Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Lyotropic liquid-crystalline mesophases and a novel, solid physical form of some water-soluble, reactive dyes

David E. Sadler[a]; Mervyn D. Shannon[b]; Patrick Tollin[c]; Douglas W. Young[c]; Michael Edmondson[d]; Paul Rainsford[d]
[a] ICI Organics Division, Earls Road, Grangemouth FK3 8XG, England [b] ICI Mond Division, Runcorn, Cheshire, England [c] Carnegie Laboratory of Physics, The University, Dundee DD1 4HN, Scotland [d] ICI Organics Division, Blackley, Manchester, England

To cite this Article Sadler, David E. , Shannon, Mervyn D. , Tollin, Patrick , Young, Douglas W. , Edmondson, Michael and Rainsford, Paul(1986) 'Lyotropic liquid-crystalline mesophases and a novel, solid physical form of some water-soluble, reactive dyes', Liquid Crystals, 1: 6, 509 — 520

To link to this Article: DOI: 10.1080/02678298608086275

URL: http://dx.doi.org/10.1080/02678298608086275

LIQUID CRYSTALS, 1986, VOL. 1, NO. 6, 509–520

Lyotropic liquid-crystalline mesophases and a novel, solid physical form of some water-soluble, reactive dyes

by DAVID E. SADLER
ICI Organics Division, Earls Road, Grangemouth FK3 8XG, England
MERVYN D. SHANNON
ICI Mond Division, Runcorn, Cheshire, England
PATRICK TOLLIN and DOUGLAS W. YOUNG
Carnegie Laboratory of Physics, The University, Dundee DD1 4HN, Scotland
MICHAEL EDMONDSON and PAUL RAINSFORD
ICI Organics Division, Blackley, Manchester, England

(*Received 25 November 1985; accepted 10 June 1986*)

A novel, solid physical form has been observed when some water-soluble, reactive dyes are isolated from aqueous solution, as sodium salts, by the addition of sodium chloride. This quasi-crystalline form has a fibrous morphology, is birefringent but is not crystalline. Dyes of this type are known to form lyotropic liquid-crystalline mesophases in water. Preliminary X-ray diffraction investigations, reported here, for the mesophases formed by two such dyes indicate that they have columnar structures of the type first proposed for the lyotropic mesophases of the disodium chromglycate/water system and subsequently for other drug and dye molecules. X-ray and electron diffraction studies of the quasi-crystalline form show that it has a closely related columnar structure. The quasi-crystalline form is postulated to result from the formation and subsequent precipitation of columnar dye aggregates, as sodium chloride is added to the aqueous dye solution.

1. Introduction

Dyes which belong to the general class known as 'reactive dyes' [1] are highly conjugated organic (occasionally metallo-organic) molecules, incorporating a reactive group capable of forming a covalent bond with fibres such as cellulose and wool, and rendered water-soluble by the substitution of sulphonate groups. The reactive dye, **1**, is a typical example (cf. figure 1). Such dyes are generally synthesized in aqueous solution and isolated as solid sulphonate salts by the addition of a suitable electrolyte (commonly sodium chloride). The physical form of the solid product affects the ease with which it can be filtered and handled and is thus of great importance in the manufacture of reactive dyes.

We now report that a number of such dyes have been observed to yield a novel solid physical form, which we term 'quasi-crystalline', on isolation from neutral aqueous solution, as sodium salts, by the addition of sodium chloride (i.e. salting-out). X-ray and electron diffraction studies show that the quasi-crystalline form consists of columns of stacked dye molecules. This structure is closely related to the columnar structures of the lyotropic liquid-crystalline mesophases formed in water by disodium chromoglycate (DSCG) [2–7] and other water-soluble drug [8, 9] and dye [9, 10] molecules. The structural feature relating these molecules is that they have polar groups distributed through a non-polar frame which is capable of adopting a planar or nearly planar conformation. Reactive dyes have similar structures, indeed some have been shown to form lyotropic mesophases in water [11]. X-ray diffraction studies, reported here, of the lyotropic mesophases formed by two reactive dyes (of the sort which give rise to the quasi-crystalline form on salting-out) indicate that these mesophases also belong to the general class of lyotropic columnar mesophases first demonstrated for the DSCG/water system [2–7] for which the term 'chromonic mesophases' has been suggested [8]. A mechanism is proposed for the formation of the quasi-crystalline form which explains its close structural relationship with the lyotropic mesophases.

2. The quasi-crystalline form

The quasi-crystalline form has been observed for the sodium salts of ten reactive dyes to date [12]. It is distinguished by a fibrous morphology. It is birefringent but not crystalline, although displaying a degree of order in comparison with truly amorphous material. In all ten cases the powder X-ray diffraction pattern consists of a broad amorphous hump on which is superimposed a broad peak at an angle corresponding to a *d* spacing in the region 3·3 to 3·6 Å. Microscope studies indicate that the quasi-crystalline form, once precipitated, neither grows in a supersaturated solution nor undergoes Ostwald ripening. Studies using accurate particle size determination have not been carried out.

