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Dye-Surfactant Interactions and Their Applications

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During the first decades of the 20th century, organic chemistry and the chemistry of dyes and intermediates developed together and could hardly be differentiated. Later, the study of dyes, particularly color-structure relationships, drew from structural and physical organic chemistry, including resonance theory, MO methods, and electronic spectra.

The principal application of dyes is in the coloration of substrates, typically textiles. During the dyeing process, synthetic fibers require surfactants or other organized assemblies such as micelles, vesicles, or layers. Such auxiliary agents will probably continue to be important in the coloration of materials resulting from current and future developments in fiber science and technology.

The application of binary dye-surfactant systems, together with an understanding of the interactions within them, is also relevant to other scientific fields, including analytical chemistry, photography, luminescence, and lasers. Of particular interest are amphiphilic dyes for which the concepts of color and surface-active properties coexist within the same molecular framework.

Dyeing Systems

For the coloration of polymeric substrates, three main techniques are employed. The oldest and most widely known is the dyeing process which involves the transfer of dyes by diffusion through dyebaths, adsorption onto the molecular surfaces of substrates, and final diffusion within the structures of the substrates. Covalent bonds may be formed during the transfer process. More recent techniques include the mass coloration (dope-dyeing) of synthetic polymers and the printing of fabrics with print pastes. The above processes need the presence of auxiliaries to optimize the dye uptake by the substrates. Many of these auxiliaries have amphiphilic structures.

The physical chemistry of the dyeing process has received much attention in the last 40 years, and many theories of dyeing have been proposed. Experimental methods are mainly based (i) on the analysis of dye uptake curves (the rate of dye transfer from the bath into the substrate) and (ii) on the analysis of dyeing isotherms (the position of the sorption-desorption equilibrium at infinite time). The state of the art in this area is described in refs 1 and 2. Our work is aimed at elucidating the complex interactions in the ternary dye-fiber-surfactant system, with a view to optimizing the tinctorial results.[3-11] This Account describes some of our results with disperse, cationic, and amphiphilic dyes.

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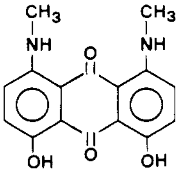
Guido Viscardi obtained his B.A. at the University of Turin, where he is currently Research Fellow of Industrial Chemistry. His research interests include the synthesis of novel dyes and functionalized surfactants and their technical applications.



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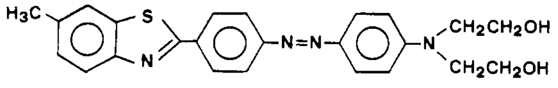

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Seventy years ago disperse dyes were introduced for the dyeing of cellulose secondary acetate and subsequently were found to be advantageous for the coloration of other synthetic fibers. In particular, disperse dyes proved to be the principal class of dyes suitable for the dyeing of polyester, the production of which consequently began to grow on a worldwide scale. The structures of disperse dyes range from simple anthraquinone derivatives 1 to more complex heterocyclic systems 2. They are sparingly soluble in water (10-100 mg/L) and therefore require the presence of a dispersing agent, which enhances their solubility.[12] These agents work by producing energy barriers which maintain dispersions in their metastable condition, thus avoiding the coalescence of dispersed particles.[13] It is still a matter of debate by which mechanism the dye is released from the micellar pseudophase to effect sorption by the fiber, i.e., whether via direct contact between micelles and fiber surface or via adsorption of single molecules from the continuous aqueous phase. A technically important interaction of surfactant systems with dyes is represented by the milling of dyes to

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(1) Zollinger, H. *Color Chemistry*; VCH: Weinhein, 1987.

(2) Johnson, A. *The Theory of Coloration of Textiles*; Society of Dyers and Colourists: Bradford, 1989.

(3) Barni, E.; Savarino, P.; Di Modica, G.; Carpignano, R.; Papa, S. S.; Giraudo, G. *Dyes Pigm.* **1984**, *5*, 15.

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(13) Rosen, M. J. *CHEMTECH* **1985**, 292.

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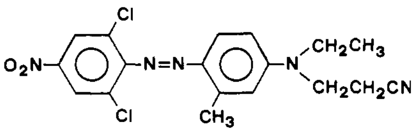
produce suitable submicron-size particles.[14] For further information on the characteristics of disperse dyes, on their use, and on the role of surfactant additives in dyeing processes, see refs 1, 2, and 15–19.

