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Diffusion coefficients for direct dyes in aqueous and polar aprotic solvents by the NMR pulsed-field gradient technique

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Abstract

The nuclear magnetic resonance pulsed-field gradient (NMR-PFG) technique was applied to determine the diffusion coefficients of selected direct dyes, including Congo Red, in D_2O and a deuterated polar aprotic solvent (DMSO-d_6). In addition, the self-diffusion coefficients of the solvents were determined in the presence and absence of dye, to reveal solvent–dye interactions. Diffusion coefficients ranged from about 1.7×10^{-10} to 4.4×10^{-8} depending on the dye, temperature and solvent employed. It is proposed that dye aggregation exists in DMSO-d_6 and D_2O, with the level of aggregation depending on the temperature and dye. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: NMR-pulsed field gradient technique; Direct dyes; Congo red; Diffusion coefficients; Aqueous and polar aprotic solvents

1. Introduction

This paper pertains to the first application of the NMR-PFG technique for measuring the diffusion of direct dyes in aqueous and organic solvents as a function of temperature. Though the present application is new, this technique has been used to characterize the diffusion of water/oil emulsions [1] and electrolytes [2].

Direct dyes, in addition to being used industrially for the coloration of a variety of substrates, have been used to define the pore structure and accessible surface of cotton fibers and microcrystalline products for many years [3–7]. Congo Red has been the most frequently used direct dye in basic research for many years. It has been used as a histochemical stain and as a specific stain for amyloids including Alzheimer plaque proteins. Azo dyes such as Trypan Blue have also been used in medical research [8].

In our work involving the use of direct dyes as probes for elucidating the supramolecular structure of cotton, we have used several dyes including the four listed in Table 1, to determine whether they produce comparable results [9]. In this regard, we found differences that may be due to either dye aggregation or molecular structure. In our most recent studies, NMR-PFG and molecular modeling experiments were used to help us explain these differences [10]. There has been very little reported about the characterization of direct dyes, in general, and with respect to diffusion there is a noticeable absence of information. The diffusion data that can be found in the literature include

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Table 1
Direct dyes

Dye	Code	Common name	CI[a]	Molecular weight (g/mol)
Direct Blue 14	DB14	Trypan Blue	23,850	960.82
Direct Yellow 4	DY4	Brilliant Yellow	24,890	624.56
Direct Red 28	DR28	Congo Red	22,120	696.67
Direct Red 2	DR2	Benzopurpurin 4B	23,500	724.73

[a] Colour index number.

studies regarding the diffusion of sulfonated dyes into cellulose membranes at 55 °C [11]. The authors were able to distinguish between pore and surface diffusivities, and for Direct Red 2 (DR2) they reported values of $11.2–2.0\times10^{-13}$ m^2 s^{-1} for the former and $3.4–4.6\times10^{-15}$ m^2 s^{-1} for the latter. Furthermore, they proposed that DR2 diffuses onto cellophane film as a dimer at 55 °C in the presence of electrolyte. In another study, direct dyes were studied in solution, the goal of which was to determine the potential of liquid crystal formation to facilitate binding to proteins [8]. In this case, the conditions employed were clearly different from those required for dyeing or for characterizing the cellulose structure. While liquid crystal formation is induced at low temperatures with high concentrations of dye and electrolyte, dyeing is performed at relatively low concentrations of dye and electrolyte and at elevated temperatures.

In 1954, Vickerstaff [12] pointed out that an unsatisfactory body of knowledge concerning aggregation in solution existed, due to the uncertainty as to whether direct dye solutions were mono- or polydispersed. It would appear that this question has not yet been fully answered. Though optical measurements show that aggregation decreases with dilution, they give an inaccurate estimate of particle size. Vickerstaff also pointed Out that diluting a concentrated dye solution resulted in instantaneous redistribution of the particle size. However, during extensive dyeing experiments, it was observed that this was not the case for DR2 [9]. This dye consistently required 3 h to re-establish equilibrium and, on dilution, absorbance values measured on a spectrophotometer increased during that time frame, irrespective of the initial concentration.

