Dyes and Pigments 1 (1980) 39–48

AGGREGATION AND LYOTROPIC MESOPHASE FORMATION IN ANIONIC DYE SOLUTIONS

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SUMMARY

A number of water-soluble anionic disazo dyes have been synthesised, the position of the solubilising groups (—SO_3^-) indicating amphiphilic properties. The (Na) mono- and di-sulphonates exhibited lyotropic liquid crystalline phases whereas tri-sulphonates crystallised normally. The dyes were examined in detail by spectrophotometry and polarisation microscopy and binary (dye/water) phase diagrams constructed. Structures for the observed phases are suggested and discussed in relation to amphiphilic surfactant behaviour and their importance in dye solid separation processes mentioned briefly.

1. INTRODUCTION

In any investigation concerning dye absorption from solution it is necessary to take into account the possibility of aggregation of the dye molecules in the dyebath. In commercial practice with, for example, water soluble dyes of molecular weight in the region of 500, the strength of the dye solution at conventional liquor ratios approximates to a concentration of 10^{-3}–10^{-4}M. There have been numerous studies of dye aggregation over this range both for anionic[1] and cationic[2] dyes and a number of experimental techniques have been used. Spectrophotometry[3] has been the most extensively employed but techniques such as light scattering,[4] polarographic diffusion,[5] vapour pressure osmometry,[6] and potentiometry[7] have also been applied to determine the molecular weight distribution of aggregates. It has been pointed out[8] that spectrophotometry is of limited use with anionic azo dyes since the broad

Dyes and Pigments 0143-7208/80/0001-0039/$02·25—
Printed in Northern Ireland

absorption curves obtained with monomers, dimers and larger aggregates cannot be sufficiently resolved and are ineffective in determining thermodynamic quantities related to aggregation.

There are also few data describing the actual structure and molecular orientation within dye micelles and aggregates other than qualitative descriptions such as the presence of 'nematic' threads,[9] polymerised dye molecules coupled with water molecules,[10] threads consisting of stacked dye cells[11] and large aggregates capable of centrifugation.[12] From these descriptions it may be concluded that these large aggregates are not simply growing nuclei and small crystals of separating dye solids. Neither are any data available relating molecular constitution to the size and type of aggregate. Some aqueous ionic dye solutions possess surface active properties[13] due to the amphiphilic nature of the solute. Consequently it has been suggested[4] that dye aggregates may parallel the structures found in lyotropic systems[14] of soaps and surfactants. Proceeding on this basis we have chosen a number of disazo-sulphonated dyes, as sodium salts, for investigation over a wide range of concentrations in an attempt to gain further insight relative to structure. In addition, the results may have technical implications in salting out processes in relation to gel formation and ultimate filtration.

2. EXPERIMENTAL

For a preliminary assessment seven disazo dyes whose detailed structures are given in Table 1 were synthesised. The dyes were obtained by diazotising 4-aminoazobenzene or the corresponding 4-aminoazobenzenesulphonic acid and coupling under alkaline conditions to either 2-naphthol or the relevant 2-naphthol-sodium sulphonate.

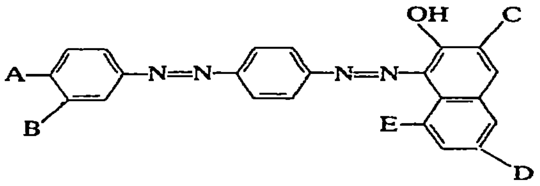
When 4-aminoazobenzene was used as the diazo component the resultant dye solid was extracted with dry acetone to remove unreacted 4-aminoazobenzene. The dye solids were dissolved in hot distilled water and salted out by the addition of sodium chloride.

It was necessary to remove all water soluble inorganic salts from the dye solids prior to examination. The dye solid (20 g) was stirred in 200 ml dimethylformamide at 100°C for 30 min. The solution was filtered hot, allowed to cool and re-filtered. An equal volume of acetone was added to the filtrate which was then allowed to stand overnight at −10°C. After filtering and washing with acetone essentially pure dye is obtained by this method.[15]

The dye structures were specifically chosen to contain one or more hydrophilic groups situated in various terminal positions in order to anticipate their amphiphilic character. Dye VIII (Sudan III) was included to complete the series. Its solubility in water at room temperature, was however, so low that further examination was not possible.

