

Changes in self-assemblies induced by temperature, concentration and light

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1. ABSTRACT

In this review, changes in aggregation induced by thermodynamic parameters, namely concentration and temperature are discussed. Most of these changes are concerned with sphere-to-rod transitions. On the other hand, the use of an external trigger such as light can induce large aggregation changes in photosurfactant systems. This is discussed in the second part of this review and several examples of light-induced aggregation changes are included, demonstrating the usefulness of this approach.

2. INTRODUCTION

The type of self-assembled structures formed by surfactants in solution can be predicted based on the geometry of the surfactant molecule. The aggregate structures that may form are restricted by the need of the amphiphilic molecule to keep the polar and non-polar groups in a favourable conformation of minimized energy. In this respect, a principal driving force behind surfactant adsorption and aggregation is the “solvophobic effect”; hence, control over aggregation and adsorption states can only be achieved by appropriate adjustments in the balance

of hydrophobic and hydrophilic interactions. This may be achieved by addition of new species; for example, adding electrolytes to ionic surfactant or modifying the pH of zwitterionic surfactants solutions, will modify the repulsion between polar groups, thereby modifying the HLB and packing of the surfactant molecule. Other possibilities to manipulate surfactant packing are feasible by changing the thermodynamic parameters involved in the formation of the self-assembled structure, for instance temperature, concentration or pressure. In addition, inducing changes in the chemical structure and geometry by an external trigger such as light is another alternative to change the aggregation state of surfactants. Therefore, the objective of the present review is to point out the two last possibilities that have not received much attention but which are however of great interest from the theoretical and practical point of view.

3. CONCENTRATION AND TEMPERATURE

3.1 Introduction to temperature and concentration aggregation changes

The surfactant geometry has a deep impact in the type of self-assembly structure formed in solution. Depending on the packing parameter, amphiphiles can form different structures such as spherical or cylindrical micelles, lamellar phases, vesicles and so forth (1). The packing parameter introduced by Israelachvili is described by the following equation:

$$P = v / la_0 \quad (\text{Equation 1})$$

where v accounts for the hydrophobic volume (surfactant tail), l is the hydrocarbon chain length (tail) and a_0 is the equilibrium area per molecule. Surfactant packing parameter relate the structural parameters of the surfactant at a molecular level with a preferred interfacial curvature of the resulting aggregates. By convention the smaller P , the higher the curvature. If $P < 1/3$ the resulting structure is spherical micelles; values of $1/3 < P < 1/2$ are related to cylindrical micelles, and so on. It was reported by Nagarajan that the surfactant tail plays an important role in the equilibrium aggregate structures as well (2). At a first approximation we can argue that the molecular structure of the surfactant controls the shape and size of the resulting aggregates. However, the final self-assembled structures can be tuned by modifying the packing parameter, since many external factors can affect the geometry of the surfactant molecule. In turn, such external triggers may induce different transitions between the shape of the aggregates. For example, the sphere-to-rod or wormlike micelle transition produces an elongation of the aggregate. This type of transition is characterized by large changes in the viscoelastic properties of the solution, and can be studied by applying the theories of De Gennes originally developed for polymer solutions (3), and modified later on by Cates *et al.* for the study of wormlike micelles in solution (4). It is well known that transformations of micellar structures can be induced by adding inorganic electrolytes (5-8) or some non-electrolytes such as alcohols (9-12). In addition, more complex structural transitions from isotropic micellar to hexagonal or lamellar liquid

crystal phases may be obtained at relatively high concentrations of surfactant, by means of elaborate phase behavior studies. These cases will not be discussed in this chapter.

Micelles are thermodynamic aggregates that exist in equilibrium with monomeric surfactant species in aqueous solution. This equilibrium is hence dependent on the relevant thermodynamic parameters such as temperature, concentration and pressure. These parameters affect the composition, critical micelle concentration (cmc) and shape of the micelles. Spherical micelles can transform into worm-like micelles by modifying some thermodynamic parameters such as concentration and temperature. These two parameters are important in order to understand the thermodynamic of self-assembly in micelles. Mainly two thermodynamic models have been proposed to study micellization: the “phase separation model” (13) and the “mass action model” (14). In general, thermodynamic models have played an important role in the understanding of the micellization process.

The effect of concentration on the structure of micelles has been studied for many years but most of the studies have been carried out inducing the transition to worm-like micelles by using different additives. The statistical thermodynamic approach for phase transitions in micellar solution have been reported by Ben-Shaul and Gelbart (15). The effect of temperature on the cmc has been reported in several books and it is recognized that the effect of temperature on the cmc is complex. It was reported by Rosen that cmc-temperature dependence seems to be found around 25 °C for ionic surfactants and around 50 °C for non-ionic surfactants (16). But a more precise dependence has been described in the literature and it is discussed in the present work. The effect of pressure on the cmc has been summarized by Moroi on the basis of the available data in the literature (17). In general, the conclusions are that for most common ionic surfactants the cmc passes through a maximum with the increase in pressure, which is around 1000 atm. In the case of non-ionic surfactants the value seems to increase in a monotonic way and then it levels off with further increase in pressure.

Most of the investigations and applications in micellar systems involve temperature and concentration as variables and have been performed at atmospheric pressure. In the next section the effects on cmc, micellar structure, as well as the morphological transitions as a function of concentration and temperature will be summarized. These parameters are important in order to understand the thermodynamics of micellization via the estimation of the Gibbs free energy, enthalpy and entropy that can be obtained through the use of different thermodynamic models.

3.2. Sphere-to-rod transition: Concentration dependence

One of the most relevant thermodynamic parameters in surfactant self-assembly is the concentration because this variable can modify the type of structure formed in solutions. Assuming a starting packing parameter

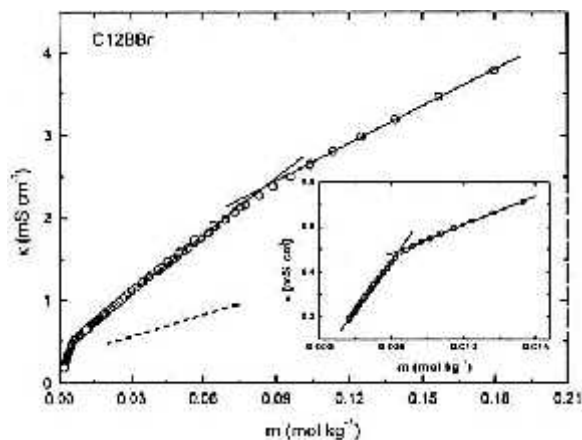


Figure 1. Specific conductivity against molality plot for aqueous solutions of C12BBr at 25°C. Reproduced with permission from (34).

in the order of spherical micelles, $P < 1/3$, a cmc above which spherical micelles start to form can be easily obtained experimentally. It is generally accepted that increasing surfactant concentration leads to structural changes in aggregation. This structural change follows the sequence spherical-cylindrical-hexagonal-lamellar in the case of ionic and some nonionic surfactants (18). Moreover, some direct spherical micelles-to-lamellar liquid crystal transitions have been reported in the case of nonionic systems (19). Nevertheless, in general, spherical micelles transform into rod-like at a precise concentration range above the cmc.