It is known that the results obtained from dyeing experiments utilising Direct Red 28 (DR28), also known as Congo Red, and DR2 are very similar, yet their behavior on dilution differs considerably. Consequently, it was deemed important to find a method that would permit characterization of the diffusion behavior of these dyes in solution. The application of such a method would prove generally useful in the interpretation of data from dyeing studies. This is also important because the aforementioned absorption data were recorded at room temperature, which precludes its use in predicting dyeing behavior at the dyeing temperature employed (60 °C).

For the present study, NMR was chosen because it can be utilized to measure the diffusion of solutes by applying pulsed field gradients to vary the field experienced by the solutes. This renders the Larmor precession frequency position-dependent, providing the frequency or phase labeling of molecules that is required to retrieve information about molecular transport processes.

The pulse sequence used for these diffusion experiments was a two-dimensional stimulated echo pulse sequence (Fig. 1). The sequence was based on three 90° radio frequency (rf) pulses (p1) that were immediately followed by a gradient pulse for each. The first and last p1s were followed by a pulsed magnetic field gradient (p16). The center rf-pulse was followed by a 5 ms spoil gradient (p19) that served to rid the x,y direction of undesired magnetization. The diffusion time (d20) as well as the width of the pulse gradient (p16) were set by the operator and permitted tailored attenuation of the gradient. This accommodated the independent characterization of various solution components diffusing at different rates. A simulated fitting (simfit) procedure was used to calculate the diffusion coefficient (D) from the measured signal intensities. The signal intensities were derived from Eq. (1):

$$I = I_0 \exp\left[-D\gamma^2 g^2 \delta^2 (\Delta - \delta/3)\right] \tag{1}$$

where:

$I =$ signal intensities in the presence of the gradient pulses

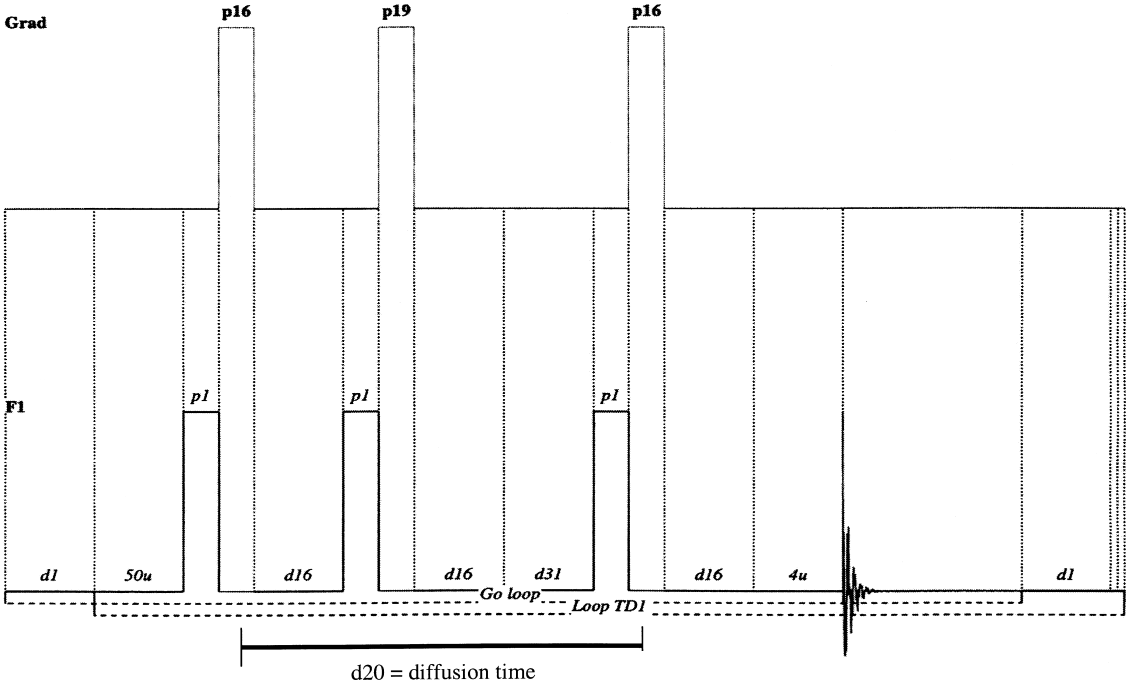

Fig. 1. 2D-stimulated NMR echo pulse sequence for diffusion measurements.