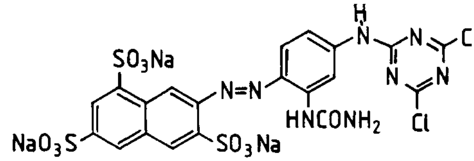
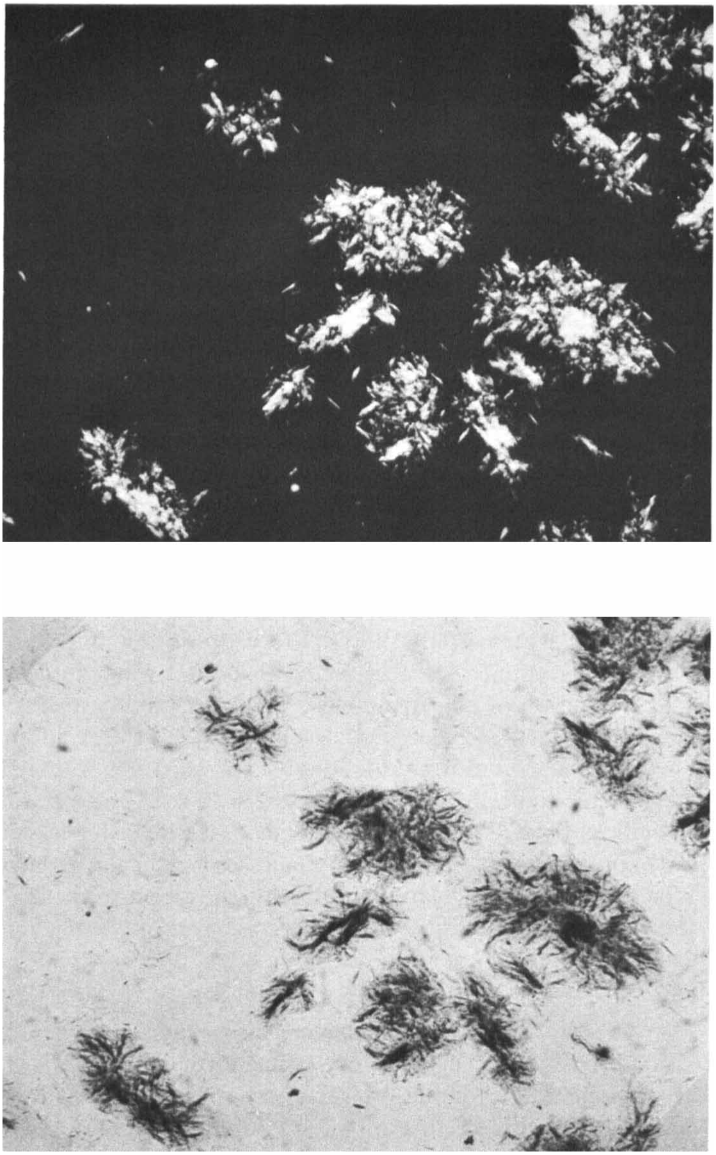


Figure 1. The molecular formula of the reactive dye **1**.

The tri-sodium salt precipitated on addition of sodium chloride to a neutral, aqueous solution of the reactive dye **1** [12] (cf. figure 1) is a typical example of the quasi-crystalline form. The fibrous morphology and birefringence can be seen by optical microscopy (cf. figure 2). The powder X-ray diffraction pattern, determined for a wet paste, consists of a broad amorphous hump on which is superimposed a broad peak at an angle corresponding to a *d* spacing of 3·5 Å (cf. figure 3). Drying the wet paste in a vacuum at room temperature removed occluded water without destroying the quasi-crystalline form, as shown by the powder X-ray diffraction pattern which remained unchanged except for a decrease in the intensity of the broad amorphous hump and the appearance of sharp diffraction lines due to sodium chloride. A differential scanning calorimetry trace for a sample dried in this manner showed a broad endotherm centred at approximately 150°C, of the type typically associated with loss of water of hydration. In agreement with this, thermal gravimetric analysis showed a weight loss associated with the endotherm from which an approximate value of four bound water molecules per molecule of **1** could be calculated [13]. On continuing to raise the temperature decomposition started at about 250°C; a true melt was not observed [14]. Removal of the water of hydration, by heating in a



(Crossed Polars)

Figure 2. The quasi-crystalline form of dye **1** observed by optical microscopy (320 ×).

vacuum at 200°C, destroyed the quasi-crystalline form; powder X-ray diffraction showed a sample treated in this manner to be completely amorphous.

