change, ΔH_{Agg} and the Entropy Change, ΔS_{Agg}

	ΔH_{Agg} (*kJ mol*$^{-1}$)	ΔS_{Agg} (*J mol*$^{-1}$ *K*$^{-1}$)
R-1	$-35{\cdot}3 \pm 0{\cdot}6$	-51 ± 2
R-2	$-20{\cdot}6 \pm 1{\cdot}6$	0 ± 5

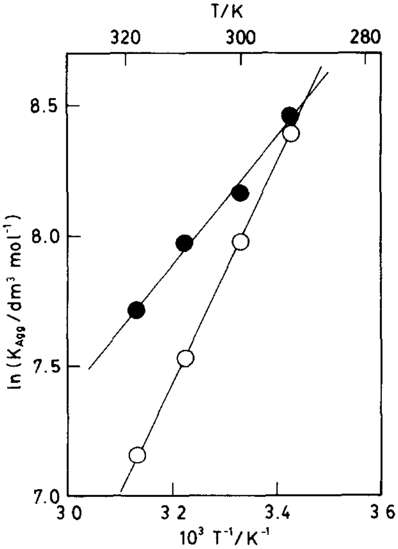


Fig. 4. Van't Hoff plots of the aggregation constants, K_{Agg}. ○, R-1; ●, R-2.

more exothermic than that for R-2, suggesting that the aggregation reaction of R-1 has favourable enthalpy in comparison with that of R-2. On the other hand, the ΔS_{Agg} value for R-1 was more negative than that for R-2, indicating that R-1 aggregates hardly more than R-2, considering the entropy. The above results clearly indicate that the hydrophobic interaction[11,12] takes part in the aggregation process. In other words, the hydrating water molecules around the dye play an important role. It is thus concluded that the difference of hydration between R-1 and R-2 is responsible for the discrepancy of the enthalpy and entropy change.

The extinction coefficients of the dye dimers, ε_{D2}, at 510 nm were determined from the slope and intercept of the linear plots shown in Fig. 3, which are a measure to elucidate the structure of the dimers. The ε_{D2} values at all temperatures were the same within experimental errors (R-1, 1510 ± 50; R-2, $1820 \pm 40\,m^2\,mol^{-1}$), suggesting that the structure of the dimers hardly varies with temperature. The extinction coefficients of the dye monomers, ε_D, at 510 nm were 2240 and 2390 $m^2\,mol^{-1}$ for R-1 and R-2, respectively, and the difference between ε_D and ε_{D2}, i.e. $\Delta\varepsilon_{D2}$ for R-1 was larger than that for R-2. This may be due to the discrepancy in the overlap of π-electron orbitals between R-1 and R-2.

3.2 Effects of urea on dye aggregation

The dependence of ε on dye concentration in the absence and presence of urea (1 mol dm^{-3}) for R-1 is shown in Fig. 5. The addition of urea decreased

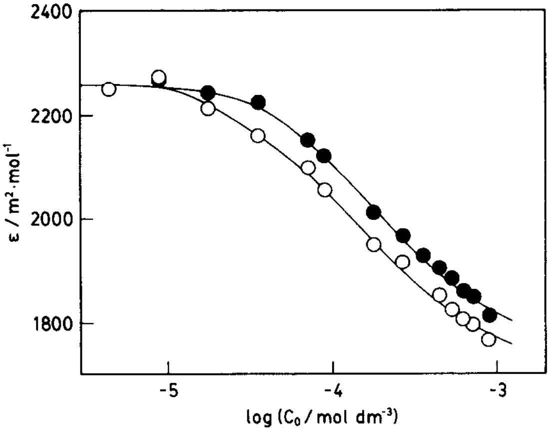


Fig. 5. Dependence of ε at 510 nm on the dye concentration in the absence (○) and presence (●) of urea (1 mol dm^{-3}) at 300 K.

the degree of the change in ε with increasing dye concentration. The same result was obtained for R-2. As in the case of the system containing no urea, the plots of $(\Delta\varepsilon/C_0)^{1/2}$ against $\Delta\varepsilon$ showed good linearity, and the aggregation constants, K_{Agg}, were determined from the plots (Table 3). The K_{Agg} values in the presence of urea were smaller than those in its absence at every temperature for both dyes. This suggests that urea has disaggregation effects. Furthermore, the ΔH_{Agg} and ΔS_{Agg} values calculated from the temperature dependence of K_{Agg} (Table 4) indicates that urea makes the aggregation reaction less exothermic and with a greater entropy change. On the other hand, the $\varepsilon_{\mathrm{D2}}$ values at 510 nm in the presence of urea (R-1, 1540 ± 40; R-2, 1800 ± 40 m^2 mol^{-1}) were coincident with those in the absence of urea,

TABLE 3

The Aggregation Constants, K_{Agg} (dm^3 mol^{-1}) in the Presence of Urea

	292 K	*300 K*	*310 K*	*319 K*
R-1	2800 ± 300	2020 ± 130	1510 ± 100	1030 ± 100
R-2	3010 ± 180	2630 ± 190	2140 ± 170	1630 ± 180

TABLE 4

The Enthalpy Change, ΔH_{Agg} and the Entropy Change, ΔS_{Agg} in the Presence of Urea

	ΔH_{Agg} (*kJ mol*$^{-1}$)	ΔS_{Agg} (*J mol*$^{-1}$ *K*$^{-1}$)
R-1	−28·0 ± 1·6	−30 ± 5
R-2	−17·4 ± 1·9	7 ± 6

resulting in no change of the dimer structure despite the presence of urea. From these results, it is concluded that the urea does not affect the dye molecules directly, but the environment around the dyes. Urea is found to be a water structure breaker by means of solubility,[13,14] viscosity,[15] and Raman spectrum[16] measurements. Thus urea breaks the water structure, and changes the condition of hydration around the dye molecules, resulting in the change of the thermodynamic parameters.

Taking into account all the results, we can conclude that the hydrating water molecules around the dyes influence the aggregation reaction thermodynamically: the number of water molecules released during the aggregation reaction differ for each dye and each cosolute.

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