I_0 = signal intensities in the absence of the gradient pulses
D = diffusion coefficient
γ = gyromagnetic ratio of protons (2.67520×10^8 rad T^{-1} s^{-1})
g = gradient strength
δ = duration of the gradient pulses
Δ = diffusion time (d20); time between the centers of the two p16 pulses.

In addition, a biexponential fitting procedure provided two-dimensional plots of –log D versus chemical shift (ppm). From these plots, information on mono- versus polydispersity of the compound in question was obtained, since the diffusion coefficients for all solute species in solution were graphically represented. Thus whilst the simfit values better facilitated direct comparisons of D for different dyes, the two-dimensional plots, for example, revealed solute polydispersity and provided information on the high and low values of the diffusion coefficients.

2. Experimental

2.1. Materials

The direct dyes (Fig. 2 and Table 1) were purchased from Aldrich Chemical Company and ACROS and purified via a previously reported method [9]. The dyes were analyzed by atomic adsorption and thin-layer chromatography to determine their purities, which were 86–96% based on their air-dry weight. Impurities consisted of inorganic salts and trace amounts of unidentified organic compounds. These substances did not appear to affect the experimental results and the conclusions drawn from them [9]. The D_2O was obtained from Aldrich Chemical Company at a grade of 99.9 at.% ^2H, while the DMSO-d_6 was obtained from Sigma at the same grade. DMSO-d_6 was chosen as the non-aqueous solvent because it is commonly employed as an internal standard for NMR-characterization of dyes [13] and does not have aromatic resonances that could interfere with the signals of interest.

2.2. Procedures

The diffusion coefficients of the direct dyes in D_2O and DMSO, as well as those for the solvent in the presence of the dyes were determined using the ^1H NMR-PFG technique. To monitor solvent–dye interactions, self-diffusion of DMSO molecules and the diffusion of H_2O molecules in D_2O were measured to provide control values for D. For all experiments, 10 mg dye was dissolved in *0.5* ml solvent, as this concentration gave a sufficiently strong NMR signal in the temperature range under consideration. The measurements were performed in 5 mm NMR tubes on a Brüker 500 MHz Avance instrument equipped with a temperature control unit. The temperatures employed were 30–60 °C, with measurements made at 10 °C intervals. The self-diffusion of the solvent molecules was relatively fast compared to that of the dye molecules in DMSO-d_6, leading to a rapid decay of the signal in the diffusion experiment when the gradient parameters for dye diffusion measurements were employed. Consequently, the gradient attenuation had to be adjusted to characterize the movement of individual components in solution.

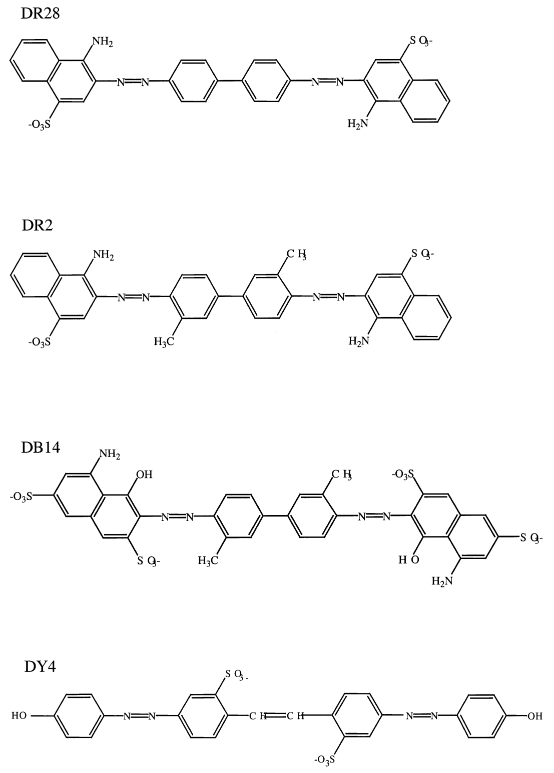

Fig. 2. Molecular structures for the direct dyes.