We have proposed the use of double-tailed surfactants and sonication to set up dyebaths for the dyeing of polyester fabrics with disperse dye **3**.[20] This dye was



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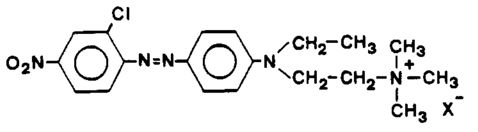
designed by chemometric procedures for its excellent fastness qualities, including lightfastness.[21] A series of comparative tests using cationic, anionic, and nonionic single- and double-tailed additives were carried out with the dye and the additives simultaneously sonicated in the bath. The best results from the point of view of both bath exhaustion and uniformity of coloration were obtained with very low concentrations of DDDAC (didodecyldimethylammonium chloride).

The use of double-tailed cationic surfactants as additives in dyeing processes was also shown to be successful in the dyeing of polyacrylonitrile with cationic dyes. Typically dyes having high affinity and low migration properties can produce superficial saturation of the anionic sites (sulfonate, sulfate, carboxylate) and an unequal distribution of the dye on the substrate. Hence colorless cations, which compete with the dyes for the anionic sites, are currently added.[22] Furthermore, in a wide comparative test with C.I. Basic Red 18 **4**, the use of DDDAC as additive exhibited by far the best retarding and leveling properties.[23] We stress the



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reciprocal beneficial effect obtained by the utilization of techniques from other scientific areas, such as use of ultrasonics and the evaluation of the effects of surfactants with tristimulus colorimetry.[24]

In our studies on amphiphilic dyes, we have investigated the behavior of some model azo dyes. Amphiphilic structures are characterized by the presence of both hydrophobic and hydrophilic moieties. Dyes **5**–**7** contain both sulfonic and carboxylic groups, whereas the latter are absent in dye **8**. They are soluble and

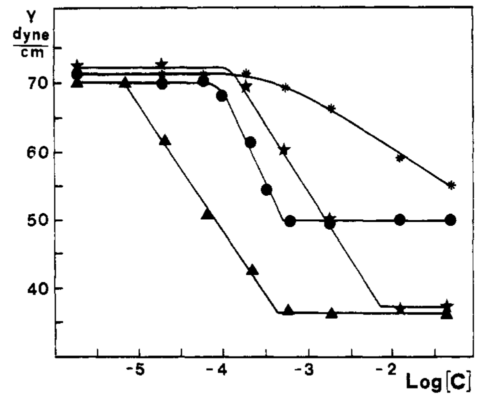


Figure 1. Surface tension data: (*) dye 5; (★) dye 6; (▲) dye 7; (●) dye 8.

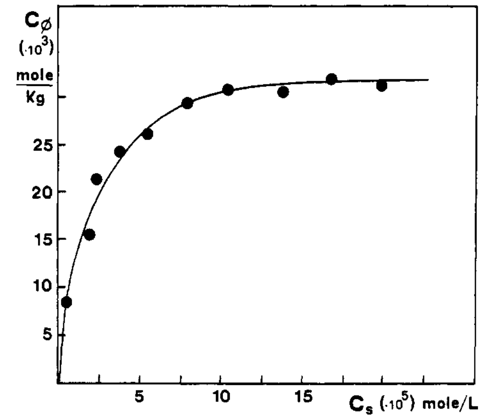
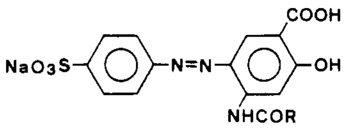
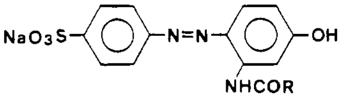


Figure 2. Dyeing isotherm of dye 8: temperature 100 °C; pH 4.8.



