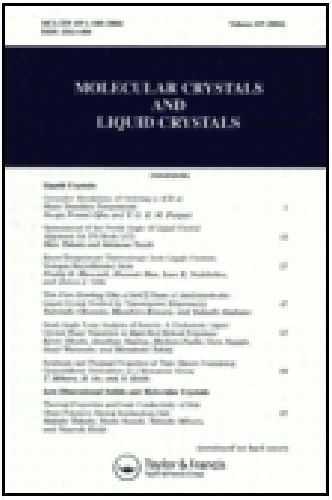

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Formation of the Liquid Crystal of a Surface-active Dye in Aqueous Methanol Solutions

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Formation of the Liquid Crystal of a Surface-active Dye in Aqueous Methanol Solutions

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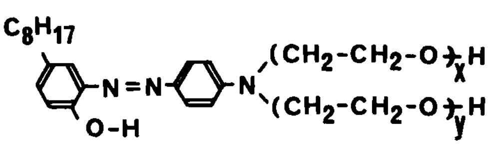
The formation of the liquid crystal phase of a surface-active dye, *p-t*-octylphenol yellow amine poly(ethylene oxide), in aqueous methanol solutions has been examined by optical microscopy. Rodlike swarms appear at relatively low dye concentrations only slightly higher than the second critical micelle concentration. They develop into liquid crystal phase when the dye concentration is further increased. It takes some hours for the formation of a stripe-like texture characteristic of nematic liquid crystals, depending on the methanol content and dye concentration. The combination of the surface active-part and the azobenzene moiety would be responsible for the formation of the liquid crystal.

INTRODUCTION

p-t-Octylphenol yellow amine poly(ethylene oxide) is a non-ionic surface-active dye which has a structure consisting of a *t*-octyl group and two poly(ethylene oxide) chains linked through 2′-hydroxy-4-aminoazobenzene. This surface-active dye has the structure shown below and exhibits a characteristic feature upon micellization in methanol + water solutions.[1-3]



$x + y = 10$

The surface tension plotted against the logarithm of concentration of surface-active dye gives two break points, each corresponding to the first and second micellization, above which the primary and secondary micelles are formed, respectively.[1] The absorption spectra change when the primary and secondary micelles are formed with increasing concentration of surface-active dye.[2] Similarly, the resonance Raman spectra also undergo some changes upon the two-step micellization.[3] Both these spectral observations reflect a slight shift in an existing tautomeric equilibrium for the 2-hydroxyazobenzene moiety.

The primary micelles, having an aggregation number of at most 15, are stabilized by the stacking interaction of planar 2′-hydroxy-4-aminoazobenzene residues in the surface-active dye. The secondary micelles are formed by the hydrophobic interaction characteristic of surfactants, as for micelles of common surfactants.

In the present work we investigate the properties of aqueous methanol solutions of *p-t*-octylphenol yellow amine poly(ethylene oxide) and examine whether they can form liquid crystal phases under appropriate conditions, as established for aqueous solutions of common surfactants. We report our microscopic observations on the formation of an optically anisotropic phase having a stripe-like texture and discuss a possible mechanism of its formation in dilute solutions.

EXPERIMENTAL

A sample of *p-t*-octylphenol yellow amine poly(ethylene oxide) with an average degree of polymerization of poly(ethylene oxide) chain groups, $x + y = 10$, was kindly donated by Dr. F. Tokiwa of the Kao Soap Co. Inc., and was the same as that previously used.[1-3] Methanol was a spectrograde reagent of the Nakarai Chemical Co. Inc., and water was redistilled from alkaline $KMnO_4$ in a glass still.

Methanol + water solutions of the surface-active dye were prepared by adding water to the methanolic solution until the desired methanol content was obtained, and then by diluting the solution with the solvent mixture. Throughout this paper the composition of the solvent is represented by the volume fraction of methanol.

The microscopic observation of the solutions was carried out using an Olympus BH microscope with or without crossed nicols at room temperature ($25 \pm 2\,^{\circ}C$). Solutions for microscopic observation were mounted in a hollow of 15 mmϕ on a slide glass and covered with a thin rectangular cover slip (24 mm × 32 mm). This cover slip of a rather large size was used in order to minimise possible evaporation of solvent components during the long times required for maturation.