3. Results and discussion

The simfit averaged diffusion coefficients (D) for the dyes in both solvents increased by two orders of magnitude, from 10^{-10} to 10^{-8} $m^2\ s^{-1}$, upon raising the temperature from 30 to 60 °C (Tables 2 and 3). This was due to increased dye mobility in solution caused by the temperature changes, and to structural changes in the dyes and solvent molecules.

3.1. Diffusion of the dyes in D_2O

The diffusion coefficients for DR2 in D_2O at 50 and 60 °C were 9.10×10^{-10} and 3.15×10^{-8} $m^2\ s^{-1}$, respectively (Table 2). As indicated earlier, the diffusion constant for DR2 on cellophane at 55 °C was 11.2×10^{-13} to 4.6×10^{-15} $m^2\ s^{-1}$ [11] Those results are not directly comparable to the present results because salt was present in the aqueous media of the prior work but not in our case. Also

Table 2
Temperature dependence for the simfit averaged diffusion coefficients (D) for the dyes in D_2O

Temperature (°C)	$D\times10^{-10}$ ($m^2\ s^{-1}$)			
	DR28	DR2	DY4	DB14
30	1.95	1.97	3.19	2.21
40	3.45	3.29	5.57	3.81
50	14.6	9.10	13.6	36.7
60	336	315	290	287

Table 3
Temperature dependence for the simfit averaged diffusion coefficients (D) for the dyes in DMSO

Temperature (°C)	$D\times10^{-10}$ ($m^2\ s^{-1}$)			
	DR28	DR2	DY4	DB14
30	1.83	1.86	1.99	1.72
40	3.54	3.61	4.48	4.23
50	6.93	11.9	9.51	12.1
60	227	443	154	179

D_2O was used in our work and its higher density versus water may have contributed an effect. Nonetheless, it can be seen that diffusion is significantly hindered in the presence of the polymer substrate.

The diffusion coefficients for all dyes in D_2O were about 1.7 times higher at 40 °C than at 30 °C (Table 2). This increase in D along with the relative uniformity among all the dye structures suggests an improvement in dye mobility. However, when D at 60 °C is compared with the value at 30 °C, it is clear that there are large differences in the rate increase for dye diffusibility. The ratio of D at 60 °C to D at 30 °C for DR28, DR2, DY4 and DB14 was 172, 160, 91 and 130, respectively. Thus, it is apparent that raising the temperature caused enhanced molecular mobility and structural changes in the aggregate form of the dyes. Marked differences in the ratios of D at 50 °C to D at 40 °C are consistent with the onset of structural changes during this 10 °C increment. The extent of these changes varied for each dye. For example, D for DB 14 was tenfold greater at 50 °C than at 40 °C, whilst that of DR28 quadrupled and D-values for DY4 and DR2 were roughly 2.5 times greater. Whilst the diffusion coefficients for all the dyes were very comparable at 60 °C, this does not mean that the structural changes resulted in similarly sized aggregates in all cases. This is an important point because the dyes differ in molecular weight, charge density, and possibly the extent of hydrophobic surface area. The aspect of hydrophobic surfaces will be discussed in the light of molecular modeling studies [10].