The idea that some structural changes occur in micellar aggregates when surfactant concentration increases was proposed in the early works of McBain *et al* (20). They showed that potassium and sodium salts of saturated fatty acids in aqueous solution exhibit changes in conductivity and osmotic activity at concentrations higher than the first break-point associated with the formation of micelles. Later Hess and Stauff, based on X-ray diffraction measurements, suggested that there is an approximately well-defined concentration range above which a change in properties reflects a change in structure of the aggregates (21, 22).

Regarding other anionic surfactants such as sodium caprylate, strong evidence of structural changes in micelles can be found in the seminal works of Ekwall *et al* (23-28); this phenomena was studied by different techniques. Sodium dodecyl sulfate was extensively studied by Miura and Kodama (29-32). They found by different techniques the existence of a second cmc in aqueous solution. Recently this transition was confirmed by NMR studies on the basis of proton chemical shift of $-CH_2$, reporting the same value of 70 mM. Lee and Woo reported that a second critical concentration, called critical micelle transition (change in shape) appears at a factor of 2 for the ratio $2^{nd} \text{ cmc}/\text{cmc}$ (33). In a more recent work by Gonzalez-Perez *et al* this relationship was not confirmed; instead, it was found that the transition appears to be strongly dependent on the alkyl chain length of the surfactant (34).

Cationic surfactants can also exhibit more than one break on the plots in various physicochemical properties of aqueous solutions as a function of concentration. Figure 1 shows the effect of concentration on the specific conductivity of dodecylbenzyl dimethylammonium bromide in aqueous solution (34). The second break indicates the starting concentration for the formation of the rod-like micelles.

Sphere-to-rod transitions with nonionic surfactant solutions have also been reported. Attwood *et al* (35) worked with a series of fatty alcohol ethoxylated, more specifically with $C_{12}E_6$ and $C_{16}E_9$ surfactants. They found changes in the osmotic pressure, corresponding to a structural transition in micelles. Light scattering studies were carried out with $C_{12}E_6$, $C_{14}E_8$ and $C_{12}E_5$ by different authors and in all cases such transition was observed (36, 37). More recently, small angle neutron scattering (SANS) measurements were performed, confirming this transition in detail for a series of C_iE_j surfactants (38). The second cmc for some nonionic surfactants have been determined using cloud point, fluorescence and viscosity methods by Mu *et al* (39). More recent thermodynamic and kinetic studies of sphere-to-rod transition have been carried out with $C_{14}E_8$ and $C_{16}E_8$ in water by Ilgenfritz *et al* (40).

As the hydrophobicity of the surfactant increases, the critical micelle concentration decreases following the classical Stauff-Klevens rule. The logarithm of cmc is a linear function with the number of carbon atoms in the alkyl chain. This is a general rule for ionic and nonionic surfactants and it is an indication of the dependence of the free energy of micellization with the chain length. As the surfactant concentration increases, at constant temperature, for ionic surfactants, the second cmc seem to follow the same rule. In the series of alkyldimethylbenzylammonium chlorides as well as alkylpyridinium halides Gonzalez-Perez *et al* found that the second cmc follows a linear relation with the alkyl chain, hence a Stauff-Klevens type relation (41). Assuming the interactions between end caps of cylindrical micelles a linear behavior has been found in the limit to zero separation between end caps, which corresponds to the micellar growth. The Stauff-Klevens relation for alkylpyridinium chlorides and bromides series is shown in Figure 2.

Analysis of the available data on the 2^{nd} cmc estimated on the basis of conductivity data has shown that the ratio of the $2^{nd} \text{ cmc}/\text{cmc}$ values varies in the range from 2 to 10 (34). It seems that there is no rule for the ratio as for different surfactants the value is different. There is not enough data available regarding the chain length dependence for the second cmc on nonionic surfactants.

Summarizing, above the critical micelle concentration the rule generally accepted is that micelles are monodisperse and non concentration-dependent. All the monomers added when the concentration is increased will be involved in the formation of new micelles. The surfactant concentration in the monomeric state remains constant when the concentration is increased and it is equal to the cmc. In ionic systems increase in surfactant

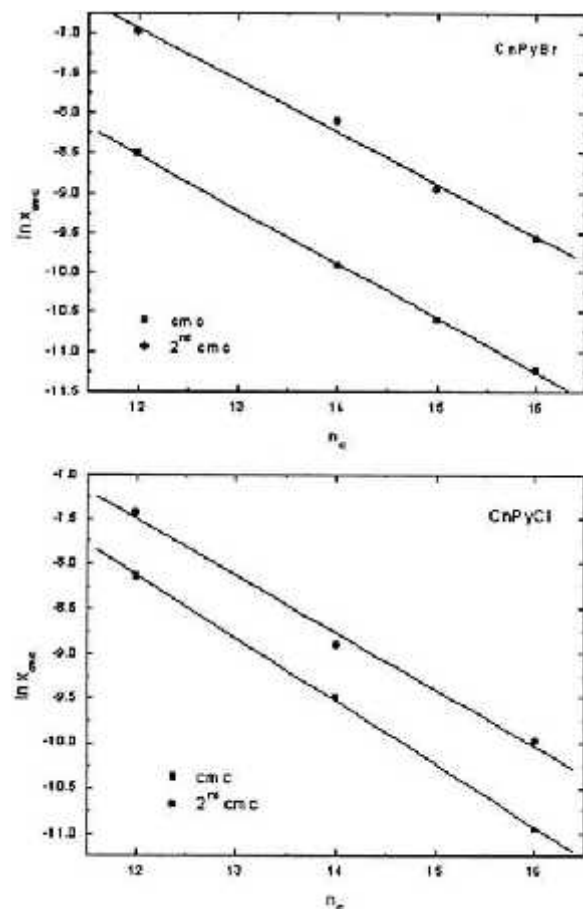


Figure 2. Logarithm of the critical micellization concentration in molar fraction units against the number of carbon atoms in the amphiphilic chain of n-alkylpyridinium bromides (up) and chlorides (b). Solid squares and circles corresponds to the measured first and second cmc's respectively. Solid lines are the corresponding linear fits. Reproduced with permission from (41).

concentration leads also to an increase in the number of counterions on the solution. This effect is shown by the linear increase in conductivity vs molality plot above the cmc. The increase in the number of ions in solution induces the increase in the ionic strength on the medium. This effect facilitates the sphere-to-rod transition as a result of the screening of the interaction between head groups, and this leads to the modification of the surface area in the packing parameter, reaching values characteristic of the formation of rod-like micelles. In the case of non ionic surfactants the increase in concentration can induce the fusion of spherical micelles and this leads to a rod-like conformation. The coexistence of spherical and wormlike micelles was reported experimentally by using Cryo-TEM for ionic and nonionic surfactants^(42, 43). This experimental evidence confirms that the second critical micelle concentration appears to be a first order transition. In general above the second critical micelle concentration the micelles are polydisperse and concentration dependent but below this second critical concentration the micelles are monodisperse and non concentration dependent.