A sample of the quasi-crystalline form of **1**, dried in a vacuum at room temperature, was studied in a transmission electron microscope. The transmission electron micrograph, given in figure 4 (*a*), clearly shows the fibrous nature of the quasi-crystalline form. The width of individual fibres is estimated to be less than about 100 Å. An electron diffraction pattern (cf. figure 4 (*b*)) obtained in the transmission electron microscope (from the area indicated by arrows in figure 4 (*a*)) consists of

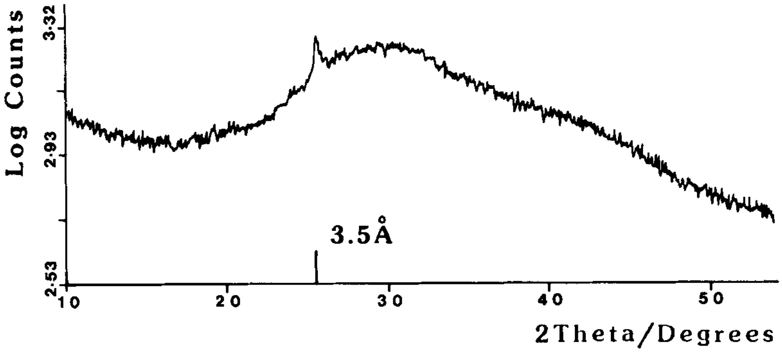


Figure 3. The powder X-ray diffraction pattern of the quasi-crystalline form of dye 1.

diffraction arcs, at a *d* spacing of 3·5 Å, oriented with respect to the fibres which make up the quasi-crystalline form. The quasi-crystalline forms of other dyes show similar, axially-oriented arcs in their electron diffraction patterns, at *d* spacings of 3·3 to 3·6 Å.

The axial orientation, with respect to the fibres, of the arcs in the electron diffraction pattern clearly demonstrates that the diffraction arises as a result of ordering along the length of the fibres. We propose that the fibres consist of columns of stacked dye molecules, together with bound water molecules, with an inter-molecular separation of approximately 3·5 Å for **1** (and between 3·3 and 3·6 Å for the other examples). Molecular models indicate that **1** can adopt a sterically favourable, nearly planar conformation suitable for such a packing. The van der Waals thickness of the molecule is of the order of 3 to 4 Å. The electron diffraction arcs were not sufficiently well resolved to allow us to distinguish between a structure in which the dye molecules stack with their planes perpendicular to the column axis and one in which the molecular planes are tilted with respect to the column axis, by measuring the variation in intensity round the arcs.

3. Lyotropic columnar mesophases

The structure proposed for the quasi-crystalline form is very similar to the columnar structures demonstrated for the lyotropic mesophases formed by a number of drug [2–9] and dye [9, 10] molecules in water. While the most widely investigated lyotropic liquid-crystalline systems are those formed by surfactants in water [15], examples of lyotropic mesophases formed by molecules which have structures consisting of polar groups distributed through a non-polar frame capable of adopting a planar, or nearly planar conformation have long been known. Thus, over 70 years ago, Sandquist [16] observed lyotropic mesophases when crystalline 9-bromophenanthrene-3-sulphonic acid was brought into contact with water and, in 1927, Balaban and King [17] reported lyotropic mesophases for naphthalene disulphonic acid derivatives [18].

The first mesophases of this type to be the subject of a structural investigation were those formed by DSCG (cf. figure 5). Three liquid-crystalline mesophases have been identified for DSCG in aqueous solution [6] of which two, the N and M phases, have been well characterized. In X-ray diffraction studies [2, 5] both the N and M phases showed a diffraction line corresponding to a *d* spacing of about 3·4 Å. In the low-angle region the M phase showed three lines at *d* spacings in the ratio $1:1/\sqrt{3}:1/\sqrt{4}$, a

