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Introduction of a Trifluoromethyl Group into Sodium 1-Phenylazo-2-hydroxy-5-benzenesulfonate

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ABSTRACT

The syntheses of sodium 1-(2-trifluoromethylphenylazo)-2-hydroxy-5-benzenesulfonate, sodium 1-(3-trifluoromethylphenylazo)-2-hydroxy-5-benzenesulfonate, and sodium 1-(4-trifluoromethylphenylazo)-2-hydroxy-5-ben-zenesulfonate is reported and the solubility of these dyes in water was found to be dependent on the position of the trifluoromethyl group. Derivatives containing a methyl group could not be prepared, showing that the coupling reaction is affected by the substituent of the diazotized aniline derivatives. The extinction coefficients of the aqueous dye solutions did not change within the concentration range 1×10^{-5} *to* 1×10^{-3} *mol* dm^{-3}*, which suggests that the dyes do not aggregate at these dye concentrations. The sorption behavior of the dyes by a nylon 6 film was investigated and compared with that of the fluorinated derivatives of sodium 1-phenylazo-2-hydroxy-6-naphthalenesulfonate. The intrinsic binding constants for the former dyes were found to be much smaller than those for the latter dyes. Copyright © 1996 Elsevier Science Ltd*

INTRODUCTION

Fluorine nuclear magnetic resonance (^{19}F NMR) experiments using fluorinated ligands can provide a great deal of information about microenvironments in polymers such as proteins,[1] since ^{19}F NMR is characterized by an

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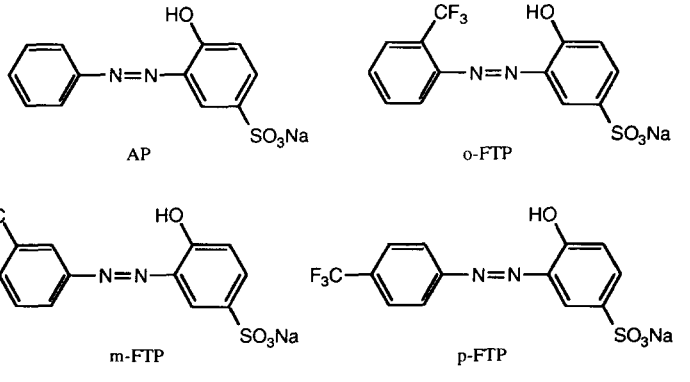
extremely wide range of chemical shifts, with the shift being highly responsive to changes in the microenvironments. Therefore, the introduction of fluorine atoms into dye molecules enables information to be obtained from both ^{19}F NMR and visible absorption spectroscopy. Such molecules can be applied as probes to explore the microenvironments in various matrices such as polymers, micelles and cyclodextrins.

We have previously reported the synthesis of various fluorinated dyes and investigated their aggregation in aqueous solutions,[2–9] interaction with a water-soluble polymer,[10–12] pH dependence,[13] and sorption by a nylon 6 film.[14,15] The properties of the fluorinated dyes were found to be quite different from those of the corresponding unfluorinated dyes and it is necessary to elucidate more fully such properties in order to apply the dyes as satisfactory probes. Furthermore, since fluorinated dyes containing one naphthalene and one benzene ring easily aggregate even below 1×10^{-4} mol dm^{-3}, they are not adequate for ^{19}F NMR experiments, which require higher dye concentrations to obtain more accurate data.

In this context, fluorinated azo dyes which do not aggregate in a higher concentration region than 1×10^{-4} mol dm^{-3} are required for the purpose of probe study. In this present paper, a trifluoromethyl group was introduced into sodium 1-phenylazo-2-hydroxy-5-benzenesulfonate, and the properties of the dyes obtained are discussed.

EXPERIMENTAL

Sodium 1-phenylazo-2-hydroxy-5-benzenesulfonate (AP) and its derivatives containing a trifluoromethyl group (*o*-FTP, *m*-FTP, and *p*-FTP) were synthesized as follows.



The corresponding aniline derivatives (0.06 mol) were diazotized with sodium nitrite (4.4 g) in the presence of hydrochloric acid (20 ml) and acetic

acid (6 ml), and the dyes were obtained by coupling of these diazonium liquors with sodium *p*-phenolsulfonate (14.0 g, 0.06 mol) in an alkaline medium (36 g of sodium carbonate in 200 ml water). *o*-FTP was insoluble in water, and was not purified. AP and *m*-FTP were purified by repeated salting-out with sodium acetate and two recrystallizations from ethanol containing a very small amount of water. *p*-FTP was purified by repeated washing with water and ethanol.

