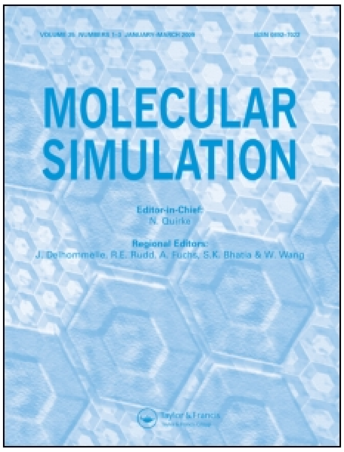

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An insight into the mechanism of the cellulose dyeing process, part 2: Simulation of aggregation, solvent and additive effects upon azo-linked aromatics and dyes

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An insight into the mechanism of the cellulose dyeing process, part 2: Simulation of aggregation, solvent and additive effects upon azo-linked aromatics and dyes

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In order to probe the complex process of dying cellulosic materials with common azo-linked dye systems, the aggregation-disaggregation process has been studied using molecular simulation techniques. In particular, the dynamics of multiple dye species in both gaseous and aqueous environments have been examined by molecular modeling methods, with emphasis upon the effects of urea upon these species in aqueous solutions. Such simulation techniques can demonstrate the natural drive for dye molecules to aggregate in solution and compare well with those results obtained from spectroscopic results. In addition, molecular modeling does predict that urea tends to cause disaggregation, by breaking up dye clusters; this also closely follows literature prediction and practical predictions.

Keywords: Cellulose; Dyeing; Aggregation; Salt; Urea

1. Introduction

1.1 Aggregation of dyes in solution

It is well documented that dyes tend to self associate in solution to form aggregates [1,2,3,4]. This self association of solubilised dyes can lead to the formation of dimers, trimers, and tetramers etc. through the combined effects of both van der Waals (in the case of π-stacking interactions) and hydrogen bonding interactions. Such aggregation has been studied by a variety of methods, with the aggregation number for particular dyes being determined under carefully defined conditions, i.e. at particular temperatures, pressures etc. Such studies clearly show that dyes tend to form aggregates very readily in aqueous solution. Work by Coates on polar dye species [2] in aqueous solution has shown that the ratio of aggregate to monomer can vary according to concentration about an isobestic point. This and related work [1] shows that the formation of aggregate species is exothermic, despite being entropically less favourable. Therefore, the breakdown of dye aggregates is a necessary prerequisite for dyeing to be possible and this has to occur at the solution-fibre interface, which necessarily requires an input of energy. Once disaggregation of the dye molecules has occurred, the dyes can diffuse into the fibre matrix and become involved in the dyeing process.

1.2 The role of salt

It has long been known that ionic additives have an important and beneficial effect on the dyeing process [5]. The simplest of these additives used in the dyeing processes are the neutral electrolytes, sodium chloride or sodium sulfate. These additives are used in the exhaust (or batchwise) dyeing of cellulose, with both anionic direct and reactive dyes. In the absence of these electrolytes, the exhaustion of the dye onto the fibre can be poor, particularly in the case of reactive dyes.

Sodium chloride, when added to a neutral dyebath, has the effect of increasing the level of exhaustion of the dye onto the fibre. The sodium chloride appears to achieve this effect by increasing the degree of aggregation of the dye molecules via the common ion effect. This has the effect of promoting exhaustion of the dye onto the fibre, since suppression of the ionisation of the dye in solution effectively reduces the solubility. This reduction in solubility modifies the equilibrium in favour of the movement of dye from solution to the fibre surface. The overall idea is therefore, to use the optimal quantity of salt to provide maximum exhaustion: Too little, and its effect will not be noticeable; too much and aggregation results to such an extent that precipitation occurs (or the aggregates become too large to diffuse into fibre matrix leading to

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surface coloration only [5]. This “salting-on” effect is a result of interactions between the dye and the electrolyte.

It is also known that cellulose fibres acquire a negative charge (zeta-potential) in aqueous media due to their low dielectric constant [6] and has the effect of repelling like-charged dyes. Hence, electrolytes tend to reduce, or even extinguish, the zeta-potential on the fibre [6,7,8], thus facilitating the transfer of dye from solution to the fibre matrix. Iyer *et al.* have proposed that the dye adsorption increases as the disrupting effect of the electrolyte cations in water increases[9]; the order being $Cs^+ > K^+ > Na^+ > Li^+$. It has also been shown that the dye binding process in different dye-fibre systems is influenced by the structure of the water around the dye molecule and fibre surfaces [10].

The effect of different sodium halides on the dyeing process has been examined and found to have little effect on dye adsorption, due to repulsion of the anion by the negatively charged surface of the cellulose. In contrast, cations strongly influence the dye adsorption by attraction onto the cellulose surface [9]. One may therefore, visualise the role of the cation as perturbing the intermolecular hydrogen bonds of water, but not perturbing water molecules bound to the cellulose matrix, since it has been indicated that water-cellulose interactions are much stronger than intermolecular water-water interactions [11].