5: R = C_3H_7
6: R = C_7H_{15}
7: R = $C_{11}H_{23}$



8, R = C_7H_{15}

self-micellizing, as can be observed by plotting their surface tension versus concentration (Figure 1).[6] Theiry efficiency and effectiveness[13] depend on the chain length and the hydrophilic character of the polar groups. The dyeing isotherms (Figure 2, dye **8**, as an example) show an asymptotic shape and can be evaluated with the Langmuir equation. The mechanism of this dyeing process is an exchange between dye anions and fiber gegenions (X^-). The maximum acid dye-binding capacity is determined by the number of basic groups present in the polyamide (see Chapter 11 in ref 1). A large number of experiments led us to some generalizations about the optimal operative conditions: (a) dyeing temperature should not be very high (ca. 80 °C); (b) long chains are preferred; (c) low pH values

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(14) *Colour Terms and Definitions*; Society of Dyers and Colourists: Bradford, 1988.

(15) Dawson, J. F. *Rev. Prog. Color. Relat. Top.* **1978**, *9*, 25.

(16) Datyner, A. *Surfactants in Textile Processing*; Marcel Dekker: New York, 1983.

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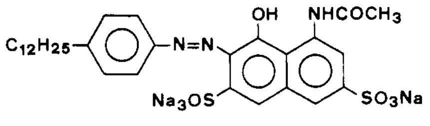
(24) Billmeyer, F. W., Jr.; Saltzman, M. *Principles of Color Technology*; Wiley: New York, 1981; p 62.

enhance the dye uptake in the fiber (positive sites are increased, whereas the ionization of the carboxyl groups is depressed); and (d) the carboxyl group of the dye seems to participate in the dye–substrate interaction, depending on pH and temperature.

Amphiphilic Dyes

In a retrospective look at amphiphilic dyes, Carbolan dyes are of special interest. Their production evolved in the 1930s to meet the dyeing requirements of wool fibers. These dyes, e.g., Carbolan Crimson B (C.I. Acid Red 138) (**9**), are simple water-soluble azo dyes into which a hydrophobic group has been introduced. These provide hydrophobic interactions, thereby preventing desorption from the fiber and yielding adequate fastness to washing.[25] The pioneering work on amphiphilic azo dyes was done by H. E. Fierz-David and W. Kuster,[26] who synthesized a series of dyes of formula **10**, with the alkyl chain R_1 covering the full range C_1 to C_{19} and one or two hydrophilic groups. The ability of dyes to lower the surface tension of water was systematically measured.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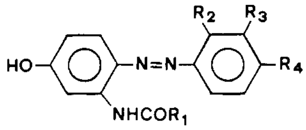
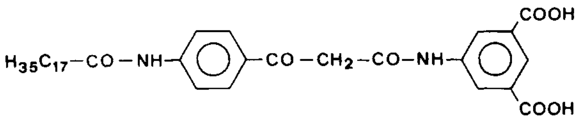

10: $R_1 = CH_3$ to $C_{19}H_{39}$
$R_2 = H, COOH$
$R_3 = H, SO_3H$
$R_4 = H, SO_3H$

Amphiphilic dyes play an important role in classical color photography. In the dye-forming processes, suitable dye precursors (couplers) **11**–**13** are incorporated in the photographic layers containing the chromogenic reaction with the oxidized developer (e.g., the quinone diiminium ion **14**), yielding the final dye (e.g., dye **15** with coupler **12**). The dyes formed with **11**, **12**, and **13** are yellow, magenta, and cyan, respectively, as required for the subtractive color process. The dye precursors have been made nondiffusing in swollen gelatin of the photographic layer by the attachment of ballasting C_{17} or C_{18}. The corresponding loss of solubility in the aqueous gelatinous emulsion is compensated by the presence of sulfonic (or carboxylic) groups.[1]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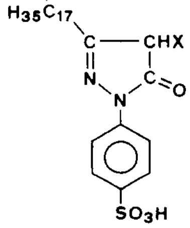
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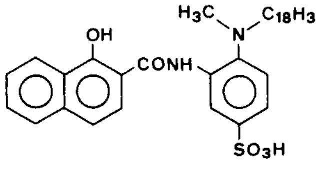
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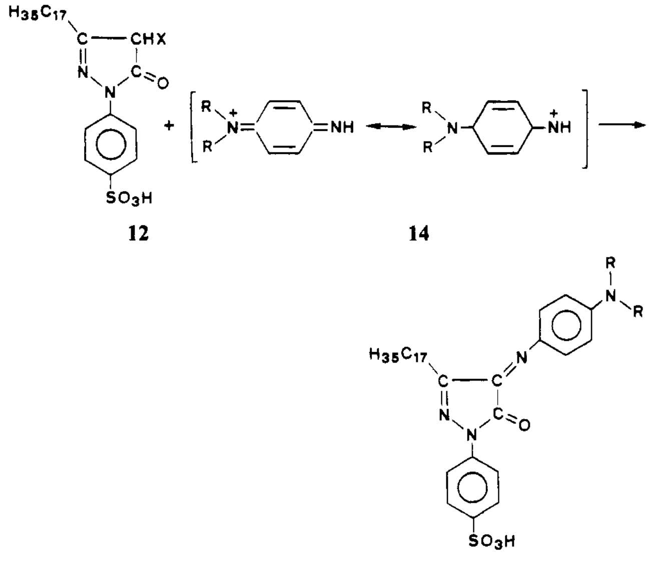
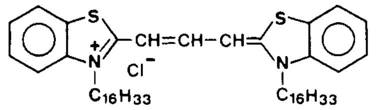