^{1}H NMR spectra of the dyes in D_2O were recorded on a JEOL EX-270 spectrometer at room temperature.

Visible absorption spectra of aqueous dye solutions with concentrations from 1×10^{-5} to 1×10^{-3} mol dm^{-3} were measured using a Shimadzu UV-3100 spectrophotometer.

The sorption isotherms of the dyes by a nylon 6 film, which was biaxially drawn and kindly supplied by Unitika Co. (having thickness and amino end group content of 15 μm and 3.53×10^{-5} equivalent per g of nylon, respectively), were determined by soaking 20 mg of the pretreated[14] nylon 6 film in the aqueous dye solution (50 ml) conditioned at pH 3 by a suitable amount of hydrochloric acid. After 1 day, the film was removed from the dye bath, rinsed in cold water, blotted with filter paper, and dried in a desiccator with silica gel. The dye sorbed by the film was extracted with 25 ml of 25% aqueous pyridine and the amount determined spectrophotometrically.

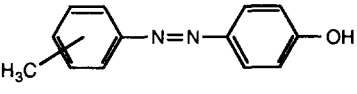
RESULTS AND DISCUSSION

Elemental analyses data are given in Table 1. The calculated values, considering water content, were in fair agreement with the experimental ones

TABLE 1
Elemental Analyses (%)

	C	H	N	F	S	Na
AP						
Calculated (as water content = 2.4%)	46.84	3.22	9.10			
Found	46.34	3.14	9.20			
o-FTP						
Calculated	42.40	2.19	7.61	15.5	8.7	6.2
Found	45.21	2.33	7.56	17.0	4.9	6.7
m-FTP						
Calculated (as water content = 2.5%)	41.34	2.41	7.42	15.1	8.5	6.1
Found	41.15	2.31	7.45	14.0	8.6	5.7
p-FTP						
Calculated	42.40	2.19	7.61	15.5	8.7	6.2
Found	41.93	2.37	7.58	14.7	7.4	7.4

except for *o*-FTP, although the experimental values for F, S, and Na had large errors because of the measuring procedure used. The discrepancies for *o*-FTP were due to insufficient purification (see above). These results indicate that the desired compounds were obtained. It is worthwhile noting that the corresponding dyes containing a methyl group could not be prepared, although according to the literature,[16] compounds of the following structure can be readily generated.



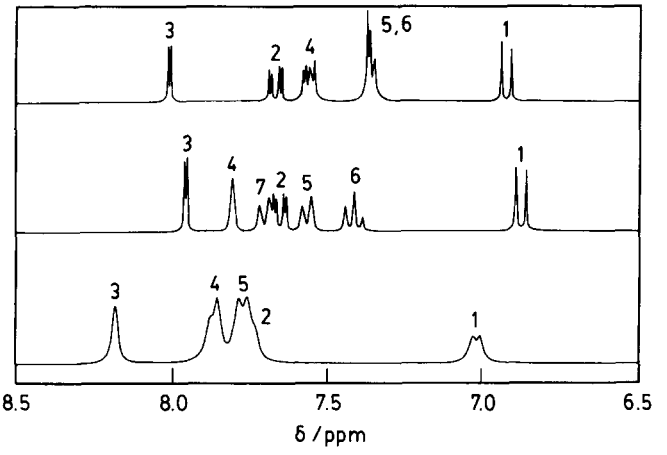
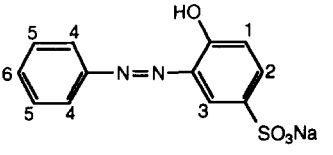
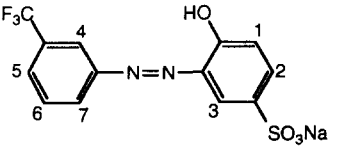


Fig. 1. ^{1}H-NMR spectra of the dyes in D_2O.