3.3. Effect of temperature on the cmc and micellar structure

Micelles are self-assembled objects that exist in thermodynamic equilibrium with monomers in the bulk above a critical concentration. Their fundamental properties are hence directly linked with the fundamental thermodynamic parameters as concentration, temperature and pressure. In particular temperature has a deep influence on the micellar structure and it also influences the critical micelle concentration. The temperature dependence of cmc is recognized as a complex phenomena related with the water surrounding the surfactants. Knowledge on temperature dependence of the cmc is fundamental in order to understand the thermodynamics of micellization that can be directly investigated by calorimetric methods or indirectly using the well known pseudo-phase separation model or the mass action model. These models give us fundamental information about the thermodynamic processes taking place on micelles as how the free energy enthalpy and entropy drives the micellization process.

At a first approximation the cmc is constant with temperature, but it has been recognized from earlier investigations that the cmc exhibits a temperature dependence that strongly affects the thermodynamic parameters. Many experimental studies suggest that the cmc is temperature dependent and in some cases, as in ionic surfactant systems it presents a U-shape. It is also generally accepted that the U-shape presents a minimum at room temperature; nevertheless, several investigations suggest that this minimum depends on certain parameters such as chain length and the type of counterions or the amount of added salt. Deep knowledge on cmc behavior as a function of temperature is hence basic in order to understand the thermodynamics of micellization. It is based on the two most accepted thermodynamic models, the phase separation model and the mass action model (17-18).

The occurrence of a minimum on the cmc vs temperature plot is a well reported phenomena in surfactant aqueous solutions. In ionic surfactants, such a minimum was reported in the preliminary works of Goddard and Benson with a series of alkyl sulfates (44). Adderson and Taylor reported similar behavior for dodecylpyridinium bromide in aqueous solution (45); more recently, a series of alkyltrimethylammonium bromide was reported by Zielinski *et al* (46), as shown in Figure 3. In nonionic surfactants this U-shape behavior was also reported (47) for octylphenoxyethoxy ethanol and for polyoxyethylene surfactants; this is shown in Figure 4 (48,49).

The existence of the U-shape in cmc vs temperature plots was explained assuming two types of hydration around the surfactant. The increase in temperature affects the water surrounding the hydrocarbon tail. The result of increasing temperature is a gradual dehydration of the hydration shell around the hydrocarbon chain, hence promoting micelle formation. An increase in temperature affects also the partial hydration of the hydrophilic head group. This effect leads to an increase in the repulsion between polar headgroups and hence acts against micellization leading to higher values for the cmc.

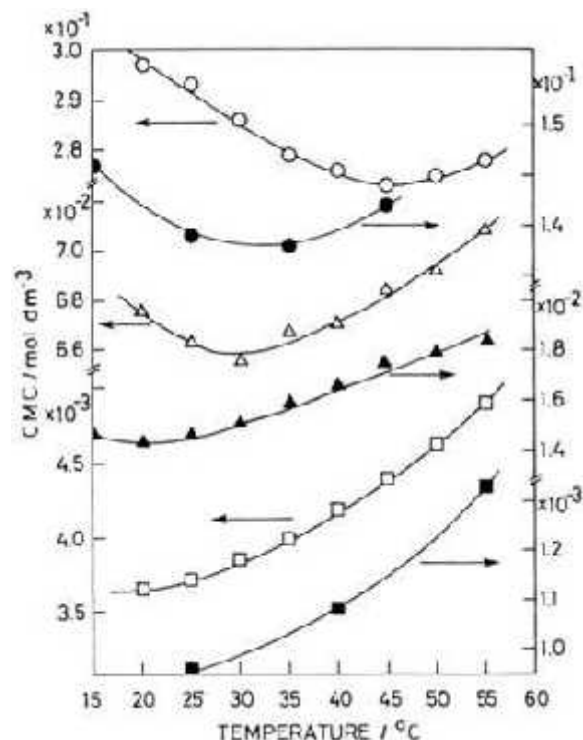


Figure 3. Effect of temperature on the critical micelle concentration of alkyltrimethylammonium bromides in aqueous solutions. (○) C8TAB; (□) C9TAB; (△) C10TAB; (◇) C12TAB; (◇) C14TAB; (■) C16TAB. Reproduced with permission from (46).

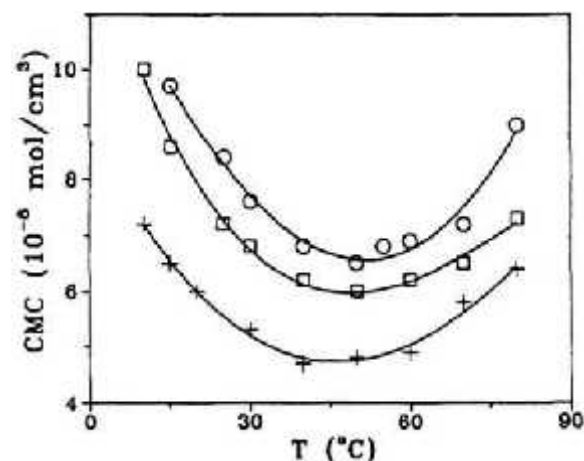


Figure 4. The variation of cmc as a function of temperature of the surfactants C12E4 (+), C12E6 (○), and C12E8 (□). Reproduced with permission from (48).

The U-shape form of the cmc vs temperature is the result of the combination of these two effects. At lower temperatures the disruption of the structural water surrounding the hydrocarbon tail is dominant and acts in favor of cmc, decreasing them. At higher temperatures the dehydration of the charged head group is dominant and this process goes against the micellization leading an increase on the cmc.

Increasing temperature has a deep effect on micelle aggregation number. It was reported by Grubic *et al* (50) that the micelle aggregation number of ionic micelles decreases almost linearly with temperature. Increase in temperature led to an increase in solubility and hence a decrease in the hydrophobicity of the surfactant molecule. Therefore, higher surfactant concentration is needed to start forming micelles at higher temperatures. Also the Brownian motion, which should be opposite to the micellization, should decrease the number of monomer forming the micelle. In the case of nonionic micelles the aggregation number increases strongly from a temperature about 20°C below the cloud point (51).