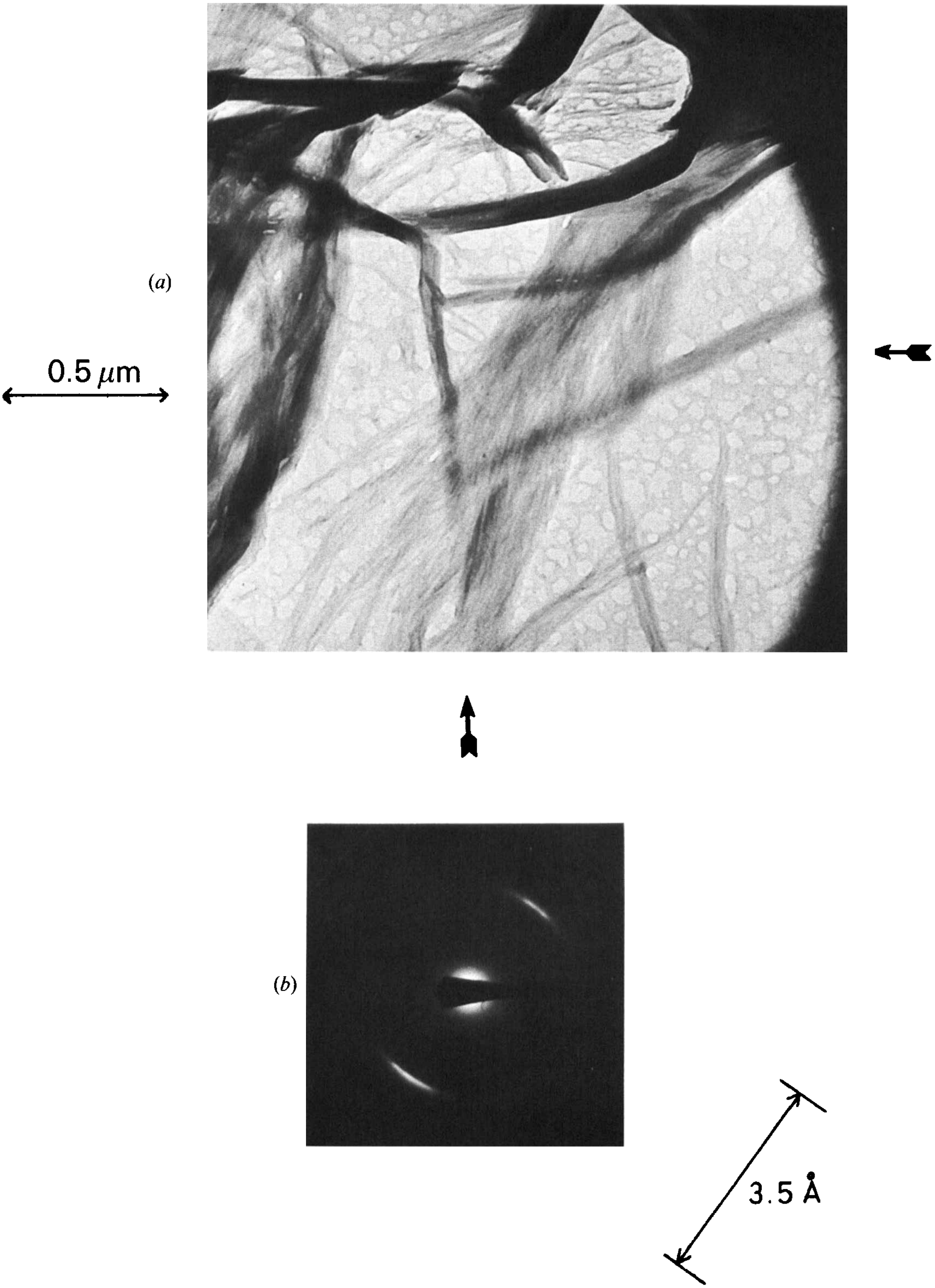


Figure 4. (*a*) Transmission electron micrograph (50 k ×). (*b*) Electron diffraction pattern of the quasi-crystalline form of dye **1** taken from the area indicated by the arrows.

relatively strong reflection at 26 to 37 Å (depending on concentration) and two weaker lines at 16 to 22 Å and 15 to 19 Å [2]. A broad low-angle reflection was seen for the N phase at an angle corresponding to a *d* spacing of 44·5 Å [2]. In a sample of the M phase partially oriented in a magnetic field, the high-angle reflection (3·4 Å) and intense low-angle reflection (37 Å) were observed to be perpendicular [5].

On the basis of these results structures have been proposed for the mesophases [2–5]. Both mesophases consist of columns of stacked DSCG molecules [3], the molecular planes lying perpendicular to the column axes [5]. The reflection at 3·4 Å corresponds to the intermolecular separation in the columns. In the N phase the columns are distributed randomly in solution but retain a degree of orientational order, forming a lyotropic nematic phase as sketched in figure 6. In the M phase, formed at higher DSCG concentration and/or lower temperatures [6], the columns are ordered into an hexagonal array (cf. figure 6). The sharp, low-angle reflections seen for the M phase correspond to the packing of the columns. N.M.R. studies [6] support the concept [3] that the columns are already fully developed in the N phase and that the N to M phase transition corresponds predominantly to the ordering of these columns.

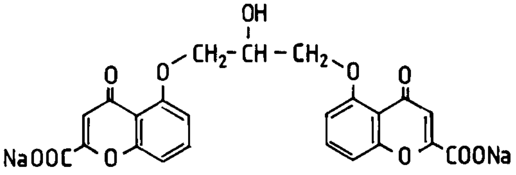


Figure 5. The molecular formula of disodium chromoglycate.

Figure 6. Proposed structures of the N and M phases of disodium chromoglycate in aqueous solution.

Subsequently, the existence of N and M mesophases has also been demonstrated for a series of drug molecules related to DSCG [8, 9] and for some dyes [9, 10] in aqueous solution. All have structures in which polar groups are distributed through a non-polar frame capable of adopting a planar, or nearly planar conformation. The term ‘chromonic’ has been proposed for this type of mesophase [8].