1.3 The role of urea

In contrast to salt, urea is used as an additive in continuous dyeing and printing processes. One of the pre-requisites for a successful cotton dyeing is sufficient solubility of the dye. In turn, this can be achieved via the addition of an auxiliary that effectively increases the solubility of the dye, leading to a more uniform dyeing and increased colour yield. These hydrotropic agents are believed to act as an amphiphilic bridge between the dye solubilisate and the aqueous medium [12]. The efficacy of urea in increasing the bonded dye yield has been attributed to several factors:

- Swelling of cellulose [13,14]
- Disaggregation of the dye, leading to increased solubility [13,14]
- Improved diffusion of the dye [13,14]
- Retarding the rate of water removal during drying [13,14]
- Acting as a solvent [13,14]

The solubilisation effects of urea upon dyes does not involve the formation of micelles and can be attributed to the ability of urea to break hydrogen bonds. This will, in effect, perturb the dye system in a similar manner to sodium chloride, although the solubility of reactive dyes increase with the addition of urea (a few exceptions have been recorded) [15]. Another function of urea is to increase the yield of the reaction between the dye and the substrate, which is observed [13,16] when the reaction is performed at room temperature. At this temperature, the partially soluble dye can only dissolve at a rate equal to its removal from saturated solution by reaction with the substrate. Thus, urea facilitates the transport of dye onto the fibre and increases the bonded dye yield.

Given the remarkably complex nature of the role of different additives used in the conventional cellulose dyeing industry, we decided to examine ways in which the dyeing process could: (a) be made less reliant upon either salt or urea; (b) be transformed into an efficient process using existing dyes; and (c) be more fully understood at the molecular level. In the first part of this work [17], we reported application of molecular modeling and simulation techniques to gain an understanding of the structural subtleties of azo-dye species. In this paper, we take these simulation methods further and examine dyes in solution and simulate their behaviour in the presence of urea.

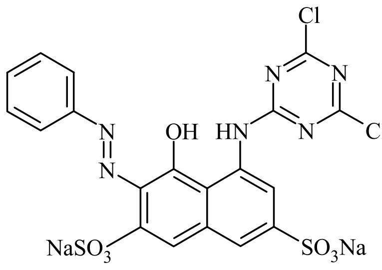
2. Methods

Dyes and all additives, with the exception of water molecules, were initially drawn using the 2D molecular builder available within QUANTA 97®. These structures were then minimised (gas phase) such that each component in the more complex models was at its own gas phase local minimum. Solvated models were constructed by combining the desired dye, before being solvated with the solvation tools in QUANTA 97®. This tool allows the inclusion of individual water molecules, as opposed to simulated solvation using a dielectric constant. All structures were subjected to minimisations using the steepest decent (SD) method to remove bad contacts, then conjugate gradient (CG) minimisations over 4000 iterations. The minimised structures were then subjected to molecular dynamics (MD) simulations, followed by simulated annealing (SA) via re-minimisation. The minimisations and re-minimisations employed sufficient iterations that all species reached their minima within the allotted 4000 iterations.

3. Results and discussions

3.1 Gas phase studies of multiple Procion Red MX-5B 1

Initially, two Procion Red MX-5B **1** molecules were placed in a relative orientation in which the sulfate



1

Molecular Formula $C_{21}H_{16}Cl_2N_6O$

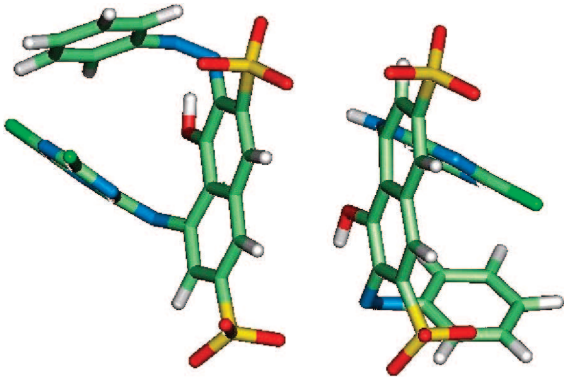


Figure 1. Starting Point for the Procion Red MX-5B **1** molecules with parallel sulfonates.

functions were close to each other, in a parallel arrangement (figure 1). Subsequent MD simulations of Procion Red MX-5B **1** molecules resulted in initial blowing apart due to the repulsive forces between the adjacent negatively charged sulfonates during the simulation process. However, the two dyes were drawn back towards each other to give the formation depicted in figure 3, with one hydrogen bond between the hydroxyl of one of the dye molecules and the sulfonate of the other assisting aggregation. In addition, the final orientation of this model results in the sulfonate-sulfonate interactions being minimsed by rotation of the two dyes relative to each other (final mimimised model after the MD and SA cycle had an energy of $-674.68\,\mathrm{kJ\,mol^{-1}}$).