The Gibbs free energy for micelle formation can be estimated from the value of the cmc and the temperature, by using the phase separation model or the mass action model which give equivalent expressions for the Gibbs free energy. The Gibbs free energy decreases with temperature, indicating that the process of micellization becomes more spontaneous at high temperatures. This is in agreement with the fact that the aggregation number of micelles is lower at higher temperatures for ionic surfactants. In addition, the cmc vs temperature influences the enthalpy of the process indirectly through the Gibbs free energy of micellization.

The hydrophobic part of the surfactant plays a role in the position of the minimum of cmc-vs temperature. For ionic surfactants like alkyltrimethylammonium bromides reported by Zielinski *et al*, it was shown that the minimum of the critical micelle concentration vs temperature decreases as the surfactant chain length increases (46). The same effect was found by Rodriguez *et al* for alkylbenzyltrimethyl ammonium chlorides (52). In nonionic surfactants like polyoxyethylene glycol monoether (OPEj) in aqueous solution, there is also a minimum in the cmc-temperature curve. In that case the minimum systematically increases as the oxyethylene chain length increases and decreases with the increase of the alkyl chain length. It was found that the temperature of the minimum for C₁₂E₄, C₁₂E₆ and C₁₂E₈ are 46, 49, and 52 °C respectively (48). For C₁₀E₈, C₁₂E₈ and C₁₄E₈ the temperature of the minimum are 61, 52, and 46 °C, respectively.

Temperature can be also used to induce a sphere-to-rod transition in ionic and non ionic surfactants. For ionic surfactants the transition was observed by decreasing temperature but for nonionic surfactants it was reported to happen by increasing temperature (53, 54). The reduction in the surfactant area per molecule affects the packing parameter, and this induces the transition to rod-like micelles. For nonionic surfactants, this transition can be obtained by thermal dehydration of the polar groups in the micelle as a consequence of the increase in temperature. In ionic systems a decrease in temperature leads a decrease in the ionization degree of the micelles. By decreasing temperature, the number of counterions in the bulk increases and hence the ionic strength, thereby reducing the surface area of the surfactant inducing the sphere-to-rod transition. In both ionic and nonionic surfactants the

transition is achieved by different methods but the final result on the packing parameter is the same by reducing the area per molecule.

It is not well reported how the second critical micelle concentration behaves with temperature. There are a few experimental indications that show an increase in the second cmc with an increase in temperature (55-57). The second dissociation seems to be accompanied by an endothermic process over the whole temperature range, whereas the enthalpy change for the first dissociation is temperature dependent (57). There is no indication about the temperature dependence of the 2nd cmc for nonionic systems. This indicates that decreasing the temperature in an ionic micellar system a sphere-to-rod transition can be induced because at lower temperatures the high ionic strength screens the interaction between the head groups and change also the packing parameter.

Summarizing, the temperature dependence of cmc and well as the second cmc can be used to better understand the thermodynamic parameters of micellization as well as sphere-to-rod transitions. Whereas the temperature dependence of the cmc is well understood, the corresponding behavior of the second critical micelle concentration is not so well described for all the types of surfactants. Sphere-to-rod structural changes in ionic surfactant systems can be obtained at high surfactant concentration by decreasing temperature. However, with non ionic surfactants systems such effect can be obtained by increasing temperature. For a better understanding of such behaviors more experimental work is needed in order to confirm a general tendency for the different surfactant types.

3.4. Outlook

Surfactant self-assembly structures in solution can be predicted by estimating the packing parameter, which is related to the geometry of the surfactant. Hence, it is possible to modify self-assembly structures by adjusting the packing parameter; this can be done by means of controlling thermodynamic parameters such as temperature or concentration. The effect of these parameters has been discussed for both ionic and nonionic surfactants. Increasing surfactant concentration can induce shape transitions from sphere-to-rod in micellar systems. It has been suggested on the basis of Cryo-tem experiments that this is a non-first order transition.

Concerning sphere-to-rod transitions induced by temperature jumps, this is obtained by decreasing temperature with ionic surfactants; in contrast, with nonionic surfactants this effect is achieved upon temperature increase. The temperature-dependence behavior of cmc is well described; however, more work is needed to explore the temperature dependence of the second critical micelle concentration. This will be useful for a better understanding of the sphere-to-rod transition. Summarizing, surfactant self-assembly behavior can be controlled by modifying purely thermodynamic parameters. This matter is still the subject of intense research amongst colloidal chemists.

4. LIGHT SENSITIVE

4.1. Introduction to light-triggered aggregation changes

The use of external triggers to induce aggregation changes in amphiphilic molecules has been the subject of many investigations. Typically, such triggers include the addition of electrolytes (ionic amphiphiles (58, 59)), switching pH (60-62) and/or temperature and concentration changes, as mentioned in the previous sections as well as other references (63, 64). Thereby, a shift in the balance of hydrophobic and hydrophilic interactions of the molecule is induced. Although light as external trigger has only been investigated over the last three decades, a certain level of complexity in the molecular design and the resulting self-assembly changes exists already. The aim of this section is to review the progress of this fascinating field of colloid science.

A photo-surfactant (photo-sensitive surfactant, light-sensitive surfactant, photo-active surfactant) is an amphiphilic molecule which contains at least one chromophoric functional group. There are various possibilities for the location of the chromophore: in the hydrophobic tail, in or near the polar head group, or even in the spacer for the case of Gemini and bolaform surfactants. The most interesting characteristic of such systems is that a required response, such as an aggregation change, can be achieved solely by the use of UV or visible light, unlike common surfactants, which require either a change in the composition of the system (pH change, electrolyte addition, or concentration, as mentioned above) or in the conditions (temperature, electrical potential for redox-active (65-67)). Since the intensity of the incident UV or visible light beam can be controlled and the aggregation state can be followed online by techniques such as Small-Angle Neutron Scattering (SANS), the aggregation changes of photo-surfactants may be induced in a spatial and timely controllable fashion.

The range of chromophores employed in the design of existing photo-surfactants has been classified as a function of the photoreaction involved and it is listed below.

- i. *cis-trans isomerizations*. Azobenzene (1) and stilbene (2) derivatives.
- ii. *Photocission reactions*. Phenylazosulfonates (3) and benzylammonium salts (4).
- iii. *Dimerizations*. Stilbene (2), N-alkylthymine (5) and anthracene (6) derivatives
- iv. *Polarity changes*. Spiropyranes (7), 1-iminopyridinium ylides (8), N-methyldiphenyl amines (9), alfa-diazoketones (10), alfa-azidoketones (11).
- v. *Polymerizations*. Acetylene or vinyl-containing surfactant molecules.