The knowledge that many water-soluble dyes, including reactive dyes [11], form lyotropic mesophases [9, 10, 17, 18] and the close resemblance between the structure we propose for the quasi-crystalline form and those of the N and M phases led us to investigate the possibility that our dyes would form lyotropic mesophases of the N and M type and to consider the possibility of a connection between formation of columnar mesophases and formation of the quasi-crystalline form. We now present our preliminary results.

4. Lyotropic mesophases of some reactive dyes

Dye **1**, shown in figure 1, forms a lyotropic mesophase (or mesophases) when prepared as a concentrated solution in water [19]. Birefringent textures are observed when the mesophase is viewed through a microscope using crossed polars (cf. figure 7). The X-ray diffraction pattern of the mesophase at high angles consists of a reflection centred at an angle corresponding to a *d* spacing of 3·4 ± 0·1 Å and is shown in figure 8. This reflection is replaced by a very diffuse band, centred at the same angle, in the isotropic solution. No attempt was made to search for low-angle reflections because of the relative instability of the mesophase with respect to precipitation of solid dye. Solid dye was not formed during the time required for the high-angle experiments. We propose that the 3·4 Å reflection results from stacking of the dye molecules to form columns of the type present in the N and M lyotropic mesophases. An attempt to distinguish between perpendicular or tilted stacking of the dye molecules with respect to the column axis, by measuring the intensity variation in the diffraction arcs, was inconclusive.

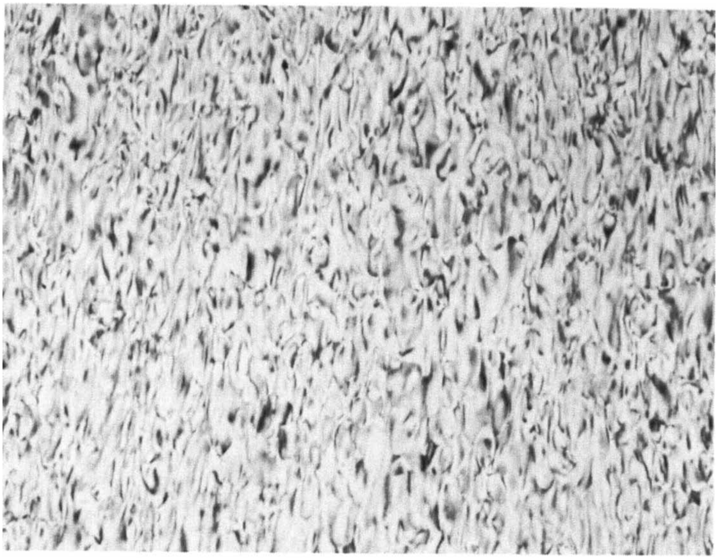


Figure 7. The lyotropic liquid-crystalline mesophase of dye **1** in water (32·5 wt% dye) viewed through crossed polars (200 ×).

Dye **2**, whose generic structure is given in figure 9, also forms a lyotropic mesophase (or mesophases) as a concentrated solution in water [19]. When viewed through a microscope using crossed polars such solutions also show birefringent textures (cf. figure 10). The mesophases of dye **2** are stable. In the absence of water loss due to evaporation no solid was observed after storage for a period of months. Preliminary X-ray diffraction studies, at one concentration, clearly show both a reflection centred at a *d* spacing of 3·6 ± 0·1 Å and another reflection with a *d* spacing of 24 ± 2 Å (cf. figure 11). There is, in addition, evidence of other reflections. We note that the mesophase has undergone partial spontaneous alignment on being drawn into the capillary tube used for the X-ray studies. The high- and low-angle reflections are perpendicular to one another, the 3·6 Å arcs being axial (bisecting the long axis of the capillary) and the 24 Å arcs equatorial. We propose that this lyotropic mesophase