TABLE 1

SULPHONATED DISAZO DYES WITH POSSIBLE AMPHIPHILIC PROPERTIES



General Structure

Dye number	*A*	*B*	*C*	*D*	*E*	*Colour index number*
I	—SO_3Na	H	H	H	H	26900
II	H	H	H	—SO_3Na	H	—
III	H	H	H	H	—SO_3Na	27150
IV	—SO_3Na	—SO_3Na	H	H	H	—
V	H	H	—SO_3Na	—SO_3Na	H	27190
VI	H	H	H	—SO_3Na	—SO_3Na	27290
VII	H	H	—SO_3Na	—SO_3Na	—SO_3Na	27305
VIII	H	H	H	H	H	26100

2.1. *Polarisation microscopy*

To detect the presence of a mesophase structure in aqueous solutions of the above dyes a range of concentrations up to 2% wt/vol. was examined between crossed polars using a Vickers M40 Photoplan microscope. A drop of each solution placed under a cover slip on a microscope slide undergoes edge-wise evaporation at room temperature causing a concentration gradient to develop inwards from the cover slip edge. The mesophase can thus be detected by its irregular heterogeneous appearance within the solution phase of the droplet.[16] Figure 1 shows this effect for a 2·0% solution of dye IV.

In this figure, region A is the isotropic solution, B is the region of nucleation and growth of droplets which gradually merge to form the lamellar mesophase C. D is the edge of the cover slip. It is of interest to observe that the dried solution outside the cover slip appears to retain the structural appearance of the mesophase. Dyes I and IV markedly show these effects over a range of concentration, as does dye V under a more limited range. Dyes II and III possess a relatively low aqueous solubility and a mesophase was not always observed. Dyes VI and VIII have a much higher aqueous solubility and an edge-wise evaporation led only to the development of a crystalline precipitate within the solution. Since the lamellar mesophase was readily observed with dyes I and IV, further examination was mainly restricted to these two, covering as wide a concentration range as possible, and including the more dilute isotropic solution.

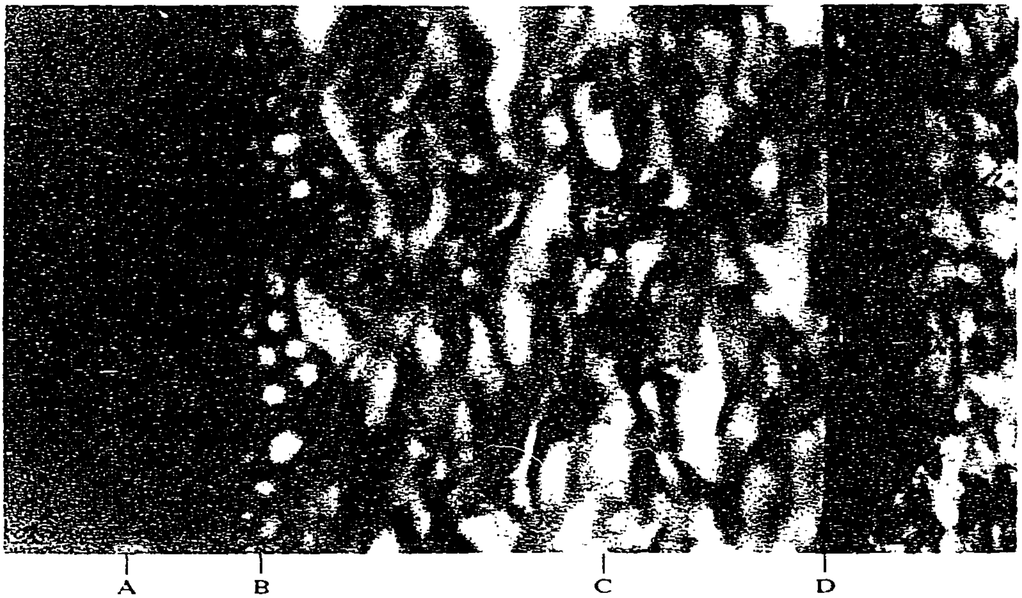


Fig. 1. Edge-wise evaporation of 2% solution of dye IV. Nominal magnification 100×. Polarisation axes parallel with figure edges. For explanation of labels see text.