The chromophores listed in this classification have been employed in systems for which light-induced changes has been studied for a variety of colloidal properties, such as aggregation changes, wetting, surface tension, and stabilization or destabilization of emulsions

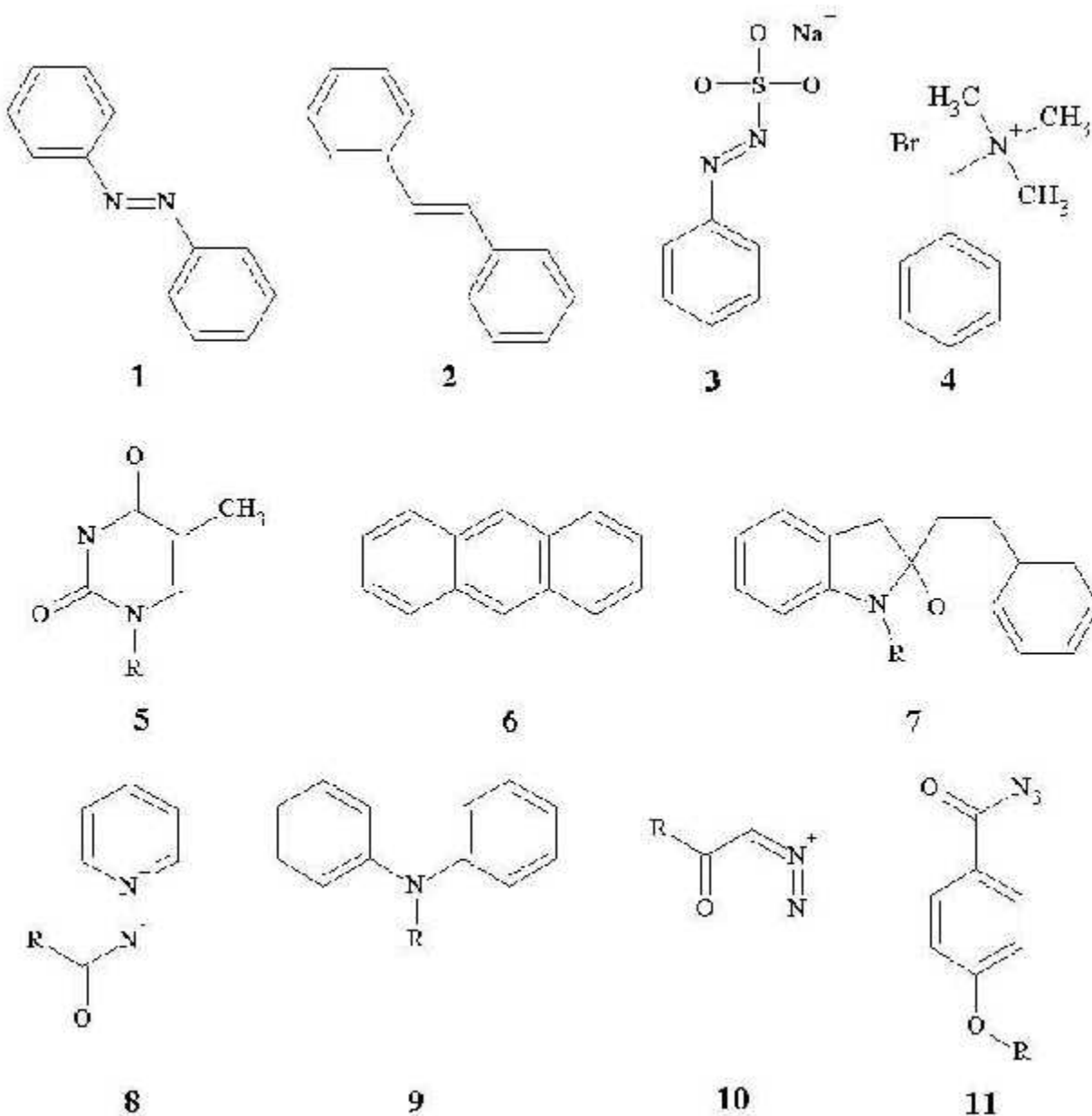


Figure 5. Chromophoric groups used in photo-surfactant systems: azobenzene (1), stilbene (2), phenylazosulfonates (3), benzylammonium salts (4), N-alkylthymine (5), anthracene (6), Spiropyranes (7), 1-iminopyridinium ylides (8), N-methyldiphenyl amines (9), alpha-diazoketones (10), alpha-azidoketones (11).

and microemulsions. The chemical structures of these chromophores are shown in Figure 5. Unsurprisingly, most of these molecules bear an aromatic group, double bonds or diazo / azido groups. The inclusion of such chromophores in the surfactant molecule is not compulsory, since there are several studies which employ small amounts of photoactive molecules in combination with conventional surfactants. Similarly, photo-surfactants have been diluted with non-photoactive surfactants or other components (e.g. gelatine) and important aggregation changes are still achievable.

In order to understand the basis of photo-induced aggregation changes, it is necessary to mention the transformations that occur at a molecular level in such photoreactions, as well as the conditions which favor one photoproduct (s) over other (s). This is the scope of Section 4. Examples of light-induced aggregation changes are discussed below, giving emphasis in outstanding systems. For other photo-induced changes in the colloidal properties of photo-surfactant systems, the reader is referred to other reviews (68-72).

4.2. Photochemistry of photosurfactants

4.2.1. Cis-trans isomerizations: Stilbene

It is well known that in order to obtain high degrees of conversion in any photo-reaction, the wavelength of choice plays an important role. In the case of *trans*-stilbene, irradiation with $\lambda=313$ nm can yield up to 91.5 % of the *cis* isomer (73). However, there are other factors that affect both the rate and the pathway of the photoreactions taking place in stilbene. For example, the substituents present and the surrounding media influence the rate of isomerization. Solvents with high viscosity may slow down the reaction, and those with high polarity may lower the efficiency of isomerization (74). The effect of other variables, such as solvation, temperature, pressure and viscosity has been studied (73-78). Regarding the photoreaction pathway, *E-Z (trans-cis)* isomerization is not the only possibility, since this reaction can be inhibited by concentration, and dimerization may take place as well. If the molecules are aggregated, then dimerization may be more likely than isomerization (73).

The molecular geometry is quite isomer-dependent. The *trans* form is nearly planar with C_{2h} symmetry whereas the *cis* isomer has a propeller-type structure with C_2 symmetry. Thanks to these properties, large changes in the colloidal properties of these systems can be induced, since changes in the architecture at a molecular level surely feeds through aggregation and adsorption changes.

Most stilbene-containing photo-surfactants have a low solubility in water. In addition, given the restrictions on the *E-Z* isomerization that entail the aggregation of these photo-surfactants, simple stilbene-containing single-chained surfactants are of little use in aqueous systems. Therefore, most of the reported investigations involve mixtures of stilbene surfactants or molecules with conventional amphiphiles.

4.2.2. Cis-trans isomerizations: Azobenzene

Photochemistry of azobenzenes is much more straightforward than that of stilbenes, since azobenzenes can undergo *E-Z* isomerization even in very viscous solutions, liquid crystals, condensed monolayers, micellar solutions, polar solvents, and even in solids (79-83). In the case of azobenzenes there is evidence for an "inversion" mechanism, which cannot occur in stilbenes (84, 85), which may explain this difference. Due to its straightforward photochemistry, azobenzene is the chromophore most commonly incorporated into photo-surfactant molecules.