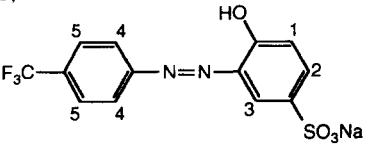
(a) AP,



(b) m-FTP,



(c) p-FTP,

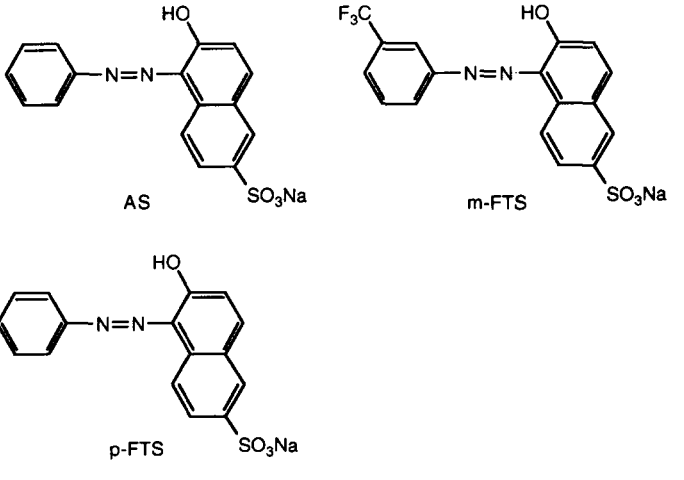


This suggests that substituents in the diazotized aniline derivatives significantly influence the coupling reaction.

To confirm the dye structures, ^{1}H NMR spectra were recorded (Fig. 1). All the signals could be assigned to each proton for the dyes and these spectra also confirmed that the desired dyes had been obtained. The broadening of the peaks for *p*-FTP is due to its low solubility in water. The solubility of the fluorinated dyes in water is thus dependent on the position of the trifluoromethyl group: *o*-FTP is insoluble, *m*-FTP much more soluble, and *p*-FTP less soluble.

The plot of extinction coefficient against dye concentration at λ_{max} for *m*-FTP is shown in Fig. 2; the extinction coefficient did not change with dye concentration and similar results were obtained for dyes AP and *p*-FTP. This strongly indicates that the dyes undergo negligible aggregation even at higher concentrations such as 1×10^{-3} mol dm^{-3} and are, therefore, applicable as probes to explore microenvironments without considering aggregation phenomena.

The sorption behavior of the dyes by a nylon 6 film was investigated in order to compare their properties with those of the sodium 1-phenylazo-2-hydroxy-6-naphthalensulfonate derivatives, whose structure is shown below.



One of the sorption isotherms obtained is shown in Fig. 3, where r and C_{free} are the amount of dye sorbed by the nylon 6 film and the concentration of free dye in the bath, respectively.

In order to analyze the sorption isotherms, the following bimodal sorption equation has been used:[14–18]

$$r = K_P C_{free} + \frac{nK_L C_{free}}{1 + K_L C_{free}} \quad (1)$$

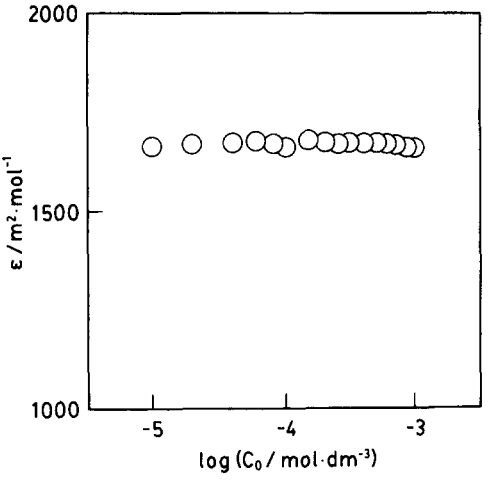


Fig. 2. Dependence of the extinction coefficient on dye concentration for *m*-FTP at 298 K.

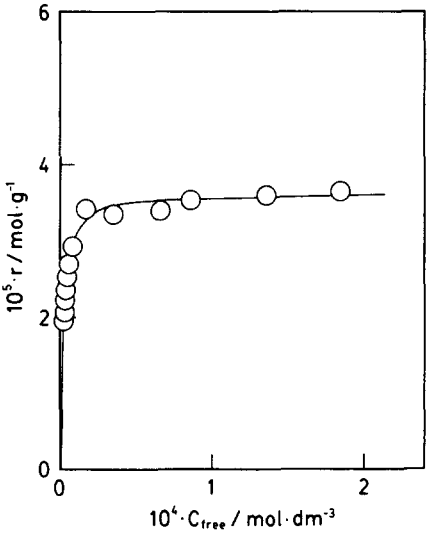


Fig. 3. Sorption isotherm of *p*-FTP for the nylon 6 film at 353 K. The solid line was calculated using the sorption parameters obtained.