In contrast, the resulting models starting from two Procion Red MX-5B **1** dyes with the sulfonates initially placed in an anti-parallel arrangement (figure 2) demonstrated that there was a strong affinity between the dyes. Interaction primarily involved hydrogen bonding interactions with 2 hydrogen bonds being evident, one between the hydoxyl and sulfonate functions and a second being between the sulfonate and azo motifs, as depicted in figure 4. However, in this case the van der Waals interactions, in the form of face-to-face (π-stacking) interactions between adjacent naphthalene rings appeared to be much stonger than the previous parallel sulfonate model (compare with figure 3) (final energy of $-791.76\,\mathrm{kJ\,mol^{-1}}$ after the MD and SA cycle, figure 4).

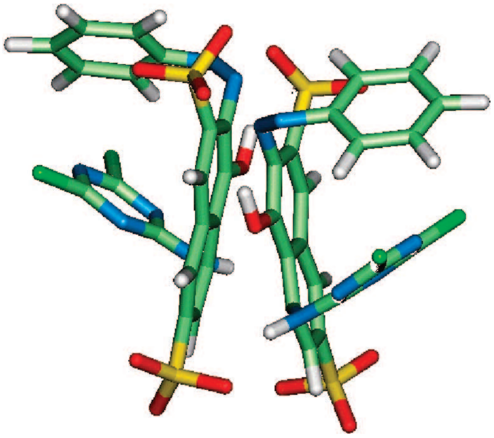


Figure 2. Starting Point for the Procion Red MX-5B **1** molecules with anti-parallel sulfonates.

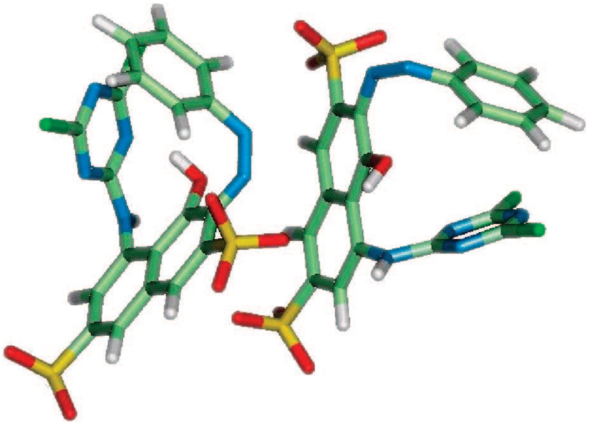


Figure 3. Two Procion Red MX-5B molecules after gas phase molecular dynamics and simulated annealing, initially placed with parallel sulfonate groups.

These gas phase studies were extended to include simulation of the behavior of three dye molecules, with two being placed in an anti-parallel arrangement and the third being placed in such a position that it was effectively end-capping the other two (figure 5). Following the MD and SA cycle, once again these gas phase studies showed the accentuated tendency of Procion Red MX-5B **1** molecules to aggregate, due to hydrogen bonding and π-stacking interactions (final energy of $-1281.26\,\mathrm{kJ\,mol^{-1}}$). These results are paralleled by spectroscopic and solution-phase experimental which, clearly shows that Procion Red MX-5B **1** aggregates readily in solution [18].

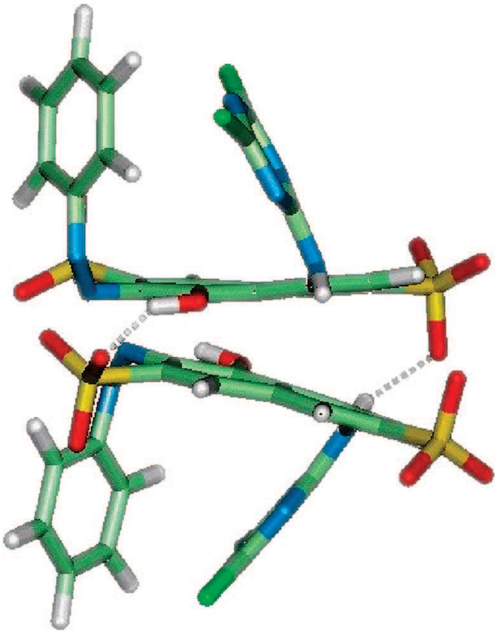


Figure 4. Two Procion Red MX-5B molecules after gas phase molecular dynamics and simulated annealing, initially placed in an anti-parallel starting position.