RESULTS

The 1, 2, and 5% methanol + water solutions were turbid at concentrations of surface-active dye above 10^{-5} M, and the 10 and 20% solutions were turbid above 5×10^{-5} M. Oily drops separated in 1, 2, 5, and 10% methanol + water solutions at dye concentrations higher than (2, 4, 8, and 16) $\times 10^{-3}$ M, respectively. Under a microscope, emulsion particles, such as those seen in Figure 1 and having a diameter of 1 to 7 μm were observed. They increased in number and grew larger, as the concentration of surface-active dye increased beyond 5×10^{-4} M for 2% methanol content and 10^{-3} M for 5 and 20% methanol content.

On the other hand, the interference color indicating formation of an anisotropic or liquid crystal phase was observed using a polarized microscope with crossed nicols. As shown in Figure 2 for 5% methanol + water solutions, rodlike swarms were exhibited at a dye concentration of 1.57×10^{-4} M; these swarms were weakly oriented in one direction at 7.86×10^{-4} M. The bright interference color developed at concentrations greater than 10^{-3} M. This anisotropic phase can be described as having a stripe-like texture. The texture could be seen even using unpolarized light, and although the stripes oriented unidirectionally, their spacings were not definite.

The development of the anisotropic phase took from a few hours to a few days, depending on the concentration of surface-active dye and the content of methanol. For example, Figure 3 shows the time