The *trans* form of azobenzene can be irradiated at 360 nm to yield the *cis* isomer, which in turn can be irradiated at 460 nm to relax back to the *trans* isomer. However, complete conversion of the *cis* or *trans* isomer is not generally accomplished (86). A photo-stationary state is reached instead, comprising a mixed population of the two isomers, and its composition depends on the wavelength used for irradiation, as well as on the substituents present in the molecule. Hence, it is advisable

to determine the optimum irradiation wavelength for each specific system in order to obtain the highest possible conversion, and in turn, the most remarkable change in aggregation or other colloidal properties.

In tune with stilbene derivatives, the geometry of the chromophore changes from nearly planar for the *trans* isomer, to bent, propeller-type for the *cis*, since one of the benzene rings occupies a plane that is displaced 56° from the azo group and the other ring (87).

As with stilbene, there are some possible side photo-reactions which could take place and lower the *E-Z* isomerization efficiency. *Cis*-azobenzenes could undergo photo-cyclization to form phenanthrene derivatives, but it seems that this requires protonation or complexation to occur (79, 88), hence this side reaction usually does not involve a problem. Other possible light-induced reaction of *cis*-azobenzenes is photo-reduction to yield hydrazobenzene and aniline derivatives, but this reaction is very inefficient and highly solvent-dependant (79, 88). A possible drawback of azobenzene-containing photosurfactants is the thermal back reaction from the *cis* to the *trans* isomer, which could lead to unwanted transformations.

4.2.3. Photocission reactions

The rupture of links between the hydrophilic head group and the hydrophobic tail of a surfactant molecule offers the possibility of a dramatic and definitive switch in the physicochemical properties of a given system. These "photo-destructible" or "photo-labile" surfactants employ functional groups such as phenylazosulfonate (89, 90) and benzylammonium (91, 92) moieties. O-nitrobenzyl moiety has also been used to create photo-labile lipids (93).

Irradiation of such surfactants with UV light enables a transition from an initially surface active molecule to a non-surface active one. A photocission reaction occurs between the head groups and the tails of the surfactants; the polar head group fragment usually remains in solution, whilst the hydrophobic tail fragment suffers phase separation, if the system is aqueous. Photo-destructible surfactants have a great potential in the paint industry where an efficient switch from a water-based system to a water-resistance final film is essential.

Phenylazosulfonates are the most widely used photo-destructible chromophores, due to their uncomplicated synthesis method and drastic photo-induced colloidal responses. Their photoreaction pathway is highly medium dependant. The photochemistry of surfactants bearing this moiety is hence somehow complicated, since in aqueous dispersions above the critical micelle concentration, molecules in the monomeric state will follow an ionic mechanism yielding alkylphenol derivatives, while the molecules forming part of a micelle will experience a more hydrophobic environment and the radical

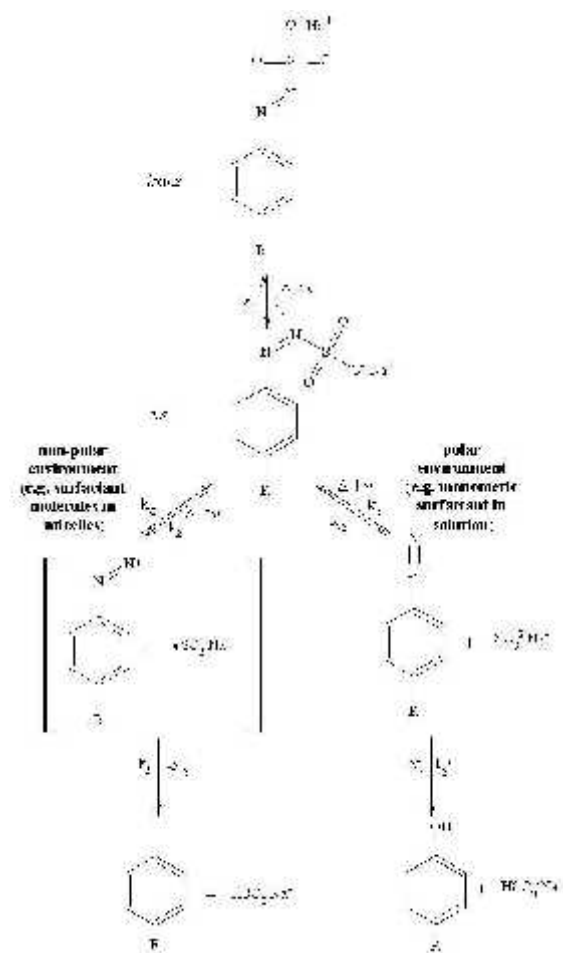


Figure 6. Mechanism of photolysis of phenylazosulfonates proposed by Nuyken and Voit (=heat). Adapted with permission from: (94).

mechanism will be favored yielding alkylbenzenes, as shown in Figure 6.

4.2.4. Polarity changes

Photo-induced polarity changes involve a modification in the hydrophilicity of the headgroup, which may arise from photo-ionization (95, 96), rearrangements (92, 97, 98) and photo-cyclization (99, 100). Examples of molecules which experience these photo-reactions include Spiropyranes, N-methyldiphenyl amines, 1-iminopyridinium ylides, diazo and azido ketones, and N-(1-pyridinio) amidates. For example, the photo-cleavage of a phosphate-phenolate bond of a water insoluble phosphotriester generates a dialkyl phosphate surfactant, which constitutes a change from a non-polar to a polar group (96).

4.2.5. Dimerizations

This kind of photoreaction occurs in molecules containing double bonds; usually dimerization results in the formation of a ring such as cyclobutane. If in addition the molecule contains other cycle (s), very dramatic and interesting changes in the molecular geometry can be

achieved. This is the case for molecules containing chromophores such as stilbene and anthracene. Prior to irradiation, such molecules are planar, since they are mainly formed by aromatic rings or as in the case of stilbene, two aromatic rings linked by an ethylene unit. On the other hand, in the cyclized photoproducts the double bond involved in the dimerization is absent and sp^3 hybridization results in the new cycle (with a tetrahedral geometry and therefore, non-planar). As an example, Figure 7 shows the molecular geometry transition involved in the dimerization of an anthracene derivative. This dramatic change gives rise to interesting responses in colloidal properties.

It must be remembered that for stilbene derivatives, *trans-cis* isomerization can also take place; however, in aggregated systems where stacking of the aromatic rings occurs there is no sufficient space for isomerization, hence dimerization would be favoured. This is usually the case in stilbene-containing surfactants in solutions above their CMC.