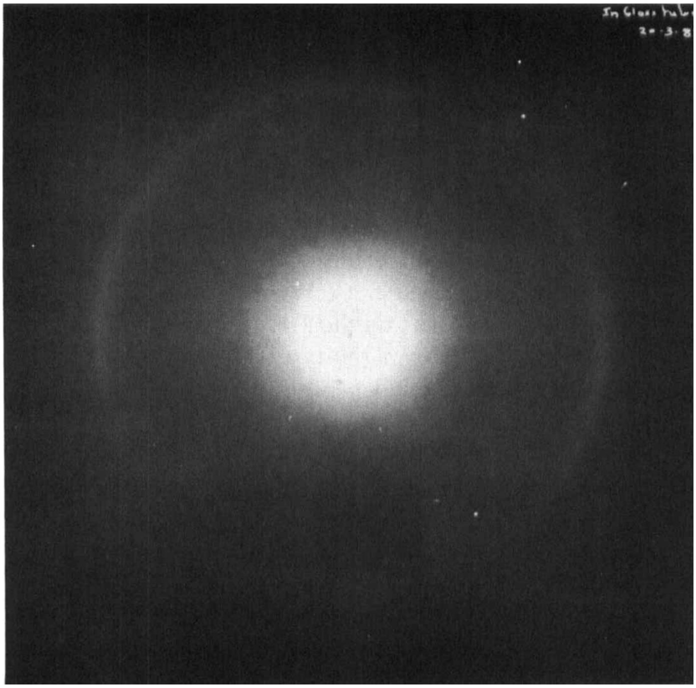


Figure 8. X-ray diffraction pattern of the lyotropic liquid-crystalline mesophases of dye **1** in water (32·5 wt% dye).

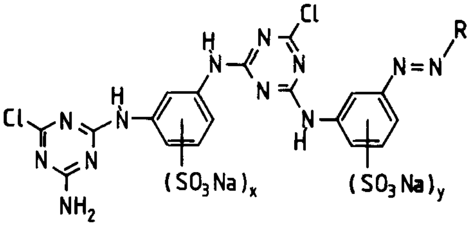


Figure 9. The generic molecular formula of the reactive dye **2**.

consists of ordered columns of stacked dye molecules, similar to the M phase, and that the columns tend to align parallel to the walls when drawn into the capillary, because of the viscous shear. The fact that the high- and low-angle reflections are perpendicular to one another allows the unequivocal assignment of the 3·6 Å spacing to packing of the dye molecules in the columns and the 24 Å spacing to packing of the columns themselves [5]. Further studies are planned to find second and third order equatorial reflections, in order to establish the symmetry of the column packing, to investigate the effect of varying the concentration on the position of the equatorial reflections and to search for an N type phase. An attempt to distinguish between perpendicular and tilted stacking of the dye molecules with respect to the column axis, by measuring the intensity variation in the diffraction arcs, gave inconclusive results.

The solid obtained on salting-out **2** from aqueous solution had the fibrous morphology and birefringence typical of the quasi-crystalline form. X-ray diffraction showed a broad peak at 3·4 Å on a very broad amorphous hump. Preliminary electron

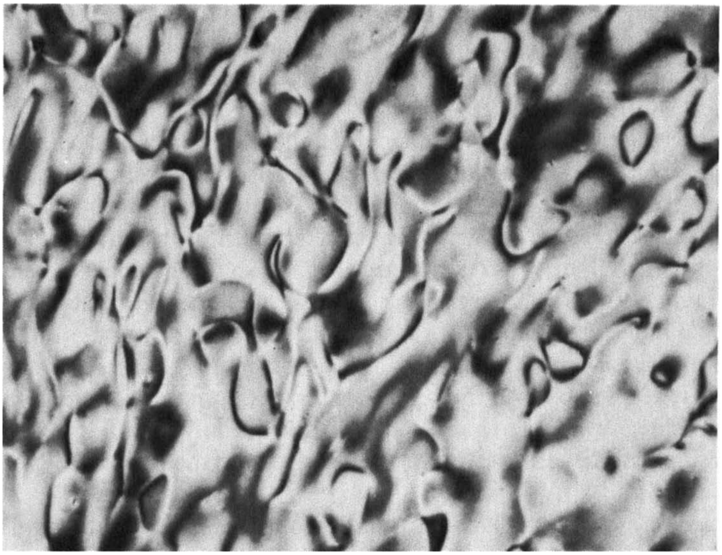


Figure 10. The lyotropic liquid-crystalline mesophase of dye **2** in water (43·7 wt% dye) viewed through crossed polars (200 ×).

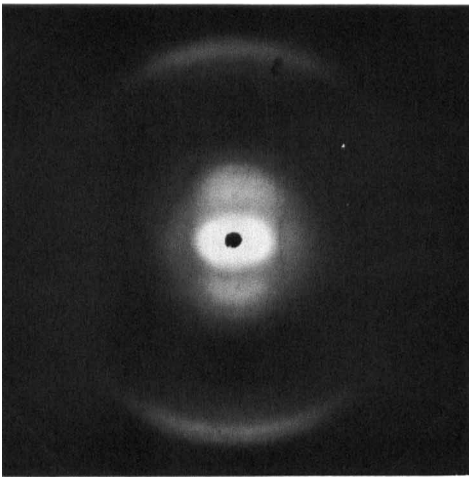


Figure 11. X-ray diffraction pattern of the lyotropic liquid-crystalline mesophase of dye **2** in water (43·7 wt% dye).

diffraction studies indicate that the ordering of the dye molecules in the columns, which produce this reflection, may be more complex than for **1**. The nature of the solid phase is under further investigation.