12 **14** **15**

Cyanine Dyes

If a *polyene* chain contains at the extreme positions an electron donor and an electron acceptor, the resulting chromogen is called *polymethine*. In *cyanine dyes* both the donor and the acceptor moieties contain at least one nitrogen atom, which is usually present in a heterocyclic ring. For a more detailed classification of cyanines and for recent trends in their main applications as sensitizing dyes in photography, see ref 27 and Chapters 3 and 14 in ref 1. We have prepared and investigated several series of cyanine dyes[28-32] containing tuned alkyl chains as described below.

The interaction of organized assemblies with hydrophobic cyanines has a beneficial effect on the deaggregation of dyes. Figure 3 shows the spectra of dye **16**, which displays a very broad absorption in water due to the formation of complex aggregates. The use of sonication does not improve the deaggregation. In methanol the dye is supposed to be in its monomeric form. The spectrum resulting from the addition of DODAC (dioctadecyldimethylammonium chloride) vesicles to the aqueous medium gives evidence for the marked deaggregation afforded by the organized surfactant.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Surfactants have been found to have an interesting effect on the photostability of dyes. Figure 4 illustrates

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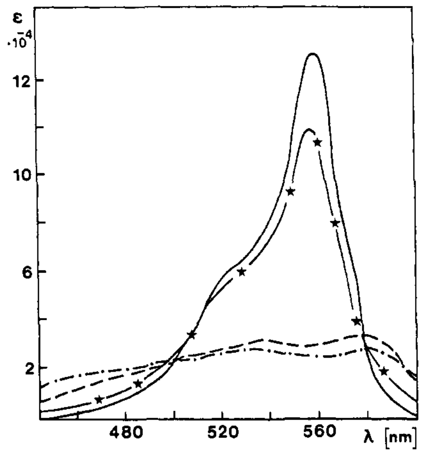


Figure 3. Electronic absorption spectra of cyanine **16**: (—) in methanol (1×10^{-5} M); (---) in water (2×10^{-5} M); (-·-) in water (2×10^{-5} M) after sonication; (★) in the presence of DODAC (5×10^{-4} M). The water samples contained 5% methanol to enhance the solubility of the dye.

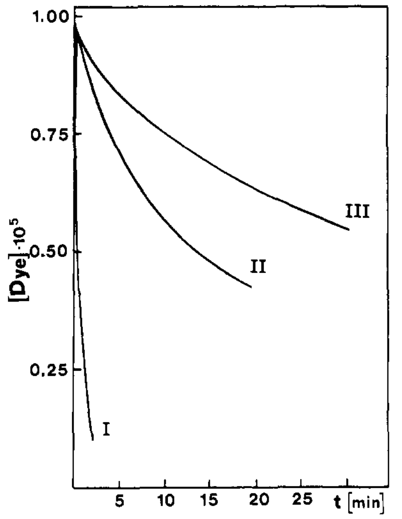
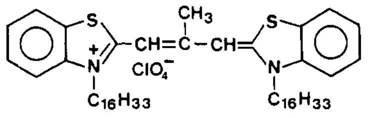


Figure 4. Bleaching of cyanine **17** irradiated at λ ≥ 300 nm: (I) in water–methanol (5% v/v); (II) with SDS 1.6×10^{-2} M; (III) with DODAC (3.4×10^{-3} M).

the bleaching curves of dye **17** under continuous irradiation with a high-pressure mercury lamp. Whereas



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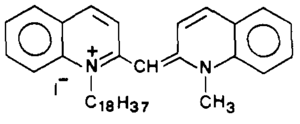
the aqueous solution decolorized in a very short time, the presence of anionic micelles (sodium dodecyl sulfate, SDS) and, more beneficially, of cationic vesicles (DODAC), enhanced the photostability by at least 2 orders of magnitude.