The accelerating increase in D can be observed from Fig. 3, which presents data obtained from the two-dimensional plots of $-\log D$ versus chemical shift (ppm) for the dyes. It can also be seen from this graph that DB14 was polydispersed at 50 and 60 °C, indicative of structural changes. In contrast, DR28, DR2 and DY4 appeared to be monodispersed at all temperatures. Variations in D may indicate differences in the number of dye molecules per aggregate and/or charge density. The observation that the red and the yellow dyes remained monodispersed at all temperatures does not necessarily mean that they maintained a particular aggregate size over the entire temperature range. Aggregate dispersion and restructuring transitions may have occurred at temperatures other than those employed in this study or may not be readily detectable. Skowronek and co-workers pointed out, for instance, that thermal transition effects for DR28 molecules assembling in water could not be detected by differential scanning calorimetry (DSC), which was attributed to a rather loose structural arrangement for the complex. The addition of NaCl caused melting transitions, as the DSC scan was consistent with aggregates having increased structural order and density.

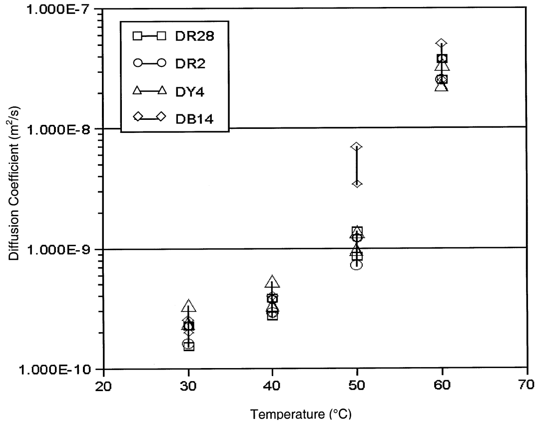

Fig. 3. Diffusion coefficient ranges for the dyes in D_2O.

As mentioned above, solutions of DR2 required several hours to reach new equilibria following dilution, unlike the other dyes. During our NMR experiments, DR2 required more than 2 h to reach equilibrium at temperatures up to and including 50 °C. Thus, our results indicate that a very rapidly established equilibrium state does not characterize all dyes. We also found that DR28 and DR2 had comparable diffusion behavior in D_2O at 30, 40 and 60 °C, once their equilibria were established. The similarity of the diffusion coefficients at 60 °C was in agreement with the results of our dyeing experiments [9].

3.2. Dye diffusion in DMSO-d_6

The diffusion coefficients for DR2 and DR28 in DMSO at 30 and 40 °C were similar (Table 3), suggesting that they diffuse at the same rate at these temperatures. The diffusion coefficient for

DR2 was much higher than that for DR28 at 50 °C and was nearly twice as high at 60 °C. This is an interesting observation since the sole difference in their molecular structures is the presence of methyl groups on the biphenyl moiety of DR2 (Fig. 2). Otherwise, they have similar molecular weights (Table 1) and the same number and type of ionic groups. This suggests that the DR2 aggregate is markedly smaller in DMSO than that of DR28 by the time 60 °C is reached and that DMSO is better able to disperse DR2 than DR28.

Comparing the diffusion coefficients for DY4 and DB 14 at 30 °C showed that the *D* for DY4 was 20% higher than that of DB 14. This difference diminished with increasing temperature and by 60 °C the *D* for DY4 was actually 10% smaller than that for DB14. These changes are relatively small considering the significant differences in the molecular structures. As mentioned, the molecular weight of DB14 is about 1.5 times that of DY4 and the former dye structure has twice the number of sulfonate groups (Fig. 2). If diffusion were based solely on the molecular weights of the dye particles in solution, this would mean that the aggregate sizes differ appreciably. It should also be noted that charge densities would differ for the resultant aggregates and would need to be taken into consideration. At 60 °C, the diffusion coefficient for DR2 was about 2.5 times higher than that of DB14 and 2.9 times greater than that of DY4, providing further evidence that the aggregate sizes and charge densities of the dyes differed.

The data obtained from the two-dimensional plots of −log *D* versus chemical shift (ppm) gave the changes in *D* as a function of temperature (Fig. 4). In DMSO, it was found that DY4 and DB14 had comparable behavior at all temperatures. This indicates a surprisingly, similar diffusion behavior given their differences in molecular weight, backbone structure, and number of charged sulfonate groups. The data also show that all four dyes were monodispersed at 30 and 40 and at 50 °C, DY4, DB14 and especially DR2 appeared to be polydispersed. Another interesting observation is that DR28 was monodispersed at all temperatures in DMSO, as observed in D_2O. However, structural changes in DR2 were affected by the type of solvent employed, as evident from its polydispersity in DMSO versus monodispersity in D_2O at 50 °C.