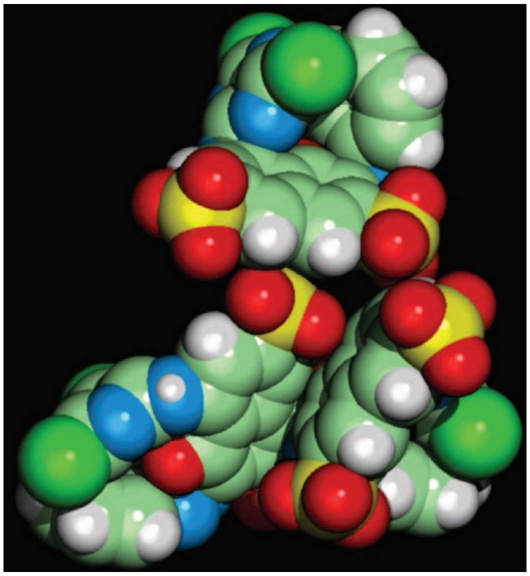


Figure 5. Three Procion Red MX-5B **1** dye molecules after MD and SA.

3.2 Aqueous phase studies of Procion Red MX-5B 1

The next step was to repeat the above modelling using Procion Red MX-5B **1**, in a simulated aqueous environment. Since water is the normal environment for dye applications using reactive dyes, we were interested to see how dye aggregation would differ in this environment, compared to the gas phase studies above. Initial minimisation studies performed previously [17] were extended to aqueous phase minimizations, with the Procion Red MX-5B **1** dye contained within a 30 Å box of water (figure 6). After MD simulations, it was found that Procion Red MX-5B **1** folds up onto itself, to form a "ball-like" structure due to hydrophobic interactions, exactly as we had found using gas-phase simulations [17], with only minor structural variations being apparent (see table 1).

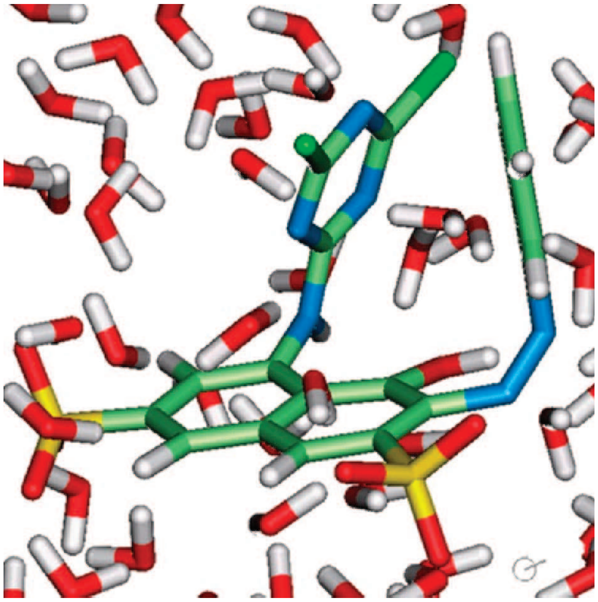


Figure 6. Procion Red MX-5B **1** molecule encapsulated within a 30 Å box of water.

The next step was therefore to examine the behavior of two and three Procion Red MX-5B **1** dye molecules in a simulated aqueous environment. The aggregate post minimisation arrangement for this two dye model is shown in figure 7. After MD simulations, it was found that in these simulated aqueous solution conditions, the dye molecules were strongly attracted to each other, as found in the gas phase simulations (*vide supra*), resulting in the formation of aggregates, as expected from the literature (figure 9) [1,2]. Simulation of the three dye molecule system (the post minimisation starting point is depicted in figure 8 was carried out in the 30 Å box of water, which equates to approximately 920 water molecules surrounding the dyes and extrapolates to a dye concentration of 0.117 M, or 306.6 water molecules per dye molecule. This means that with respect to the simulation, there was sufficient water to ensure complete solvation of the dye molecules. MD simulations were performed at 300 K, followed by SA on this hydrated system, following the previously outlined routine. The result was that here again, the dye molecules were strongly attracted to each other. This attraction being the result of a combination of hydrophobic, π-stacking and hydrogen bonding interactions, as depicted by figure 9 for the anti-parallel, two dye model (final energy for the parallel arrangement was -17213.71, versus $-17171.50\,\mathrm{kJ\,mol^{-1}}$ for the anti-parallel arrangement). The three dye model producing aggregated systems in our results with a final energy of $-19368.69\,\mathrm{kJ\,mol^{-1}}$ figure 10 (water molecules have been removed for clarity). It is interesting to note that the dyes effectively encapsulate themselves to form a hydrophobic cluster held together by hydrogen bonds, with a hydrophobic core and hydrophilic coat formed by the sulfonate groups.