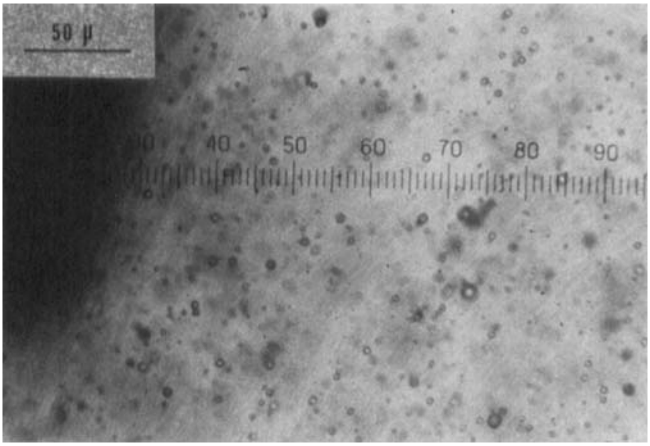
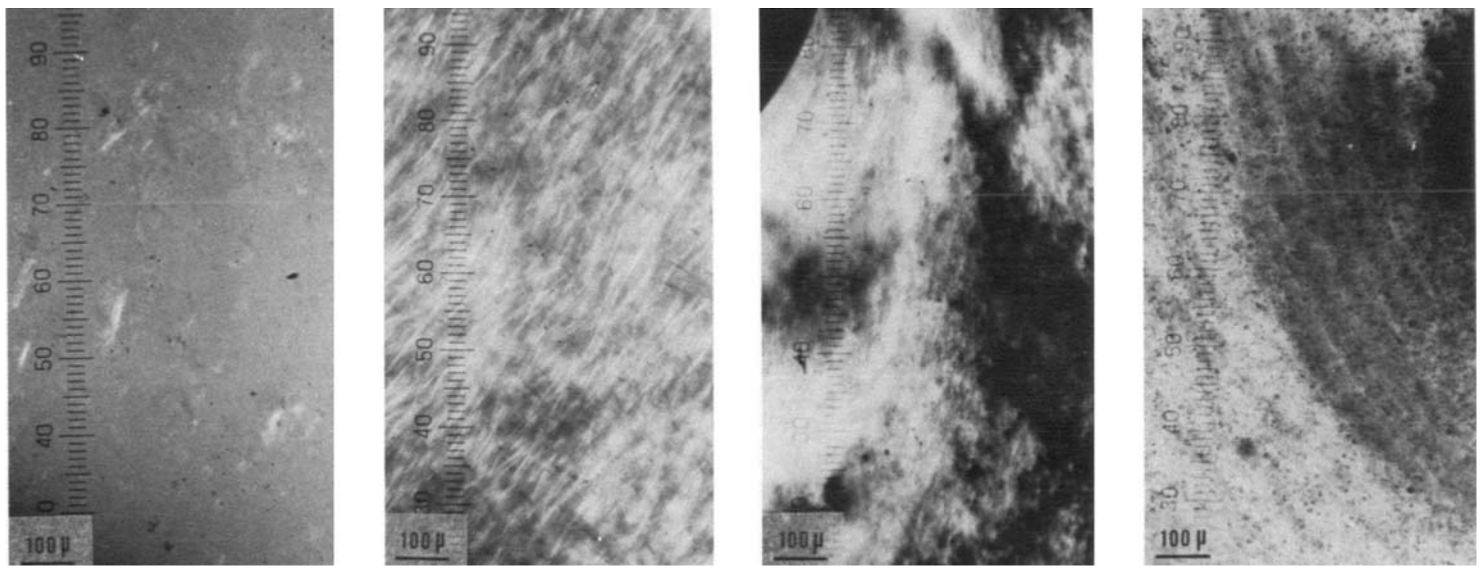
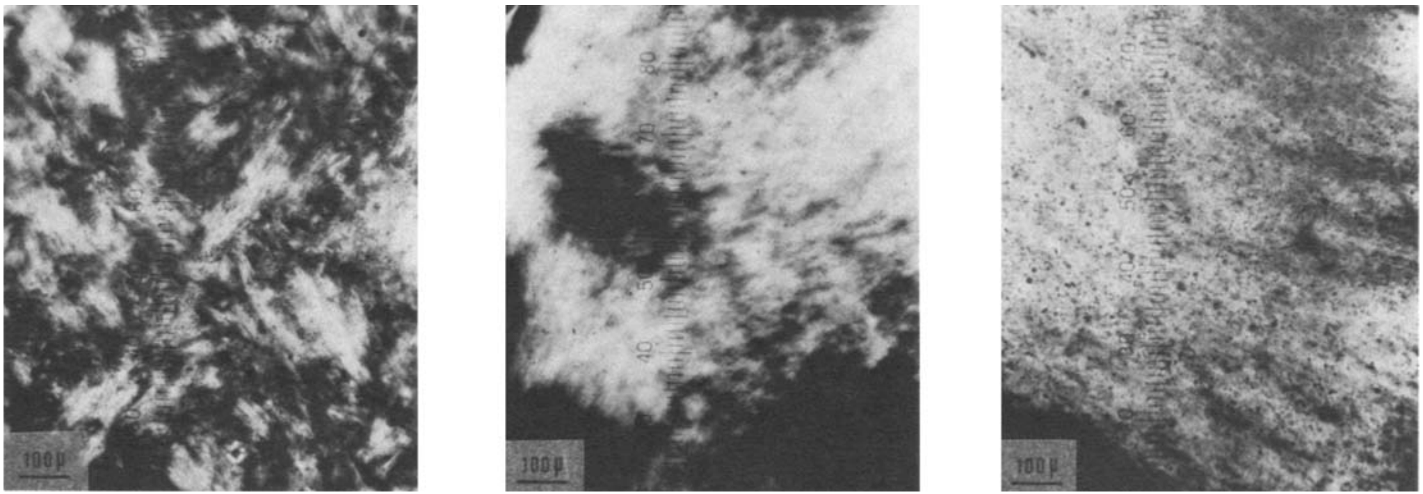


FIGURE 1 Micrograph of the emulsion formed in a 5% methanol + water solution of the surface-active dye at 7.99×10^{-3} M.



(a) (b) (c) (d)

FIGURE 2 Micrographs (crossed nicols) for 5% methanol + water solutions of the surface-active dye. Concentration: (a), 1.57×10^{-4} M; (b), 7.86×10^{-4} M; (c), 3.93×10^{-3} M; (d), 7.99×10^{-3} M.