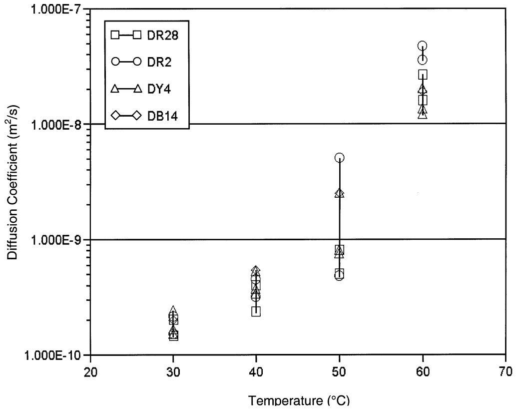

Fig. 4. Diffusion coefficient ranges for the dyes in DMSO.

3.3. The effects of the dyes on the solvents

Although the single simfit averaged values are presented here, it is critical to point out that both DMSO and water exhibit extremely wide ranges in the 2D-plots, indicating their polydispersity. The diffusion coefficient for H_2O was determined in these experiments, in the presence of dye dissolved in D_2O and in the presence of D_2O alone. The source of the H_2O present in these solutions was twofold. First, the D_2O contained residual H_2O and second, the dyes had a moisture content of approximately 4–5%. We found that the diffusion of H_2O was greater at all temperatures in the presence of the dyes as compared to the H_2O in D_2O alone (Table 4). For instance, at 30 and 40 °C the diffusion coefficients for H_2O were about four times greater in the presence of dyes than in D_2O alone. By 60 °C the *D* for H_2O in the presence of the dyes was only 1.2–2.0 times greater than that for water in D_2O alone. Since it is generally accepted that H_2O exists in the form of clusters, particularly at lower temperatures [14], it is proposed that the dyes disrupt such clusters. This reduction in the size of the H_2O clusters produced a higher diffusion coefficient.

Elevated temperatures also induced the breakup of H_2O clusters, as evident from the progressive increase in the H_2O diffusion coefficients with increasing temperature (Fig. 5). By 60 °C the *D* value was more than 50 times greater than the value at 30 °C. It is interesting that the rate of increase in the diffusion coefficient for H_2O in D_2O was greater than that for H_2O in the dye solutions, only at 40 to 50 °C. Thus, it would appear that this temperature range represents a transition during which the dispersion of H_2O clusters in D_2O was induced solely by thermal means. The increase in diffusion coefficients on raising the temperature from 50 to 60 °C was about tenfold for the H_2O in D_2O, while the increase was eight to 15-fold for H_2O in the presence of dye. This was the largest increase in *D* observed for any 10 °C temperature rise and was the temperature range that had the largest effect on water, whether or not dye was present.

In contrast to the results for H_2O, the diffusion coefficients for DMSO in the presence of the dyes were lower than the control values at all temperatures (Table 5). A notable difference between the DMSO control sample and H_2O in D_2O control sample was that the diffusion coefficient for the former increased markedly with increasing temperature and was 17 times greater at 40 °C than at 30 °C. In contrast, the diffusion coefficient for H_2O in D_2O alone was only 1.3 times higher for the same temperature range. With every subsequent 10 °C temperature increase, the *D* for DMSO roughly doubled (Fig. 6). It is possible that DMSO complexes existed at 30 °C but were broken up immediately when the temperature was increased, and that every subsequent doubling of *D* was due to an increased mobility of the DMSO molecules rather than to structural changes. By 60 °C, the *D* for the DMSO control sample was 80 times greater than the value at 30 °C.