3.3 Simulation of the effect of urea upon Procion Red MX-5B 1 aggregation

Having examined dyes in both gas and aqueous phase environments, the next step was to examine the effect of urea upon aggregation. For this simulation, the starting arrangement was the three dye molecule system above, with two being placed in an anti-parallel arrangement and the third being placed in such a position that it was effectively end-capping the other two (*vide supra*, i.e. as shown in figure 5). To this model was added nine urea molecules, placed in close proximity to the dyes, but in a random fashion. This arrangement was then solvated within the confines of a 10 Å solvation sphere; this enclosure again contained sufficient water molecules to allow solvation of the dyes.

This system was then minimized to give the structure shown in figure 11 (energy of $-3498.47\,\mathrm{kJ\,mol^{-1}}$) and

Table 1. Comparison of molecular properties for Procion Red MX-5B 1 from gas phase and aqueous phase simulations.

	*Procion Red MX-5B **1***	
	Gas phase [17]	*Aqueous phase*
Final Energy kJ mol^{-1}	− 173.75	− 2098.74
Dihedral angle Φ_1[17]	275.8	240.3
Dihedral angle Φ_2[17]	43.4	43.4
Bond length -N=N-Å	1.245	1.246
Bond length Ar-N-N-Å	1.350	1.371
Bond length Naph-N=N-Å	1.376	1.381

this system contains 447 hydrogen bonds within the whole solvated structure. This hydrogen bond total is a summation of all the dye–dye, dye–urea, dye–water, urea–urea, urea–water, water–water interactions. This minimised model was then subjected to MD simulations and the results are shown in figure 12, where one can observe the fact that the urea molecules caused breakdown of the aggregated dye system. This is achieved by interfering with the hydrogen bonding pattern that occurs in the absence of urea, i.e. both between adjacent dyes, and between water and dye molecules. The total number of hydrogen bonds is considerably reduced in the presence of urea to 306 for the entire system (figure 12). These effects are evident even after the initial minimisations and become more extensive after full MD and SA, resulting in a final energy of − 8884.67 kJ mol^{-1}. These results again mirror those reported in the literature for effect of urea upon dye aggregation (*vide supra*), i.e. that urea strongly interrupts the many weaker hydrogen bonds interactions between dyes, and replaces these with fewer, stronger hydrogen bonds between the dyes molecules and urea. This effect becomes clearer if figure 12 is examined in the absence of water molecules, then one can observe the true extent of the hydrogen bonding network between the dyes and the urea molecules, as shown in figure 13. This figure shows that there is no dye–dye hydrogen bonding, but there are five dye-urea hydrogen bonds. If we compare this model with those obtained for the aqueous phase simulations of a similar starting model without the urea

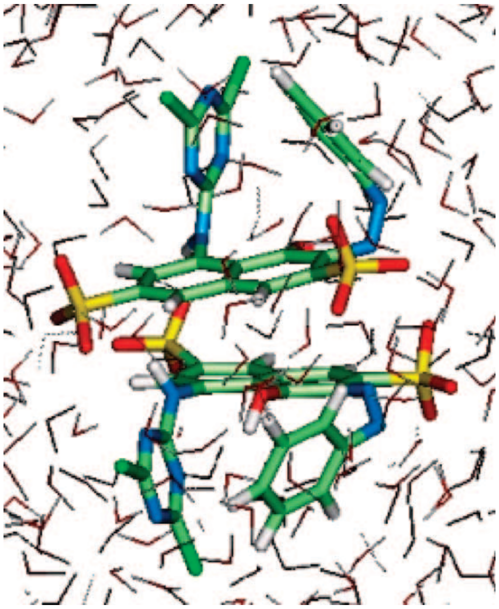


Figure 7. Mimimised structure of two Procion Red MX-5B dyes within a 30 Å water matrix prior to MD and SA studies.

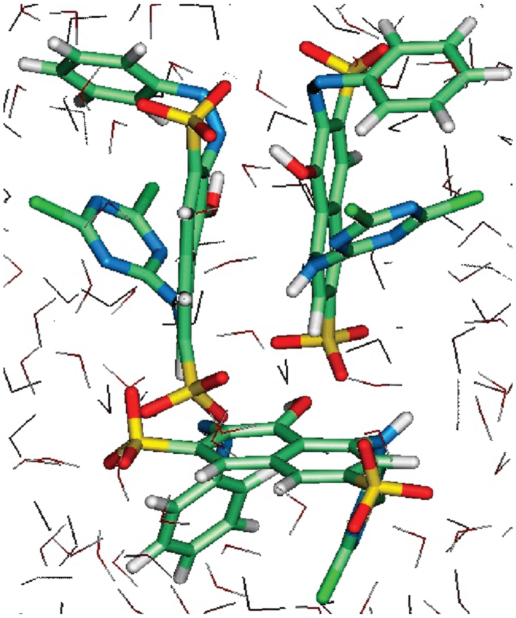


Figure 8. Mimimised structure of three Procion Red MX-5B dyes within a 30 Å water matrix prior to MD and SA studies.