2.2. *Absorption spectrophotometry*

Aqueous solutions of dye I over the range $<7{\cdot}7\times10^{-6}$M ($3{\cdot}5\times10^{-4}$%) to $2{\cdot}2\times10^{-2}$M ($1{\cdot}0$%) were examined using a Unicam SP800 spectrophotometer with matched glass cells varying in path length from 50 μm to 10 cm to accommodate the large changes in absorbance over this range. Optical densities were determined at λ_{max} which showed a gradual hypsochromic shift from 515 nm to 485 nm as the concentration increased.

The relation between optical density and concentration is given in Fig. 2. The optical density values given were obtained by applying Lambert's law and converting all experimentally determined values to their equivalent values for a standard 1·0 cm cell. Linear relationships were found over different concentration regions, the most marked deviations from linearity being at points A and B on this figure.

The former occurs at a dye concentration of $3{\cdot}96\times10^{-3}$M (0·18%). By expanding the concentration scale below 0·10% a second well-marked point of inflexion at B at a concentration of $7{\cdot}71\times10^{-5}$M ($3{\cdot}5\times10^{-3}$%) is observed. It has been suggested[17] that such points correspond to critical micelle concentrations (CMCs). The value of $3{\cdot}96\times10^{-3}$M at point A lies within the range of CMCs found for other amphiphilic dyes, and the lower value (B) may correspond to possible dimer formation. In both cases however, deviations occur over

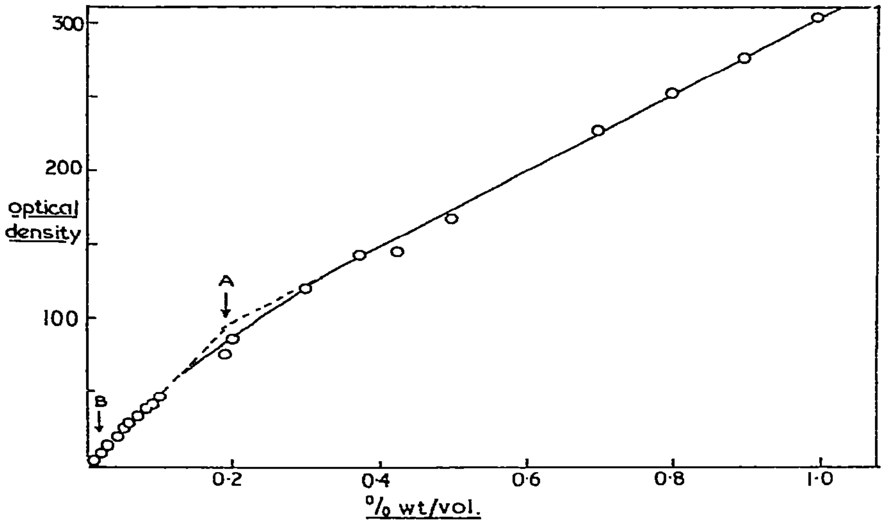


Fig. 2. Optical density–concentration relation for dye I in aqueous solution.

relatively large concentration ranges on either side of these critical points and it may be assumed that there is a gradual progression in the average state of aggregation up to the point of formation of a lamellar liquid crystalline state.

The limitations of high absorbance, coupled with the necessarily small path lengths required, precludes spectrophotometry as a means of studying solutions and mesophase formation above a concentration of approximately 1·0%. Since the presence of the mesophase can be detected by polarisation microscopy the latter has been used, both at ambient and elevated temperatures to construct phase diagrams for both dye I and dye IV.

2.3. *Binary phase diagrams*

Aqueous dye solutions of known concentration were placed in the sample holder of a hot stage cell which has been previously described.[18] The glass cell is capable of holding a thin (50–100 μm) layer of dye solution without solvent loss at temperatures up to 140°C (±1·0°C). Thus the relation between concentration and the temperature at which structural changes in solution are observed, can be determined and plotted as a binary phase diagram. Figure 3 shows the diagram for the mono-sulphonated dye I–water system. All observed changes were found to be thermodynamically reversible and the temperature of transition, mesophase $\rightleftharpoons$ isotropic solution, was verified from the endothermic peak temperature extrapolated to a zero heating rate by differential thermal analysis using a DuPont 900 Thermal Analyzer.