5. Mechanism of formation of the quasi-crystalline form

The structures proposed for the quasi-crystalline form and for the lyotropic mesophases of **1** and **2** are clearly closely related. Other workers have also related the solid form obtained on salting-out dyes from aqueous solution with their lyotropic mesophases. Thus Balaban and King [17] considered that the 'caseous' form they obtained on salting-out naphthylamine disulphonic acid derivatives from aqueous solution might be 'dehydrated' liquid crystals. Berg and Haxby [20] have shown that salting-out a saturated aqueous solution of a cyanine dye leads first to aggregation to form a lyotropic mesophase and then to precipitation of solid dye, as the salt concentration is increased.

The quasi-crystalline form of dyes such as **1** and **2** were obtained by adding sodium chloride to aqueous dye solutions at dye concentrations well below those at which the mesophases were observed [19, 21]. Thus it is not surprising that lyotropic mesophases were not observed, in either case, prior to precipitation of the quasi-crystalline form. However, it is generally the case that aggregation in solution occurs at concentrations below those required to form lyotropic mesophases [22], transformations taking place from isotropic molecular solutions, to isotropic solutions of aggregates, to lyotropic mesophases as the concentration of the solute is increased [15]. Furthermore, addition of electrolyte is known to lower the solute concentration required for aggregation and to increase the degree of aggregation at a given concentration for ionic surfactants [23]. All these phenomena have been demonstrated for the particular case of DSCG [7, 24].

We propose a mechanism for the formation of the quasi-crystalline form in which addition of sodium chloride promotes the formation of columnar aggregates of the dye molecules in aqueous solution, which then precipitate as the salt concentration increases. This mechanism would explain both the morphology of the quasi-crystalline form and the apparent absence of growth and Ostwald ripening. There is no reason to assume that the existence of the quasi-crystalline form is limited to reactive dyes or to isolation with sodium chloride.

Some of the reactive dyes we have studied form crystalline phases on salting-out from aqueous solution [12]. The formation of the quasi-crystalline form rather than a crystalline phase, on salting-out dyes such as **1**, might result from the presence of impurities, which should be more readily accommodated by the quasi-crystalline ordering than in a crystalline lattice, or could be the result of aggregation of the dye in solution prior to formation of the solid phase. Formation of large aggregates would be expected to interfere with the growth of a crystal, generally assumed to take place by the sequential addition of small growth units to the crystal surface [25], but would lead naturally to formation of the quasi-crystalline form.

6. Conclusions

A novel, solid quasi-crystalline form has been observed on salting-out some reactive dyes from aqueous solution. It has a structure consisting of columns of stacked dye molecules together with bound molecules of water. It is postulated to result from the formation and subsequent precipitation of columnar aggregates of the dye molecules as sodium chloride is added to the aqueous solution.

The structural investigation, by X-ray diffraction, of lyotropic liquid-crystalline mesophases of two reactive dyes (of the type which produce the quasi-crystalline form) in aqueous solution has been reported. Both have structures based on columns of stacked dye molecules which are closely related to those of the columnar N and M mesophases reported for DSCG [2–7], related drug molecules [8, 9] and some other water-soluble dyes [9, 10].

7. Experimental

The dyes studied were obtained from the routine manufacturing processes and contained organic, reaction by-products (up to *c.* 15 per cent). No attempt was made to remove these impurities. Both **1** and **2** have a single, well-defined structure. We have not been given permission to reveal the structure of **2** and so a generic structure is given instead.

The quasi-crystalline form of **1** was obtained by the addition of solid sodium chloride (20 per cent wt/vol) to a neutral aqueous solution (7·6 per cent wt/vol **1**, 5·4 per cent wt/vol NaCl) at 20°C. The powder X-ray diffraction pattern was observed for a wet paste using a PW 1130 Philips X-ray generator, standard rotating specimen holder, Cu/K_α radiation, graphite monochromator and scintillation counter. The transmission electron micrograph for a sample dried *in vacuo* at room temperature was obtained using a Philips EM 400 T, operated to minimize electron loss. The electron diffraction pattern was obtained by the selected area diffraction technique from a region of approximately 0·5 μm in diameter (the centre indicated by arrows in figure 4 (*a*)). Small crystals of sodium chloride were used as an internal standard to calibrate the camera length. Differential scanning calorimeter studies were carried out using a Perkin Elmer DSC2 and thermal gravimetric analysis on a Stanton Redcroft TG 750.

Electrolyte was removed from dyes **1** and **2** by ultrafiltration (Amicon Model 402 ultrafiltration apparatus, Amicon YM2 ultrafiltration membrane, theoretical cut-off molecular weight > 1000) yielding **1** (< 2·1 per cent wt/wt NaCl) **2** (< 0·22 per cent wt/wt NaCl). Lyotropic liquid-crystalline mesophases were prepared from these dyes by dissolving them in distilled water at room temperature.