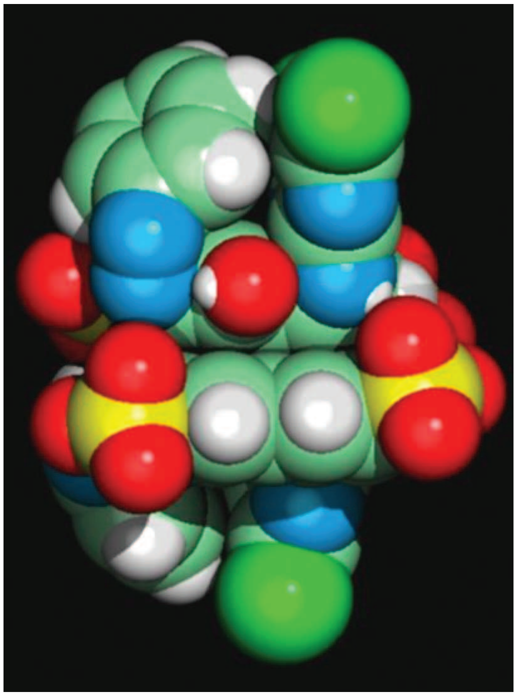


Figure 9. Anti-parallel arrangement of two Procion Red MX-5B dyes within a 30 Å water matrix following MD and SA studies with water removed for clarity.

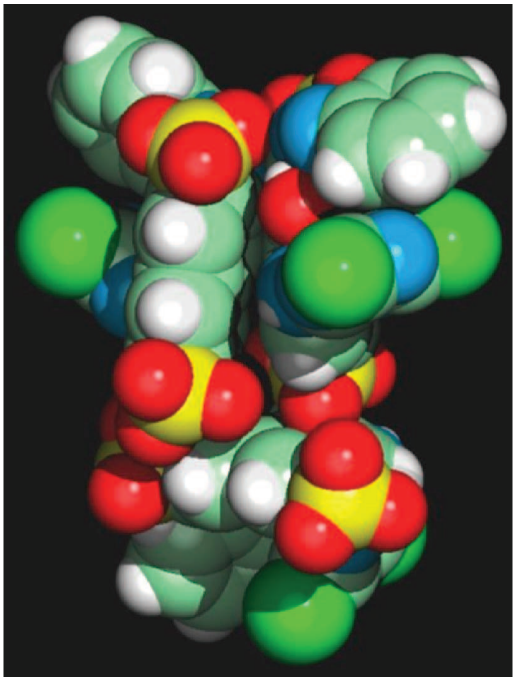


Figure 10. Final model for the three Procion Red MX-5B dyes within a 30 Å water matrix following MD and SA studies with water removed for clarity.

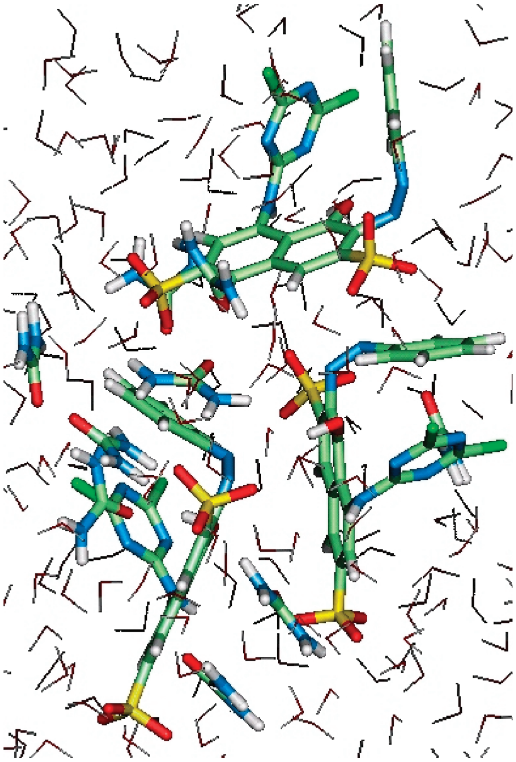


Figure 12. Final structure of three Procion Red MX-5B **1** dyes within a 30 Å water matrix with 9 urea molecules present following MD and SA.

present (figure 14), one dye–dye hydrogen bond can be found. These observations support the fact that there is a breakdown in the hydrogen bonding network between dyes upon addition of urea and de-aggregation results. Thus, it would appear that the key factor in the role of urea upon aggregation is the formation of multiple of fewer stabilising hydrogen bonds between dye, urea and water, leading to aggregate collapse and dye solubilisation.