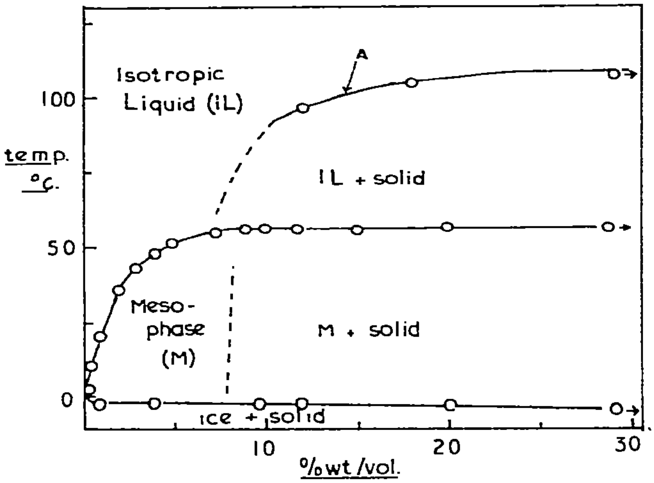


Fig. 3. Binary phase diagram for C.I. Acid Red 151 (dye I) and water. A corresponds to 14% wt/vol. solution.

Above a concentration of approximately 7–8% the appearance of solid dye particles both in the presence of the mesophase and isotropic solution up to a temperature of 100°C can be noted. The concentration boundary limiting the presence of these particles is ill-defined partly by limitations in microscope resolution. Cooling an isotropic solution, e.g. A in Fig. 3, from above 100°C shows first the growth in size and number of these particles. At 54°C the

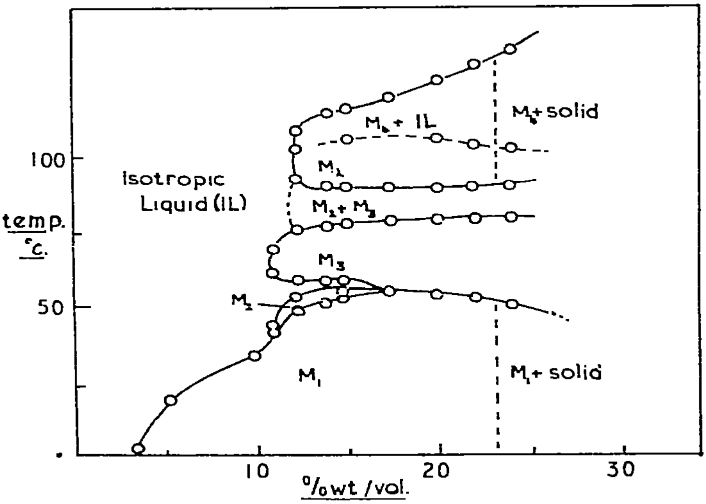


Fig. 4. Binary phase diagram for dye IV and water.