(a) (b) (c)

FIGURE 3 Micrographs (crossed nicols) for a 5% methanol + water solution of the surface-active dye at 7.99×10^{-3} M. Incubation (maturation) time: (a), three hours later; (b), after one day; (c), after two days.

dependence of the appearance of an interference color for a 5% methanol + water solution at a dye concentration of 7.99×10^{-3} M. After a few hours, the interference color developed only partly, and the anisotropic domains formed, in which rodlike swarms associated with each other. A stripe-like texture with a unidirectional orientation and a bright interference color spread over a wide region after a day, and the liquid crystal phase was sufficiently matured after two days. It might be suspected that such a long time for maturation would have caused evaporation of solvent components and concentration of the surface-active dye with the result that the development of the liquid crystal phase was induced by the increase in concentration. However, it is much more likely that the time taken for the development of the anisotropic phase is due to the coalescence of anisotropic domains and the rearrangement of rodlike swarms after the coalescence.

It certainly appears that the liquid crystal is formed through the formation of rodlike swarms and their weak orientation. The values of the concentration of surface-active dye for the appearance of the anisotropic phase at different methanol contents are listed in Table I. It may be noticed that the formation of anisotropic phase depends on the methanol content and is most complete in 5% methanol + water solution. At 4×10^{-3} M, the liquid crystal is sufficiently matured in 5% methanol, but only incomplete maturation was attained for 2% methanol. In 20% methanol, only a weak orientation of rodlike swarms was obtained at the same dye concentration.

TABLE I

The concentrations of surface-active dye for the appearance of anisotropic phase[a]

Methanol content	2%	5%	20%
Formation of rodlike swarms	1.49	1.57	7.49
Weak orientation of rodlike swarms	7.49	7.86	37.5
Incomplete maturation of liquid crystal	37.5		
Formation of liquid crystal		39.3	
		79.9	
C_0^{I}	0.291	0.138	0.320
C_0^{II}	2.34	1.00	1.03

[a] The concentration of surface-active dye is expressed by the unit 10^{-4} M.

DISCUSSION

It has been demonstrated that *p-t*-octylphenol yellow amine poly(ethylene oxide) can form anisotropic phases in aqueous methanol solutions. This is indicated by the bright interference color observed by polarized microscopy; this proves the occurrence of a liquid crystal. The liquid crystal was built up through the appearance of rodlike swarms and their weak orientation in one direction or their mutual association to form an anisotropic domain, as the dye concentration was raised or the maturation time was increased.

It was found that micellization of the surface-active dye occurs in two steps in methanol + water solutions.[1-3] While the primary micelles are stabilized by the stacking interaction of dye, the secondary micellization is caused by the hydrophobic interactions characteristic of surfactants. Although the aggregation number of the secondary micelles has not been determined, it is possible that they are rodlike because of the strongly hydrophobic nature of the dye; this is also indicated by the insolubility in pure water, and in the formation of a multimolecular layer on the surface of aqueous methanol.[1] The values of the first and second critical micelle concentrations, C_0^{I} and C_0^{II}, are also included in Table I; these were determined by surface tension measurements.[1]

Rodlike swarms were formed around or above the second critical micelle concentration. It seems likely that these swarms are stable at moderate concentrations of surface-active dye and would be composed of rodlike micelles formed above the second critical micelle concentration. In more concentrated solutions, swarms associate together to form anisotropic domains which eventually develop into a uniform liquid crystal phase with a stripe-like texture. Since such a texture is oriented in one direction but stripes are not separated regularly from their neighbors, i.e., by an equal spacing, the formation of a nematic liquid crystal phase may be suggested.

Common surfactants can form liquid crystal phases in moderately concentrated solutions; these are called the middle phase and the neat phase.[4,5] It was found that the surface-active dye forms a liquid crystal phase in dilute solutions, such as those having concentrations as low as 10^{-3} M. Owing to its strong hydrophobic nature, the surface-active dye could form rodlike swarms which might develop into liquid crystal phase in diluted solution. Such properties of a dye capable of forming rodlike swarms and a liquid crystal phase could be assisted by the azobenzene moiety, which often results in the formation of thermotropic liquid crystals.[6,7] The combination of the surface-active nature with the hydrophobicity of long, rigid dye part in a molecule would be responsible for the formation of a lyophilic liquid crystal in dilute aqueous solutions.

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