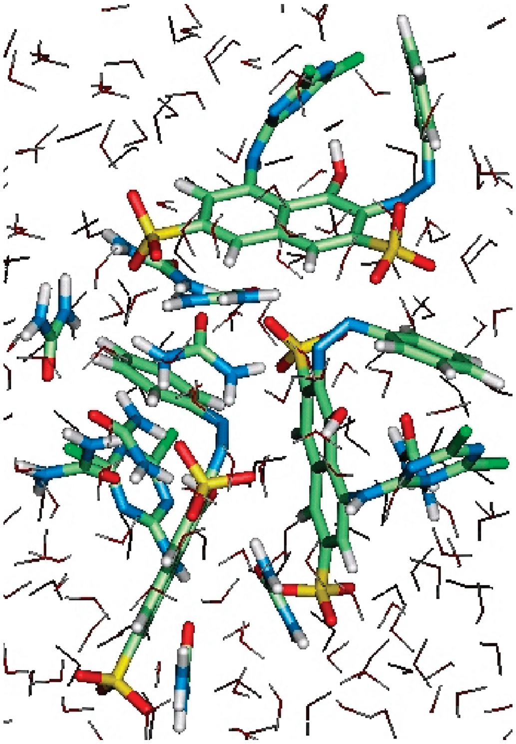


Figure 11. Minimised structure of three Procion Red MX-5B **1** dyes within a 30 Å water matrix with 9 urea molecules present.

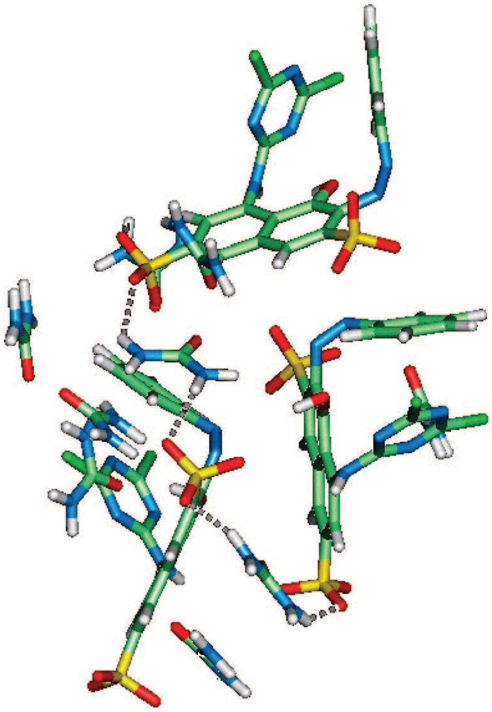


Figure 13. Final structure of three Procion Red MX-5B **1** dyes within a 30 Å water matrix with 9 urea molecules present following MD and SA with water removed to show the true extent of the dye-urea hydrogen bonding.

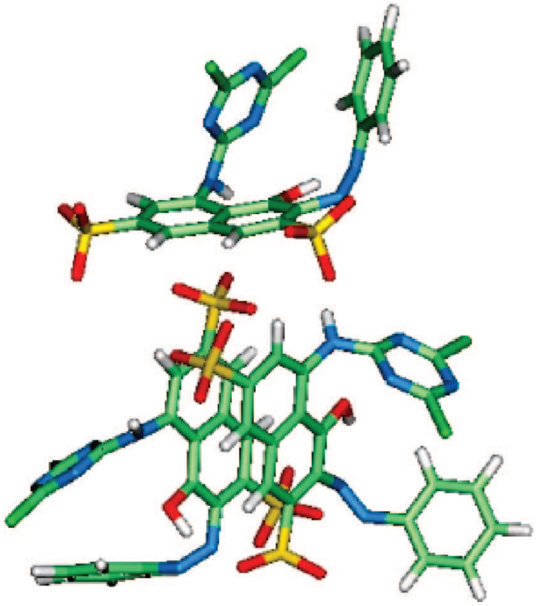


Figure 14. Model derived from the aqueous phase simulations of three procion Red MX-5B molecules in the absence of urea for comparison to figure 13 with urea.

4. Conclusion

Molecular simulation on Procion Red MX-5B **1**, in both simulated gas and aqueous phases (along with spectroscopic evidence), show that dyes tend to readily self-associate. This self-association in turn leads to the formation of poly-molecular aggregates. Extension of the aqueous phase molecular modelling studies to look at the effect of added urea, shows that urea affects the dissolution of the dye species by breaking up the poly-molecular aggregates by interruption of inter-dye hydrogen bonds in particular, an effect which is well documented in the literature [19]. These effects of dye aggregation and dis-aggregation in solution, in the presence of either salt and urea, have been clearly observed by spectroscopic methods [19]. It is therefore reasonable to conclude that molecular simulation of the behaviour of dyes in solution and in the presence of additives is possible. This follows experimental observations and should therefore be practicable for extension to the molecular design of potential replacements of dye-bath additives.