4.2.6. Photo-induced polymerization of surfactants

Unlike the photo-reactions listed above, which induce a change in the aggregation state, photo-induced polymerization of surfactants induces the retention and definitive stabilization of a given structure. Surfactants containing photo-polymerizable units such as diacetylene can be left to self-assemble in solution and then irradiation with an appropriate wavelength would lead to the creation of covalent bonds which would stabilize the structure whilst (ideally) keeping the shape and size constant. This approach represents a convenient way to improve useful but usually unstable structures with short lifetimes such as vesicles. The principle has been employed by Ringsdorf *et al*, who studied a series of polymerizable amphiphiles with the diacetylenic unit, such as the one shown in Figure 8 (92, 101). The molecules formed small unilamellar vesicles (~100 nm diameter, ~10 nm wall thickness). Electron microscopy showed that the structure of the vesicles was maintained after polymerization. The polymerized vesicles could not be broken down by organic solvents.

4.3. Examples of photo-induced aggregation changes.

4.3.1. Vesicle transitions

Due to their great potential as delivery systems, much effort has been devoted to the development of photo-responsive vesicles. Transitions leading to their disruption (93, 102), formation of spheroidal or ellipsoidal micelles (103, 104) and cylindrical micelles (105, 106, 111, 112), needles (107), and precipitation (108) have been reported. Photo-induced formation of vesicles from an insoluble solid has also been reported (96). The range of chromophores used in these systems is varied. Due to space restrictions, only some outstanding examples are discussed.

Disruption of vesicles represent an interesting approach. A major challenge in gene therapy, for the transduction and expression of exogenous genes in mammalian cells, is to develop artificial nanoparticles that are highly efficient as

Temp., conc. And light-induced aggregation changes

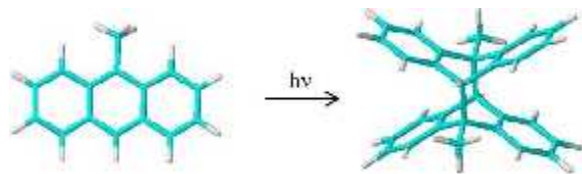


Figure 7. Changes in the molecular geometry taking place in the dimerization of an anthracene derivative: flat monomer (a) to non-planar dimer (b).

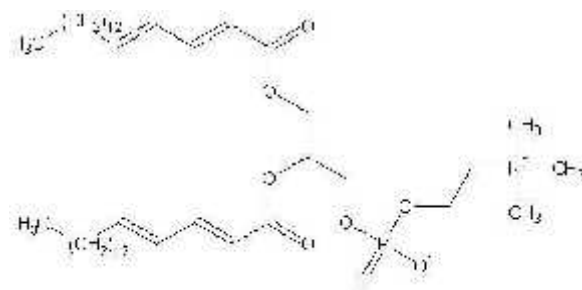


Figure 8. Photo-polymerizable phospholipid used by Ringsdorf *et al* (92, 101). Reproduced with permission from (92, 101).

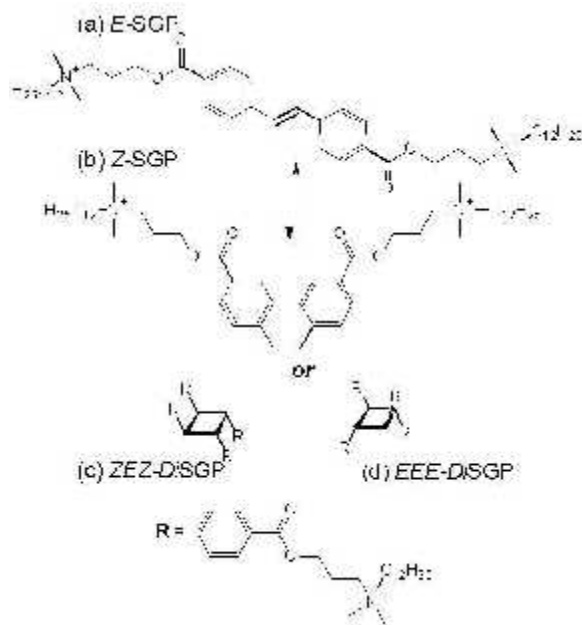


Figure 9. Structure and photoreactions of SGP: a) *trans* isomer *E*-SGP, b) *cis* isomer *Z*-SGP, c) *cis*, *anti*, *cis* dimer *ZEZ*-DiSGP and d) all-*trans* dimer *EEE*-DiSGP. Reproduced with permission from (104).

non-viral vectors. Nagasaki *et al* developed cationic lipids bearing an *o*-nitrobenzyl moiety as a photo-cleavable spacer between its hydrophilic (lysine or arginine) and hydrophobic (didodecyl tertiary amide) regions (93). These lipids could be used to prepare non-viral vectors, which are made up of lipid aggregate (vesicles) / DNA complexes, also called lipoplexes; such a system represents a photo-

responsive gene delivery system. UV irradiation was used during gene delivery to destabilize lipoplex membranes and to facilitate membrane fusion. Photo-cleavage of lipids would not only make the membrane of the vector unstable to facilitate the fusion with endocytic vesicles, but it also promote the dissociation of cationic lipid/DNA lipoplexes, thus aiding the escape of DNA from the endocytic vesicles, increasing the efficiency of transfection in a substantial way.

Eastoe *et al* reported for the first time the photo-induced conversion of vesicles to micelles, using a novel stilbene-containing Gemini photosurfactant (SGP) (103). The structures of this cationic photo-surfactant, as well as its possible photo-products are shown in Figure 9.

^1H NMR studies were consistent with dimerization in aqueous solutions. The initial *E*-SGP (*trans* isomer) was found to aggregate as polydisperse vesicles (two populations between 20 and 80 nm of diameter), whilst upon irradiation, a transition to small charged micelles (4 nm in diameter) was observed (SANS data, Figure 10). The progressive change in structure was also followed by SANS and intermediate irradiation states were found to consist of a mixture of vesicles and micelles, and as the reaction proceeded the vesicles became smaller with a sharper size distribution. After only a few minutes the final state of small charged micelles was reached. This analysis was consistent with the macroscopic aspect of the samples, which changed from a slightly milky appearance (consistent with vesicles) to a transparent solution (consistent with small micelles). The dramatic change in aggregation was explained in terms of significant perturbations in molecular geometry. The initial *E*-SGP molecule has a flat and rigid *trans*-stilbene spacer, whilst after irradiation the photo-cyclized dimer (DiSGP) contains a cyclobutane group, which makes the spacer twisted and more flexible (Figure 11).

Other colloidal responses, such as a decrease in surface tension and decrease in contact angle onto hydrophobic surfaces, further confirm the more efficient packing of *ZEZ*-DiSGP. A similar change in aggregation was observed in systems where SGP was diluted with conventional surfactants such as dodecyltrimethyl ammonium bromide (DTAB), and gemini surfactants 12-4-12 and 16-4-16 (104). Furthermore, other interesting colloidal responses brought about by SGP have been reported by Eastoe *et al* (109, 110). The main drawback of SGP was that reversibility could only be achieved up to 50%.