Table 4
Temperature dependence for the simfit averaged diffusion coefficients (*D*) for H_2O in D_2O in the presence and absence of direct dyes

Temperature (°C)	$D\times10^{-10}$ (m^2 s^{-1})				
	DR28	DR2	DY4	DB14	Control
30	21.9	21.5	25.1	22.7	5.43
40	29.0	29.4	27.0	25.2	7.31
50	64.9	38.2	42.1	41.1	28.0
60	545	558	532	336	283

Table 5
Temperature dependence of the simfit averaged diffusion coefficients (*D*) for DMSO in the presence and absence of direct dyes

Temperature (°C)	$D\times10^{-10}$ (m^2 s^{-1})				
	DR28	DR2	DY4	DB14	Control
30	6.96	8.20	6.54	2.33	7.72
40	8.99	12.6	9.99	2.54	133
50	15.2	62.1	23.5	24.9	276
60	223	512	257	137	618

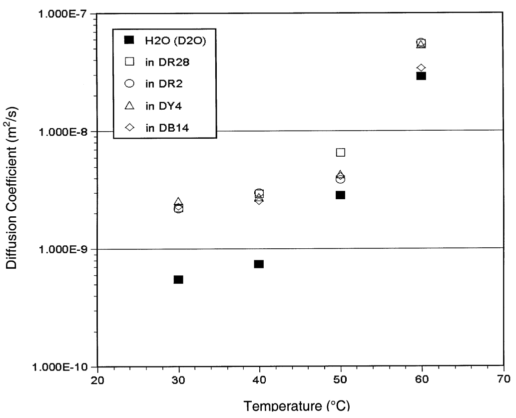

Fig. 5. Diffusion coefficients for water in dye/D_2O and D_2O.

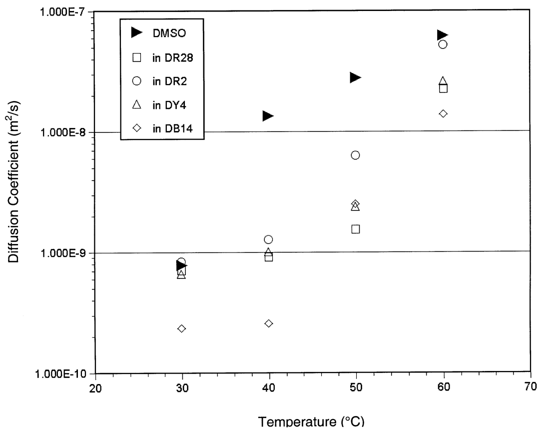

Fig. 6. Diffusion coefficients for DMSO as solvent for the direct dyes.

It is known that there is an exceptionally high degree of structural order in H_2O [14] and that DMSO molecules apparently are also well-structured [15]. It has been pointed out that the degrees of structural order within solvents are reflected in a ratio of their dielectric constants (ε) to their dipole moment (μ) and in their enthalpy of vaporization (ΔH_V). Though ε/μ is about 3.6 times greater for H_2O versus DMSO, the latter has a relatively large ΔH_V. The contribution of dipole moment to ΔH_V is only 10 kJ mol^{-1} less for DMSO than for H_2O. It is important to note also that the contribution of London forces to ΔH_V is approximately 11% for water versus about 45% for DMSO [14].

At 30 °C, the diffusion coefficient for the DMSO control was nearly equal to that of the DMSO in the presence of DR2, DR28 and DY4. However, it was 3.3 times greater than the *D* for DMSO in the presence of DB14. These results suggest that DB14 significantly hindered the diffusion of DMSO. Upon raising the temperature to 40 °C, the DMSO control had a *D* value that was 11 to nearly 53 times greater than that for the DMSO solvating the dyes. DB14 had the largest adverse affect on DMSO at 40 °C. Surprisingly, at 50 °C DR28 had the most adverse effect on DMSO. This was also the temperature at which the behavior of the red dyes differed the most. Whilst DR28 hindered DMSO diffusion the most and was monodispersed, DR2 was the least hindering and was polydispersed. Based on these observations and the extreme difficulty associated with reestablishing the equilibrium of DR2 following dilution in aqueous media, it is evident that DR2 is more hydrophobic than DR28.

