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Entropy Contribution to an Azo Dye Aggregation in Aqueous Solution

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SUMMARY

The temperature dependence of the aggregation of a monoazo dye in aqueous solution was investigated by means of ^{19}*F-NMR. The chemical shifts for concentrations of* $1{\cdot}0 \times 10^{-2}$ *to* $5{\cdot}0 \times 10^{-5}$ *mol* dm^{-3} *fall on the same curve at various temperatures. The aggregation is suggested to be of a athermal and entropy-driven nature.*

1 INTRODUCTION

The aggregation of dyes in aqueous solution has been widely investigated by researchers in the field of biochemistry, interface chemistry and photographic chemistry as well as dyeing chemistry. NMR Spectroscopy is one of the most promising methods in investigating aggregation phenomena.[1–3] Using a dye molecule which carries an appropriate marker atom for NMR measurements, significant information on the aggregation behaviour can be obtained.[4,5] In this work we have investigated the effect of the temperature on the aggregation behaviour of the fluorine-containing monoazo dye **I**.

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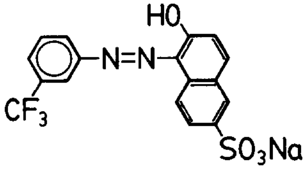
2 EXPERIMENTAL

Dye **I** was synthesized by conventional diazotization and coupling reactions. The dye was purified by repeated recrystallization from aqueous ethanol and by passing through a silica-gel column. The concentration of the investigated aqueous solutions were $5{\cdot}0 \times 10^{-2}$ to $5{\cdot}0 \times 10^{-5}$ mol dm^{-3}. ^{19}F-NMR measurements were performed on a Bruker WH-90 spectrometer at 84·7 MHz. The temperature was kept constant within ±0·2°C. CF_3COOD/D_2O was used as an external reference and for field stabilization.



I

3 RESULTS AND DISCUSSION

In Table 1, ^{19}F chemical shifts and linewidths of the CF_3 group are given as a function of the dye concentration and temperature. On the one hand, the

TABLE 1

^{19}F Chemical Shifts[a] and Linewidths[b] of the CF_3 Group of I

Temperature (K)	*Concentration (mol dm^{-3})*					
	$5{\cdot}0 \times 10^{-2}$	*$1{\cdot}0 \times 10^{-2}$*	*$5{\cdot}0 \times 10^{-3}$*	*$1{\cdot}0 \times 10^{-3}$*	*$5{\cdot}0 \times 10^{-4}$*	*$5{\cdot}0 \times 10^{-5}$*
295	13·10 (94)					
296	13·11 (95)					
299	13·12 (110)					
303	12·95 (165)	13·13 (6)	13·16 (4)	13·23 (3)	13·26 (3)	13·31 (3)
308	12·85 (152)	13·10 (7)	13·13 (8)			
313	12·49 (133)	13·11 (8)	13·14 (5)	13·22 (3)	13·26 (2)	
323	12·51 (35)	13·12 (12)	13·15 (7)	13·21 (3)	13·26 (3)	
327	12·57 (19)	13·11 (9)	13·16 (4)	13·22 (2)	13·25 (3)	13·28 (3)
333	12·63 (9)					
343	12·79 (3)					

[a] In ppm (between ±0·07 and ±0·02 for narrow and broad resonance lines, respectively).
[b] In Hz, in parentheses (between ±0·1 and ±8 for narrow and broad resonance lines, respectively).

change of chemical shift with temperature at the highest concentration investigated ($5{\cdot}0 \times 10^{-2}$ mol dm^{-3}) is quite distinct and shows a minimum at 313 K. We attribute this to the superposition of the multiple aggregation equilibrium at this high concentration and probably the complex azo–hydrazone tautomeric equilibrium. In this concentration range the gelation of the dye solution is visually observed at low temperatures. The linewidths at this concentration, which show a maximum at 303 K, indicate this complexity. Accordingly, the quantitative interpretation of the data was performed without using these values.

On the other hand, as shown in Fig. 1, chemical shifts in the concentration range $1{\cdot}0 \times 10^{-2}$ to $5{\cdot}0 \times 10^{-5}$ mol dm^{-3} are rather temperature-independent. The aggregation thus seems to be an athermal reaction.