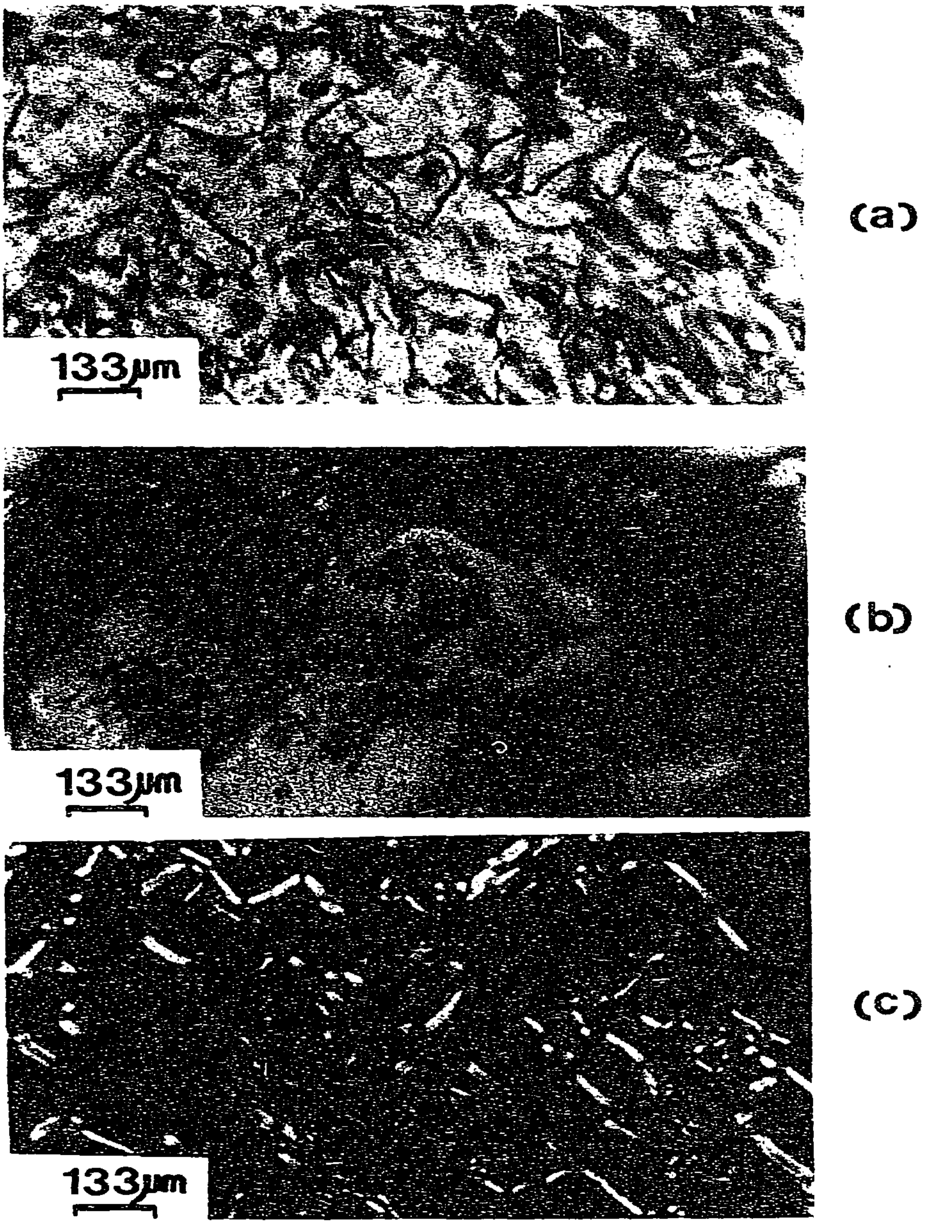


Fig. 5. Observed modifications between crossed polars of 14% wt/vol. solution dye IV at (a) 20°C, (b) 53°C and (c) 110°C. Polarisation axes parallel with figure edges.

smectic mesophase nucleates as droplets which rapidly merge to form a continuous phase in which the particles are embedded. At concentrations <7·0% wt/vol. only the mesophase with no particles is observed.

A repeated procedure using the di-sodium sulphonate, dye IV, shows a more complex structural behaviour of the mesophase, illustrated in Figs. 4 and 5. The higher aqueous solubility of this dye causes a general shift of the structured phase to higher concentrations, an isotropic solution existing up to 3% wt/vol. at 20°C. Above 10% concentrations the structured phases are observed from ambient up to 110–120°C. Within these defined conditions a number of modifications in the structure can be observed. No solid particles were observed below a concentration of approximately 22% and again the limiting boundary condition was ill-defined.

The microscopic appearance of some of the modifications of structure within the mesophase is given in Fig. 5. Figure 5(a) shows the smectic phase of a 14% wt/vol. solution of this dye at room temperature where disclination lines and points can clearly be seen. On heating this phase (M_1 Fig. 4) to slightly above 50°C lenticular droplets are observed (M_2 Fig. 4 and (b) Fig. 5). The droplets which are oriented, possibly nucleating and growing on the inner surfaces of the glass cell, are similar to the 'batonnets' observed by Gray and Winsor[19] on cooling the isotropic aqueous solution of sodium caprylate. These lenticular droplets can be described as thread-like smectic structures wound on a spindle. They are however transient and merge into the M_3 (Fig. 4) phase above 60°C. The latter has a smectic appearance which is not so well defined as M_1 and has a smeared or brushed appearance. The transition $M_1 \rightleftharpoons M_3$ may be due to the formation of a higher energy tilted smectic subphase. Between 78 and 90°C the M_2 batonnets reappear and predominate above 90°C finally merging to give the M_4 network structure (Fig. 5(c)) interspersed with isotropic liquid. Above 120°C the M_4 structure breaks down to give the isotropic liquid. If a more concentrated (22%) solution is examined in this way, on cooling from 120°C it is possible to detect the gradual appearance of solid particles. Since the smectic mesophase appears at higher temperatures than with dye I the particles of dye IV are more limited in their growth and amount than in the first example.