It is also noteworthy that a 30 to 40 °C temperature increase gave a *D* value for DMSO in the presence of dye that was only 1–1.5 times greater at 40 °C than at 30 °C. This is in complete contrast to the *D* value for the DMSO control, which reflected a 17-fold increase on heating from 30 to 40 °C. It is possible that the dyes (with their Na^+ counter ions) exhibited a structuring effect such that, even with increases in temperature, the dispersion of the DMSO complexes into smaller structural units was prevented. By 60 °C, the *D* value for DMSO in DR28 and DY4 was roughly 36 times greater than at 30 °C, while the *D* value for DMSO in DR2 and DB14 was about 60 times greater. In contrast, the diffusion coefficient for DMSO alone increased 80-fold upon raising the temperature from 30 to 60 °C. Thus, it is apparent that DMSO in the presence of the dye did not diffuse as rapidly as the DMSO control, even at elevated temperatures. In addition to a possible structuring effect by the ions, it is feasible that the dyes might be obstructing the movement of solvent molecules at elevated temperatures.

3.4. Comparison of dyes in D_2O versus DMSO

At 30 °C, the *D* values for the two red dyes were comparable in D_2O and DMSO (Tables 2 and 3). It cannot be concluded, however, that the size of the aggregates for the red dyes were similar in both solvents at this temperature, since the solvents differ in molecular weight, density, dielectric constant, and structural form. Consequently, their effects on the *D* of the dyes differ. It is of interest to note that at 50 °C the *D* for DR28 in D_2O was about twice that of DMSO. As discussed above, it appears that DR28 has been converted to smaller aggregates at 50 °C in D_2O, which did not seem to be the case in DMSO. Though DR28 and DR2 differ only by 2 methyl groups, the *D* for the former at 60 °C was about 1.5 times greater in D_2O than in DMSO, while the reverse was true for DR2. The *D* value for DR2 was approximately 1.4 times higher in DMSO than in D_2O. While DR28 was better solvated in D_2O at 60 °C, DR2 was better solvated in DMSO. Since London forces contribute about 45% to the ΔH_V of DMSO, it is apparent that DMSO would more readily solvate those dye molecules with greater hydrophobic surface characteristics. Molecular modeling studies were employed to better explain these observations.

In the context of discussing hydrophobicity/hydrophilicity, it is worth noting that DY4 was the only dye that had a higher *D* value in D_2O than DMSO at all temperatures (Tables 2 and 3). Based on these results, it is apparent that DY4 is the most hydrophilic of the four dyes investigated. Comparing its molecular structure to that of DR28 (Fig. 2), it can be seen that both dyes have two sulfonate groups; however, DY4 also has two hydroxyl groups. The hydrogen-bonding ability of these hydroxyl groups enhances the solvation of DY4 in aqueous media to a greater extent than is possible for DR28. On the other hand, DR2 was much better solvated in DMSO at all temperatures except 30 °C and, thus, it appears to be the least hydrophilic of the four dyes. DR28 and DB14 are similar in that their *D* values were higher in D_2O than in DMSO at temperatures except 40 °C. The hydrophilicity of these two dyes falls between that of the previous two dyes.

4. Conclusions

It has been shown that the direct dyes employed in this study undergo aggregation in DMSO and D_2O to varying degrees depending on the temperature employed. The observed aggregation is disrupted with increasing temperature and the degree to which this occurs varies with the dye and solvent. The present results suggest that Direct Yellow 4 is the most hydrophilic dye of the four studied, while Direct Red 2 is the most hydrophobic. It is evident that the methyl groups of Direct Red 2 render this dye more hydrophobic than its structural analog Direct Red 28.

It is also clear that direct dyes affect the diffusion coefficients of the solvents employed and vice versa, in different ways depending on the solvent. For instance, while the presence of direct dye raises the diffusion coefficients for D_2O it depresses the diffusion coefficients for DMSO.

We believe that the NMR-PFG technique can also be used for other dye classes that can be dissolved in solvents such as DMSO-d_6 and D_2O.

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