With use of an isodesmic model,[6,7] assuming multiple equilibria, the aggregation constant K of the dye was estimated by means of eqn (1):

$$(\Delta\delta/C_0)^{1/2} = -(K/2\Delta\delta_{D_2})^{1/2}\Delta\delta + (2K\Delta\delta_{D_2})^{1/2} \qquad (1)$$

In the multiple equilibria of

$$\text{monomer} \rightleftharpoons \text{dimer} \rightleftharpoons \text{trimer} \rightleftharpoons \cdots \rightleftharpoons n\text{-mer}$$

successive aggregation constants were assumed to be identical and denoted as K. In eqn (1), C_0 is the total concentration of dye, $\Delta\delta = |\delta - \delta_D|$, $\Delta\delta_{D_2} = |\delta_{D_2} - \delta_D|$, and δ is the chemical shift observed. δ_D and δ_{D_2} are the chemical shifts of the monomeric and dimeric species, respectively.

An example of the plot of $(\Delta\delta/C_0)^{1/2}$ against $\Delta\delta$ is shown in Fig. 2; $\delta_D = 13{\cdot}30$ ppm was used as an extrapolated value from Fig. 1. From the slope and

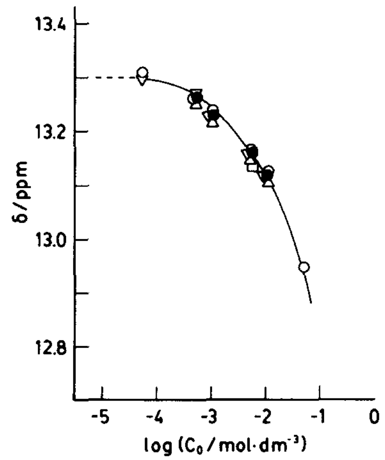


Fig. 1. Concentration dependence of ^{19}F chemical shifts: ○, 303 K; □, 308 K; ●, 313 K; △, 323 K; ▽, 327 K.

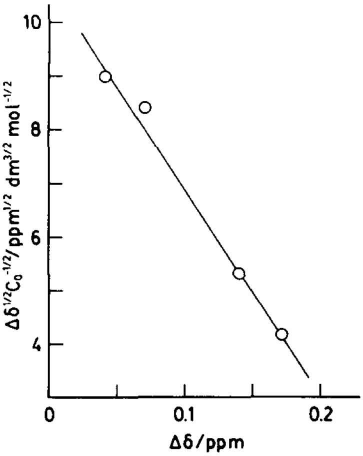


Fig. 2. $(\Delta\delta/C_0)^{1/2}$ vs $\Delta\delta$.

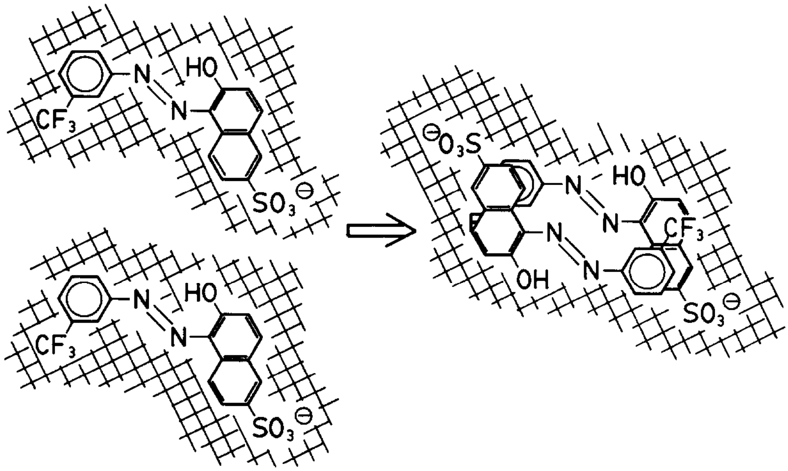


Fig. 3. Diagrammatic representation of dimer formation through hydrophobic interactions.

intercept in Fig. 2, K was determined as 410 ± 40 dm^3 mol^{-1} at 303 K, which is in good agreement with the value 430 ± 40 dm^3 mol^{-1} at 298 K in a previous report.[4]

As discussed above, the aggregation of the dye is an athermal reaction with $\Delta H = 0$ J mol^{-1}. Thus we obtain $\Delta S = 50$ J mol^{-1} deg^{-1}. Bearing in mind the entropy change of the process

benzene (in water) → benzene (pure)

to be 59 J mol^{-1} deg^{-1},[8] which is very similar, dimer formation of the dye in an antiparallel stacking mode[4,5] (Fig. 3) is supposed to be driven by hydrophobic interactions. The magnitude of ΔS obtained for **I** seems to indicate the degree of overlapping of the aromatic nuclei.

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