where K_P is the partition coefficient ($dm^3\ g^{-1}$), n the number of binding sites for Langmuir type sorption (mol g^{-1}), and K_L the intrinsic binding constant for Langmuir type sorption ($dm^3\ mol^{-1}$). The first and second terms in the right-hand side of eqn (1) express the uptake of dye by partition and Langmuir type sorption, respectively. The K_P values were calculated from the slope of a straight line in the high concentration region of the sorption

isotherms, resulting in almost zero values for all the dyes. This suggests that the isotherms obtained in the present study can be analyzed by means of a single Langmuir type sorption mechanism, namely

$$r = \frac{nK_L C_{free}}{1 + K_L C_{free}} \tag{2}$$

The n and K_L values were determined using a modified eqn (2); re. eqn (3).

$$\frac{1}{r} = \frac{1}{nK_L} \cdot \frac{1}{C_{free}} + \frac{1}{n} \tag{3}$$

The plot of $1/r$ against $1/C_{free}$ gave good linearity (Fig. 4), the slope and intercept of which provided the n and K_L values. The sorption isotherm curve calculated by using the parameters thus obtained fitted in with the experimental data very well (Fig. 3).

The n and K_L values calculated above are given in Table 2. The n values for AP, *m*-FTP, and *p*-FTP were similar, which are in fair agreement with the amino end content of the nylon 6 film (3.53×10^{-5} mol g^{-1}). This shows that all the amino end groups dissociate into cations and are acceptable for the dyes. Furthermore, this demonstrates that all the dye molecules have one anionic group that is a sulfonate, i.e. they have high purity.

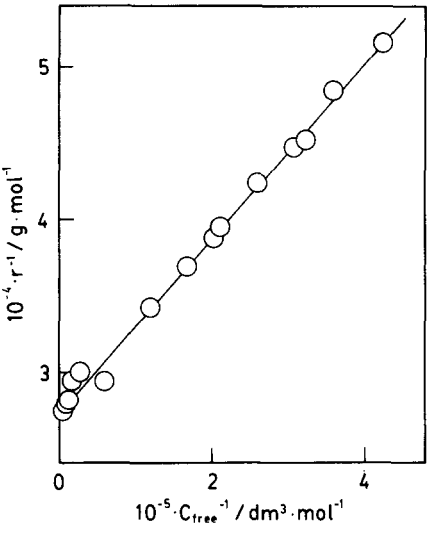


Fig. 4. Plot of $1/r$ against $1/C_{free}$ for the sorption of *p*-FTP at 353 K.

TABLE 2
The n and K_L Values at 353 K

	$10^5 n$ (mol g^{-1})	$10^{-5} K_L$ (dm^3 mol^{-1})
AP	3.47	3.24
AS[a]	3.4	15.9
m-FTP	3.50	5.03
m-FTS[a]	3.6	17.3
p-FTP	3.63	4.88
p-FTS[b]	4.0	19.0

[a]Ref. 14, [b]Ref. 15.

The K_L values for sodium 1-phenylazo-2-hydroxy-5-benzenesulfonate derivatives were much smaller than those for sodium 1-phenylazo-2-hydroxy-6-naphthalenesulfonate derivatives. Several interactions, including electrostatic interaction between the anionic group of the dyes and the cationic group of the nylon 6 film, are effective in the present system; hydrophobic interaction is also effective. Therefore, the nature of the aromatic rings influences the intrinsic binding constants.

It is of interest to note that the K_P values were almost zero in the case of sodium 1-phenylazo-2-hydroxy-5-benzensulfonate derivatives, whereas those for sodium 1-phenylazo-2-hydroxy-6-naphthalenesulfonate were more than 0.02 dm^3 g^{-1}. This strongly suggests that the structure of the dyes affects the partition type sorption.

Thus the replacement of a naphthalene ring by a benzene ring reduces not only the aggregation constant but also the binding constant with the nylon 6 film. This reduction could make it possible to investigate the microenvironment with less perturbation of the system. The dyes prepared in the present paper are under application as probes and data will be reported later.

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