A peculiar feature of amphiphilic cyanine dyes is represented by the buildup of layers of dyes according to the technique first developed by I. Langmuir and K. Blodgett.[33] The basic principles and the potentiality of LB films have been recently outlined in *Accounts*.[34] Recently new sophisticated techniques have been introduced for a more complete and reliable characterization of LB organized molecular assemblies. A recent article[35] investigates in depth the correlations of phase diagrams and crystallization behavior with the optical properties of a mixture of a single-tailed cyanine dye **18**–stearic acid (cosurfactant) mixture. This charac-



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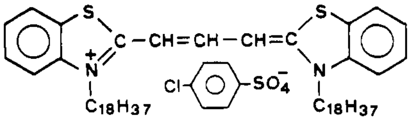
terization employed a variety of methods including pressure–area isotherms, fluorimetry, absorption measurements, electron diffraction, and fluorescence microscopy. In particular, the last technique permits a direct observation of the lateral structure formation in monolayers, e.g., during phase transitions.

The hydrophobic tails of amphiphilic cyanine dyes are usually hydrocarbon chains. Recently structural modification of the tails has been used to obtain new information on the intermolecular interaction between the hydrophobic moieties. For example, M. Matsumoto and co-workers have substituted the C_{18} chains in the symmetrical dye **19** with the so-called "mesogenic units", which contain phenylcyclohexyl groups (dye **20**).[36] This substitution results in larger anisotropic



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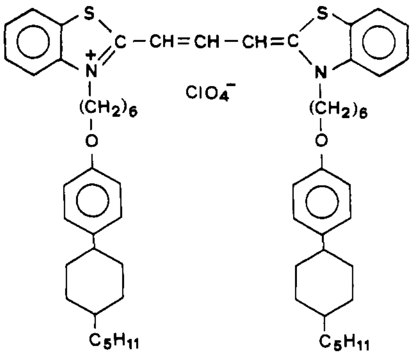

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polarizability of the mesogenic groups. This leads to stronger interaction between the hydrophobic parts because of the increased dispersion force and the introduction of a permanent dipole. Interesting data have been obtained on cluster formation at the air–water interface, on in-plane spectral anisotropy of LB films with cadmium icosanoate, and consequently, on the flow orientation of the crystallites at the air–water interface during the deposition process.

Analytical Applications

In the presence of dyes (chromophoric reagents) or of colored binary complexes (sensitized systems), surfactants have contributed to the development of new spectrophotometric and fluorimetric methods for the determination of micro amounts of metal ions, anions,

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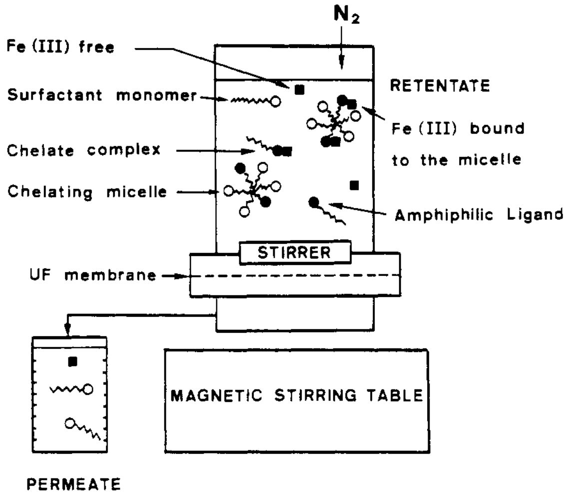
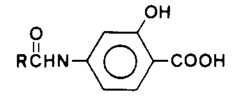


Figure 5. Scheme of the micellar-enhanced ultrafiltration device.