The X-ray diffraction pattern of the lyotropic liquid-crystalline phase of **1** (32·5 wt%) was obtained for a sample contained in quartz capillary (0·3 mm) with Cu/K_α radiation (Ni filter), a pin-hole collimator and a Philips flat-plate camera with a specimen-to-film distance of approximately 70 mm. The experimental accuracy for a sharp reflection (3 to 6 Å) was judged to be ± 0·1 Å. The X-ray diffraction pattern of the lyotropic liquid-crystalline phase of **2** (43·7 wt%) was obtained for a sample in a quartz capillary (0·5 mm) with Cu/K_α radiation (Ni filter) using a pin-hole camera of the type described by Langridge *et al.* [26], with a specimen-to-film distance of approximately 60 mm. The experimental accuracy for a sharp reflection was judged to be ± 0·1 Å (3 to 6 Å) and ± 2 Å (20 to 30 Å).

References

[1] Venkataraman, K., 1972, *The Chemistry of Synthetic Dyes*, Vol. 6 (Academic Press).
[2] Hartshorne, N. H., and Woodard, G. D., 1973, *Molec. Crystals liq. Crystals*, **23**, 343.
[3] Lydon, J. E., 1980, *Molec. Crystals liq. Crystals*, **64**, 19.
[4] Hartshorne, N. H., and Woodard, G. D., 1981, *Molec. Crystals liq. Crystals*, **64**, 153.
[5] Goldfarb, D., Luz, Z., Spielberg, N., and Zimmermann, H., 1985, *Molec. Crystals liq. Crystals*, **126**, 225.
[6] Goldfarb, D., Labes, M. M., Luz, Z., and Poupko, R., 1982, *Molec. Crystals liq. Crystals*, **87**, 259.
[7] Perahia, D., Goldfarb, D., and Luz, Z., 1984, *Molec. Crystals liq. Crystals*, **108**, 107.
[8] Attwood, T. K., and Lydon, J. E., 1984, *Molec. Crystals liq. Crystals*, **108**, 349.
[9] Attwood, T. K., 1984, Ph.D. Thesis, University of Leeds.
[10] Attwood, T. K., Lydon, J. E., and Jones, F., 1986, *Liq. Crystals*, **1**, 499, have carried out a detailed investigation of several dye mesophases in aqueous solution by X-ray diffraction and have shown them to have structures similar to those seen for the disodium chromogylcate/water system. We thank the authors for a copy of the manuscript prior to publication.
[11] Bayer Patent, 1980, EP 0029958 A3; 1981, DE 3149129 A1.
[12] All the dyes studied were unpurified samples obtained from the routine manufacturing process.

[13] A vacuum-dried sample of the quasi-crystalline form of **1** contained 4 ± 2 molecules of water of hydration per molecule of **1**.

[14] All the sodium salts of the highly sulphonated water-soluble, fibre-reactive dyes which we have studied undergo decomposition before they can melt, whether X-ray diffraction shows them to be truly crystalline, quasi-crystalline or amorphous.

[15] Tiddy, G. J. T., and Walsh, M. F., 1983, *Aggregation Processes in Solution*, edited by E. Wyn-Jones and J. Gormally (Elsevier), p. 151.

[16] Sandquist, H., 1915, *Berichte*, **48**, 2054.

[17] Balaban, I. E., and King, H., 1927, *J. chem. Soc.*, p. 3068.

[18] We thank a referee for drawing [16, 17] to our attention. For further examples see Kelker, H., and Hatz, R., 1980, *Handbook of Liquid Crystals*, Chap. 11 (Verlag-Chemie).

[19] Dyes **1** and **2** form mesophases in aqueous solution, at room temperature, in the approximate concentration range 30 to 50 wt% dye (< 2 wt% NaCl).

[20] Berg, R. A., and Haxby, B. A., 1970, *Molec. Crystals liq. Crystals*, **12**, 93.

[21] The dyes were isolated under the normal manufacturing conditions: addition of 5 to 25 wt% NaCl to dye solutions containing 5 to 10 wt% dye.

[22] Dye aggregation in aqueous solution is a common phenomenon and aggregates consisting of stacks of planar dye molecules have frequently been proposed. Burdett, B. C., 1983, *Aggregation Processes in Solution*, edited by E. Wyn-Jones and J. Gormally (Elsevier), pp. 241–70. Duff, D. G., and Giles, C. H., 1973, *Water, A Comprehensive Treatise*, Vol. 4, edited by F. Franks (Plenum), pp. 169–207.

[23] Moore, W. J., 1983, *Basic Physical Chemistry* (Prentice-Hall), p. 415.

[24] Champion, J. V., and Meeten, G. H., 1973, *J. pharm. Sci.*, **62**, 1589.

[25] Mullin, J. W., 1972, *Crystallisation*, second edition (Butterworths).

[26] Langridge, R., Wilson, H. R., Hooper, C. W., Wilkins, M. H. F., and Hamilton, L. D., 1960, *J. molec. Biol.*, **2**, 19.