# Gelation of an Aqueous Fluorinated Dye Solution

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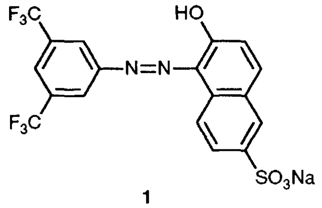
The gelation of aqueous solutions of sodium 1-(3,5-bistrifluoromethylphenylazo)-2-hydroxy-6-naphthalenesulfonate is investigated by means of $^{19}$F NMR spectroscopy.

The aggregation behaviour of azo dyes containing a trifluoromethyl group in aqueous solutions has been investigated by means of $^{19}$F NMR and visible absorption spectroscopy.[1–4] It is consequently found that the monoazo sulfonic dye containing a trifluoromethyl group at the *ortho* or *para* position to the azo group forms only a dimeric aggregate, while the dye having the group at the *meta* position forms a polyaggregate, and its aqueous solutions with more than $1 \times 10^{-2}$ mol dm$^{-3}$ becomes gelatinous.

For the purpose of increasing the gelation ability and raising the sensitivity in NMR measurements, a monoazo sulfonic dye containing two trifluoromethyl groups at the *meta* position to the azo linkage, *i.e.* sodium 1-(3,5-bistrifluoromethylphenylazo)-2-hydroxy-6-naphthalenesulfonate **1** was prepared and its aggregation behaviour in aqueous solutions investigated using a Bruker AM-X400 NMR spectrometer (376 MHz for $^{19}$F nucleus) at 298 K under the same conditions as described in our previous papers.[1,2]

All the NMR spectra observed over the concentration range from $1.78 \times 10^{-5}$ to $1.78 \times 10^{-2}$ mol dm$^{-3}$ consisted of one singlet, suggesting that both trifluoromethyl groups exist in the same environment. The chemical shifts, δ, of the fluorine atoms as a function of the dye concentrations, $C_o$, are shown in Fig. 1. The signals showed progressive shifts to lower magnetic field with increasing dye concentration, indicating that the fluorine atoms in the dye aggregate are located above the aromatic ring as for the dye containing one trifluoromethyl group.[1] Furthermore, the chemical shifts became approximately constant at concentrations of more than $5 \times 10^{-3}$ mol dm$^{-3}$. From this, it is thought that all the dye molecules take part in the aggregate at those concentrations, resulting in the gelation of the aqueous solution.



**1**

To estimate the aggregation constant, $K_{agg}$, eqn. (1) (isodesmic model[1,5]) and eqn. (2) (monomer–dimer model,[2,5,6]) were used.

$$(\Delta\delta/C_o)^{\frac{1}{2}} = -(K_{agg}/2\Delta\delta_{D2})^{\frac{1}{2}}\cdot\Delta\delta + (2K_{agg}\Delta\delta_{D2})^{\frac{1}{2}} \qquad (1)$$

$$(\Delta\delta/C_o)^{\frac{1}{2}} = -(2K_{agg}/\Delta\delta_{D2})^{\frac{1}{2}}\cdot\Delta\delta + (2K_{agg}\Delta\delta_{D2})^{\frac{1}{2}} \qquad (2)$$

where $\Delta\delta = |\delta - \delta_D|$, $\Delta\delta_{D2} = |\delta_{D2} - \delta_D|$ and δ is the observed chemical shift. $\delta_D$ and $\delta_{D2}$ are the chemical shifts of the monomer and dimer species, respectively. Both these equations lead to the linearity of the plot of $(\Delta\delta/C_o)^{\frac{1}{2}}$ against Δδ. This plot for aqueous solutions of compound **1** is shown in Fig. 2, where $\delta_D$ 14.925 was used as an extrapolated value to infinite dilution in Fig. 1. The extrapolation to determine $\delta_D$ was carried out as follows. By using an adequate $\delta_D$ value, $K_{agg}$ and $\delta_{D2}$ were estimated by means of eqn. (2) in the concentration region lower than $4 \times 10^{-4}$ mol dm$^{-3}$. The δ values at all of the concentration points measured were calculated by using the parameters obtained above. By repeating this calculation using several $\delta_D$ values, we determined the $\delta_D$ value that gave the smallest error between the calculated and observed δ values. Fig. 2 clearly indicates that the plot of $(\Delta\delta/C_o)^{\frac{1}{2}}$ against Δδ appears to be divided into two linear parts with a crossover point between 3 and $4 \times 10^{-4}$ mol dm$^{-3}$. Considering the fact that visible absorption spectra of the dye **1** aqueous solutions have isobestic points in the