3. DISCUSSION

In considering the progressive increase in concentration from very dilute solutions of amphiphilic dye up to the point of mesophase formation, the blue shift of −30 nm in λ_{max} for dilute solutions of dye I is indicative of the presence of aggregates having a 'ladder' or 'staircase' arrangement of anions in which the aromatic planes can stack alternately one on top of each other.[20] As the concentration increases the stacks will increase in length. Whilst each aggregate or stack maintains an independent existence such solutions would appear isotropic. This threadlike stacking may be related to the ribbon structure observed microscopically at higher concentrations as seen in the network of Fig. 5(c) or when influenced by adsorption at the glass interface as the batonnets of Fig. 5(b). It is difficult to visualise how the conventional Hartley spherical micelle could originate from such mainly uni-dimensional structures. The mesophase structure shown in Fig. 5(a) could therefore result from the merging of the stacks to form a two-dimensional array as suggested in the model given in Fig. 6.

This merging would be equivalent to the smectic phase observed with other lyotropic systems caused by lateral molecular interaction and entrapment of water between individual layers. In the early stages of formation the layers would be present as domains containing parallel-oriented entities interspersed with layers of more dilute dye solution. The latter could act as lubricating layers allowing relative movement of the sheets of dye anions, the system as a whole remaining fluid-like but viscous. Between the extensive sheets or rafts, disclination lines would be apparent as thread-like continuities (Fig. 5(a)).

At higher concentrations it is probable that a stage would be reached where no free water was available for smectic mesophase formation. The individual layers would be more closely spaced and any excess dye present would remain in the solid form.

At room temperature the number of water molecules per dye anion at the

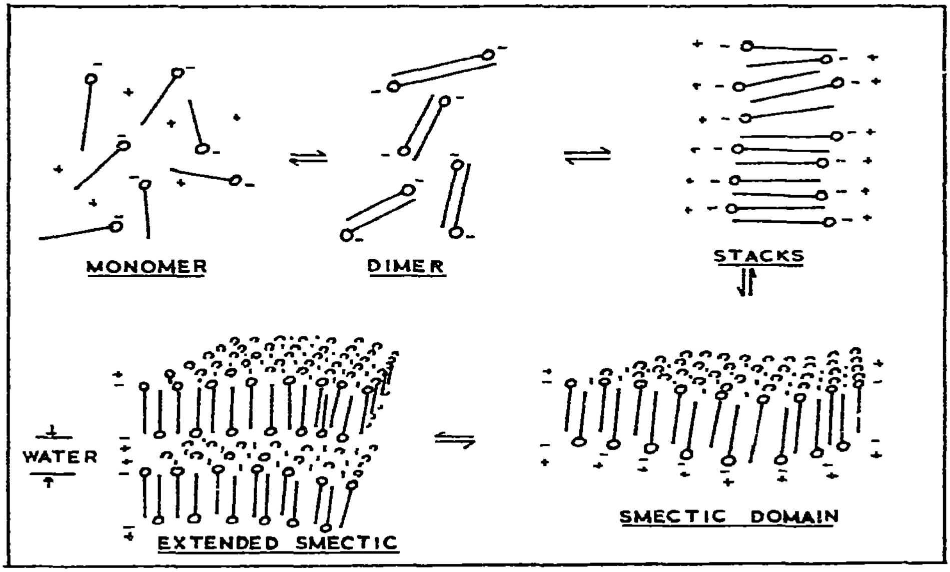


Fig. 6. Aggregation of amphiphilic dyes on increasing concentration in aqueous environment.

onset of the smectic phase is approximately 10^4 for dye I and approximately 500 for dye IV. These values are particularly high and indicate that the extended smectic phase is likely to be a heterogeneous dispersion of such a phase in a more dilute solution. By ultra-centrifuging the dyes at concentrations within the smectic phase region it is possible to separate the high molecular weight phase. With dye I the supernatant solution strength was found to be constant over a large range of concentrations and very much less than the concentration (0·2% wt/vol.) corresponding to the onset of the smectic phase. A review[21] of the earlier literature of aggregation in direct dyes quotes values of aggregation numbers of up to 200. Where such dyes are amphiphilic in nature the above observations would indicate that these numbers could be therefore considerably under-estimated at the higher dye concentrations.

Although the experimental observations are consistent with the proposed model it is appreciated that further quantitative data are necessary. The model differs from that proposed for amphiphilic surfactants[14] in that the planar hydrophobic structures of the dye anions are considerably less flexible, and through π-bond overlap can mutually interact more strongly, than the corresponding aliphatic chains of normal surfactants. Long range lateral order can therefore be established at much lower concentrations in dye solutions.

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