and biological compounds. These methods are mainly based on the dramatic microenvironmental changes experienced by the chromophore (or lumophore) in the organized media. A review on dye–surfactant interactions, with particular attention to connections with analytical chemistry, has been made by M. E. Diaz Garcia and A. Sanz-Medel.[37] A further review of organized assemblies in analytical chemiluminescence spectroscopy has been recently published.[38]

Analytical problems also include chemical separation procedures. In this respect, dye–surfactant associations appear to be useful. Micellar extractions and micellar-enhanced ultrafiltration have been investigated in the separation of iron(III) using nonionic surfactant/amphiphilic ligand mixed aggregates. In ref 39 descriptions of the techniques and of the experimental results obtained by using tuned-chain [(alkylcarbonyl)amino]salicylic acids as ligands are reported. Ligands **21–25** are the dye precursors of the amphiphilic dyes **5–7**.[40] Figure 5 depicts the scheme of the micellar-enhanced ultrafiltration device. The amphiphilic ligand (dye) forms a chelate complex with Fe^{3+} which is formally uncharged. The latter, in turn, is strongly bound within the host micelle made up by a nonionic or a cationic surfactant. The successive removal of these aggregates from the feed solution is achieved by using an ultrafiltrating membrane having a pore size small enough to reject the micelles. Figure 6 graphically illustrates some experimental data.



21, R = CH_3
22, R = C_3H_7
23, R = C_7H_{15}
24, R = C_9H_{19}
25, R = $C_{11}H_{23}$

Cationic micelles function better than nonionic micelles in the effective removal of the complexes. Indeed, the same separation efficiency obtained in working with a dye having a C_{11} chain in nonionic micelles is achieved by using the more soluble C_7 derivative in hexadecyltrimethylammonium nitrate (HTAN). Moreover, the use of a cationic surfactant introduces more selectivity in the separation, due to the electrostatic repulsion of uncomplexed cations which remain in the aqueous bulk phase. Micellar-mediated techniques afford novel separation procedures whose advantages include low costs, low toxicity of the aqueous surfactants relative to organic solvents, and low alteration or denaturation of biomolecules.

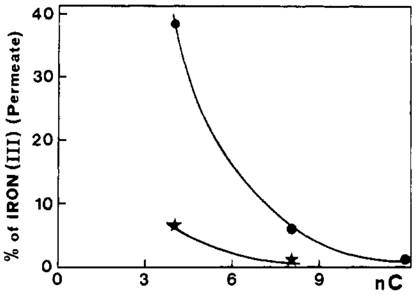


Figure 6. Micellar-enhanced ultrafiltration performances in different surfactant systems; nC = number of carbon atoms in R in dyes **5–7**: (●) nonionic surfactant $C_{12}E_8$; (★) cationic surfactant, hexadecyltrimethylammonium nitrate (HTAN). Membrane: Spectra-Por C, cutoff molecular weight 10 000 daltons; $I = 0.1$ M $NaNO_3$; $[HNO_3] = 0.002$; $[\text{ligand}] = 1 \times 10^{-3}$; $[\text{surfactant}] = 2 \times 10^{-2}$; $[\text{iron(III)}] = 1 \times 10^{-4}$.

Miscellaneous

Subjects in the area of dye–surfactant interactions are impressively diverse. Related articles reviewed by *Chemical Abstracts* during the 1980s are distributed over 20 out of 80 sections. These sections include “Surface-active agents”, “Dyes”, and “Surface chemistry, colloids”, as well as “Immunochemistry”, “Wood products”, and “Energy technology”. Clearly there is wide interest in dye–surfactant pairing. Here we describe some selected examples, reporting only a few references from which further bibliography can be deduced.

A high-contrast rapid-processing photographic material with a support and hydrophilic colloid layers has been proposed. The silver halide emulsion layer contains AgX grains that are spectrally sensitized with suitable merocyanines and a fluorocarbon surfactant.[41] More recently, an analogous material has been claimed as suitable for laser exposure.[42] The above examples illustrate applications that exploit the interactions between sensitizing dyes and fluorine containing surfactants.