5. Experimental

5.1 General computational procedures

All molecular modelling work was undertaken on a Silicon Graphics O_2 workstation with a 180 MHz CPU, 64Mb of RAM running IRIX 6.2. QUANTA was used in the initial stages and was upgraded to QUANTA 97®. Hardcopies of structures were prepared using Snapshot for screen capture and XV for RGB to JPEG conversion.

1. *Minimisation studies of Procion Red MX-5B 1 within a water matrix*

   A Procion Red MX-5B **1** molecule was constructed within the molecular editor of the QUANTA 97® package, this structure was then subjected to gas phase minimisation's over 4000 iteration using the SD, then CG algorithms. This structure was then solvated, with a 30 Å box of water, using the solvation option within the calculation menu. The resultant model was then re-minimised as until the structure would minimise no more initially by SD, then by CG methods.
2. *Molecular dynamics studies of Procion Red MX-5B1 within a water matrix*

   Solvated dynamics simulations were studied by performing dynamics simulations on the model generated from procedure 1. The simulations were carried out as in our previous paper using 4 ps time scale for each of the dynamic simulation components.
3. *Gas phase minimisation of two Procion Red MX-5B 1 molecules.*

   A Procion Red MX-5B **1** molecule was constructed using the molecular editor interface within QUANTA 97®. This was then subjected to gas phase minimisation over 4000 iterations using both the SD and CG algorithms. A clone of this structure was made and the two entities placed back-to-back with the sulfonate groups in an antiparallel arrangement, before re-minimisation using the SD algorithm to remove bad contacts. The structure was then minimised as outlined using the CG algorithm.
4. *Gas phase dynamics simulations of two Procion Red MX-5B 1 molecules.*

   Using the model created in procedure 3 dynamics simulations were performed at 300 K with a 4 ps time span for each of the heating, equilibration and simulation components of the dynamics simulation. This structure was then annealed using the methodology outlined in previous procedures.
5. *Aqueous phase minimisation of two Procion Red MX-5B 1 molecules.*

   The Procion Red MX-5B **1** model that was created in procedure 3 was solvated using the solvation option within QUANTA 97®. The resultant model was then minimised using the both the SD methodology to remove bad contact due to the random placement of the water molecules. The structure was then minimised using the CG algorithm until the model would not minimise further.
6. *Molecular dynamics simulations of two Procion Red MX-5B 1 within a water matrix*

   The model that resulted from experiment 5 was subjected to dynamics simulations as in 4 and re-minimisation using the CG algorithm over 4000 iterations.
7. *Gas phase minimisation of three Procion Red MX-5B 1 molecules*

   A Procion Red MX-5B **1** molecule was constructed using the molecular editor interface within QUANTA

97®. This was then subjected to gas phase minimisation over 4000 iterations using the SD and CG algorithms (as above). Two clones of this structure were made and the three entities placed back-to-back with the sulfonate groups in an antiparallel arrangement with the third on one of the ends, before re-minimisation using the SD algorithm to remove bad contacts. The structure was then minimised as previously outlined using the CG algorithm.

8. *Gas phase dynamics simulations of three Procion Red MX-5B 1 molecules*

   Using the model created in procedure 7 dynamics simulations were performed at 300 K, the structure was then annealed using the methodology already outlined in earlier procedures.

9. *Aqueous phase minimisation of three Procion Red MX-5B 1 molecules*

   The Procion Red MX-5B model created in procedure 1 was solvated using the solvation option within QUANTA 97® as mentioned previously. The resultant model was then minimised using the CG algorithm until the model would not minimise ant further.

10. *Molecular dynamics simulations of three Procion Red MX-5B 1 within a water matrix.*

    Using the model created in procedure 9 dynamics simulations were performed at 300 K with a 4 ps time span for each of the heating, equilibration and simulation components. This structure was then annealed using the methodology already outlined in previous procedures.

11. *Aqueous phase minimisation of three Procion Red MX-5B 1 molecules in the presence of urea.*

    Using the methodology previously (procedure 7) described a structure consisting of three Procion Red MX-5B **1** dye molecules and 9 urea molecules were constructed within a 10 Å water matrix. The urea, being manually placed in a random arrangement, but in close proximity to the dye aggregate beofre the solvation function was activated. This structure was then subjected to minimisation using the steepest descent then CG algorithms over 5000 iterations.

12. *Aqueous phase Procion Red MX-5B 1 urea minimisation-dynamics-annealing studies.*

    Using the post minimisation model constructed in procedure 11, dynamics and annealing studies were performed as outlined in earlier procedures. Using the CG algorithm for the annealing process and 4 ps for the time interval for each of the simulated dynamics components.

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