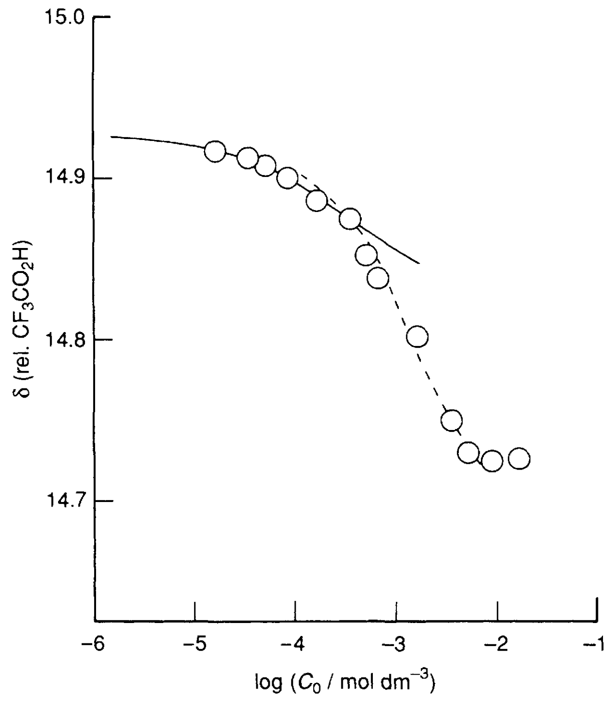


**Fig. 1** Dependence of chemical shifts on dye concentration at 298 K. The solid line is the fitted curve using the parameters obtained from eqn. (2) and the dotted one is the fitted curve determined by eqn. (1).

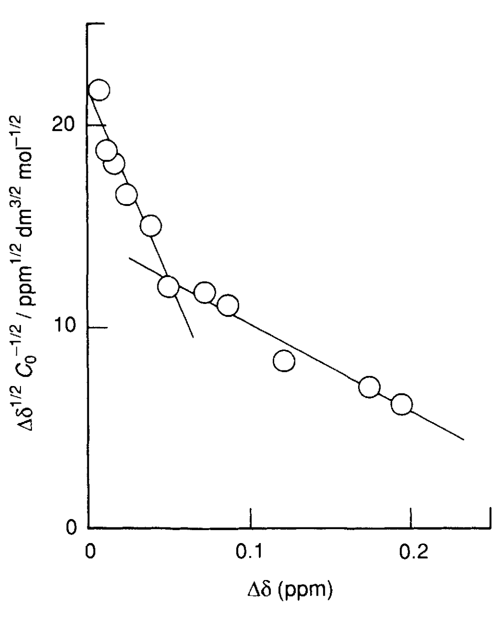


**Fig. 2** Plot of $(\Delta\delta/C_o)^{\frac{1}{2}}$ *versus* Δδ at 298 K

concentration range of less than 5 × $10^{-4}$ mol $dm^{-3}$, while not at greater concentration, we demonstrate that only the dye dimer is formed in the lower concentration region and the polyaggregates with several numbers of aggregation are formed in the higher concentration region. Therefore, the linear plots in the higher and lower concentration region were analysed using eqns. (1) and (2), respectively, with the result that the aggregation constants, $K_{agg}$, were calculated as 620 ± 80 $dm^3$ $mol^{-1}$ for the polyaggregation and 2100 ± 400 $dm^3$ $mol^{-1}$ for the dimerization. The latter value was consistent with the aggregation constant (2240 ± 20 $dm^3$ $mol^{-1}$) determined by means of visible absorption measurements assuming monomer–dimer equilibrium below 5 × $10^{-4}$ mol $dm^{-3}$. The solid line in Fig. 1 is the fitted curve calculated using the parameters obtained from eqn. (2) and the dotted one shows the fitted curve determined by eqn. (1). The above results suggest that the gelation of the aqueous dye solution investigated in the present paper involves both dimerization and polyaggregation. The detailed results including visible absorption spectra will be reported in due course.

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