Dyes in surfactant systems can also function as luminescence probes for the investigation of the structure and dynamics of organized molecular assemblies.[43] Drastic changes are shown in the spectral properties of dyes when the latter interact with micelles or bilayer membranes (vesicles and lamellae) set up with biomaterials (lecithin) or with synthetic surfactants.[37,44,45] Several examples of this application follow. (1) The highly fluorescent and solvatochormic hydrolysis product of the cationic dye C.I. Basic Blue 12 (Nile Blue

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(37) Diaz Garcia, M. E.; Sanz-Medel, A. *Talanta* **1986**, *33*, 255.

(38) Hinze, W. L.; Srinivasan, N.; Smith, T. K.; Igarashi, S.; Hoshino, H. In *Multidimensional Luminescence*; Warner, I. M., Mc Goun, L. B., Eds.; JAI Press: Greenwich, CT, 1990; Chapter 8.

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(40) Barni et al., manuscript in preparation.

(41) Hanyu, T.; Yorozudo, H. (Konica Co.) Jpn. Kokai Tokkyo Koho JP 62,265,651 87,265,651; *Chem. Abstr.* **1988**, *108*, 213837p.

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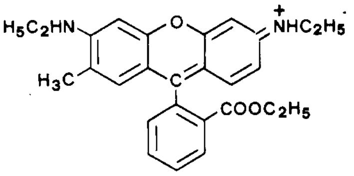
A, a biological stain) is a useful probe of the surfactant phase of a C_7H_{16}–Aereosol OT–H_2O reverse micellar system with the total luminescence spectroscopy (TLS) technique.[46] (2) Liphophilic, solvatochromic dye probes have contributed to the spectroscopic determination of the effective dielectric constants of the interfacial region of several ionic and nonionic micelles.[47] (3) The damage of heat stress (followed by sublethal recovery) on the permeability barrier of the outer membrane of *Escherichia coli* cells has been evaluated by using the fluorescent dye *N*-phenyl-1-naphthylamine.[48] (4) A color reaction between 3′,4′,5′,6′-tetrachlorogallein–Mo(VI) complex in a Triton X 405–poly(vinyl alcohol) micellar medium and human serum albumin has resulted a highly sensitive method for its determination.[49] (5) The entrapping of dyes and drugs and their solubilization, stabilization, and release into a surrounding environment have been studied in photosensitive phospholipid vesicles,[50] in soybean phosphatidylcholine oligolamellar liposomes and potato mitochondria,[51] in lysolecithin micelles and lecithin liposomal membranes,[52] and in carboxyfluorescein-loaded vesicles.[53] In contrast, one group has concluded that cyanine dyes did not prove to be suitable probes for sensing the plasma membrane potential in yeasts.[54]

Rhodamine 6G (**26**) is by far the most used dye for dye lasers. Several hundreds of dyes have been employed, allowing operation to occur over a wide spectral range (250–1300 nm) with a continuous tunability. The dyes must have high photochemical stability and fluorescence quantum yield. Surfactant systems have recently been combined with dyes. Binary solvents made up by surfactants are able to solubilize dye molecules (two to three molecules for each micelle), resulting in a stable colloidal suspension which increases the lasing efficiency and the thermal stability of the dye solution.[55]



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Concluding Remarks and Future Opportunities

In the 1970s progress in the development of textile dyes appeared to come to a relative standstill. All fibers were readily dyed in a wide chromatic range and with excellent performances. Furthermore, caution pervaded the production and the indiscriminate use of dyes because of their possible toxicity, particularly induced by precursors such as aromatic amines.

At the beginning of the 1990s, we witness a lively change in the situation. Humans definitely prefer a colored world, as evidenced by a world consumption of dyes in 1988 of 600 kilotons. Production strategies must be adapted to environmental requirements, including the use of renewable raw materials. The recent development of "materials science" presumably will bring out novel substrates which, in turn, will demand novel dyes and auxiliaries.

For nonconventional, high-technology, specialized applications of dyes, the demand has increased dramatically in recent years, and the dye–surfactant combination represents one of the most vital areas of technical research and development.

In conclusion, it is interesting to note that until recent years the studies of analytical chemists, physical chemists, physicists, biologists, pharmacologists, etc. depended on structures available commercially or by occasional contacts. More recently, the use of tailor-made dyes and surfactants has been spreading, and consequently, dialogue with synthetic chemists has become closer. This symbiotic and interdisciplinary trend of research offers the best opportunities for the future.

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