Abbot *et al* came up with another interesting example of molecular design: a bolaform photo-surfactant bearing an azosulfonate chromophore in the spacer (111), bis (trimethylammoniumhexyloxy)-azobenzene dibromide (BTHA, shown in Figure 12). Bolaform surfactants assume conformations that are more constrained than those of conventional surfactants, since both headgroups maintain contact with the aqueous phase, either in the aggregates or at the air-water interface. Therefore, *trans*

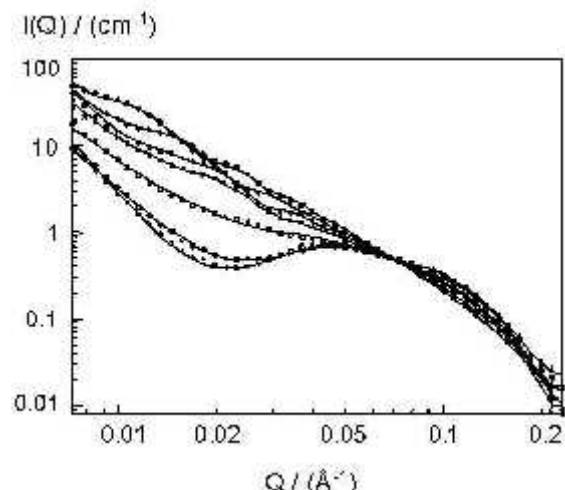


Figure 10. SANS data for a 10 mM aqueous solution of SGP surfactant as a function of irradiation time (103). In order of decreasing intensity 0 (○), 10 (+), 20 (*), 30 (×), 55 (□), 95 (○) and 125 s (★) irradiation time. The fitted lines are for polydisperse vesicles (bi-layer thickness = 20 Å) in equilibrium with charged micelles (radius = 20 Å, fractional molecular charge + 0.25 and variable Debye length between 100 and 35 Å). Reproduced with permission from (103).

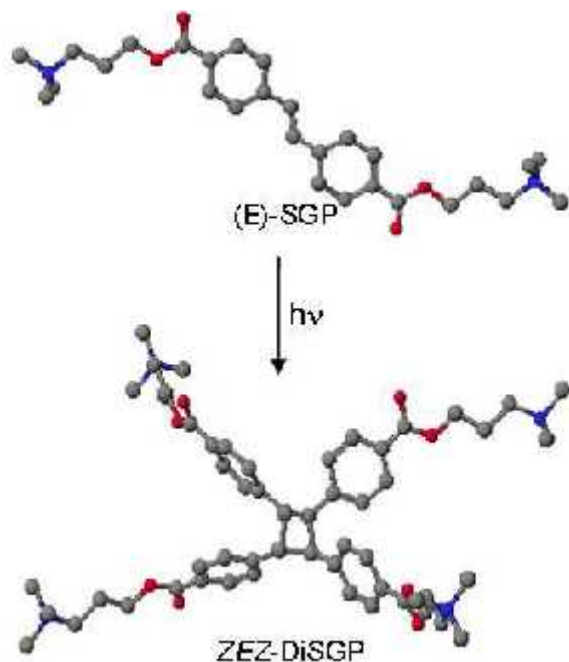


Figure 11. Changes in molecular geometry upon irradiation of (E)-SGP to form ZE-Z-DiSGP. Reproduced with permission from (103).

cis isomerization of bolaform surfactants would lead to significant changes in aggregation and adsorption.

Several studies have been carried out with BTHA in aqueous systems alone and in mixtures with

Sodium Dodecyl Sulfate (SDS) (105a, 105b, 111); the most interesting results were obtained with the mixtures SDS-BTHA. In such mixed systems, dynamic surface tension was reduced by up to 25 mN m⁻¹ upon irradiation. Dynamic Light Scattering (DLS), Quasi-elastic Light Scattering (QLS) and SANS demonstrated a light-induced aggregation change. Vesicles were obtained prior to UV irradiation with both SDS-rich and BTHA-rich mixtures. However, after UV irradiation, the behaviour was different, depending on the SDS-BTHA ratio. With SDS-rich compositions, a reversible vesicle-to-micelle transition was observed, whilst for BTHA-rich compositions, UV-irradiation resulted in the irreversible formation of a precipitate. Surprisingly, for other (intermediate) compositions, UV-irradiation only resulted in a small reduction of vesicle volume fraction, practically no change in vesicle size, and coexistence of vesicles with micelles. This behaviour was explained in terms of a segregation of *cis* isomer into the micelles and *trans* isomers into the vesicles, as favoured by their molecular conformation.

Baglioni *et al* reported a similar kind of transition using the same system (aqueous BTHA and SDS) (112). Since higher concentrations of SDS + BTHA were investigated, the results were slightly different. SANS and DLS were consistent with a mixed population of large and small vesicles, in coexistence with small oblate ellipsoids (6 nm). After irradiation, the size of the large vesicles was decreased, whilst the size of small vesicles and oblate ellipsoids remained almost constant. However the volume fraction of surfactant in small and large vesicles was decreased and oblate ellipsoid-shaped aggregates were dominant. The variety of results obtained in the studies by Abbott *et al* (105a, 105b, 111) and Baglioni *et al* (112) clearly indicates the richness of the BTHA-SDS system, since the size and shape of the obtained aggregates are highly dependent on the concentration and composition of the samples.

In both BTHA studies, reversibility of the photo-reaction as well as the aggregate transition was achieved. This is expected since the chromophore used was azobenzene. However the samples had to be continuously irradiated as the thermal back reaction was rather fast even in the dark. It would appear that BTHA and SGP systems complement each other, in that SGP can give a definitive switch from vesicles to micelles, whilst BTHA offers full reversibility, although continuous irradiation is necessary. In addition, the range of aggregate size is different for both systems (smaller aggregates were obtained with SGP).

Eastoe *et al* achieved a vesicle-to-needle transition using a mixture of light-inert cetyltrimethyl ammonium bromide (CTAB) and an anionic photo-destructible surfactant (sodium 4-hexylphenylazosulfonate, C₆PAS) (107). CTAB and C₆PAS spontaneously formed vesicles in water. SANS and TEM (Figure 13a) were consistent with polydisperse single-shell hollow spherical vesicles of about 18 nm diameter. When the sample was irradiated with UV light, C₆PAS was selectively photo-degraded to yield a final state which consisted of mixed

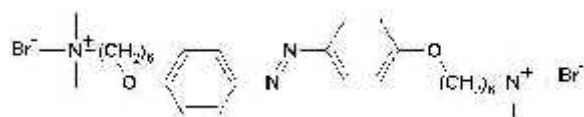


Figure 12. Azobenzene-containing bolaform surfactant BTHA (Bis (trimethylammonium hexyloxy)-azobenzene dibromide) used by Abbot *et al* (105, 111).

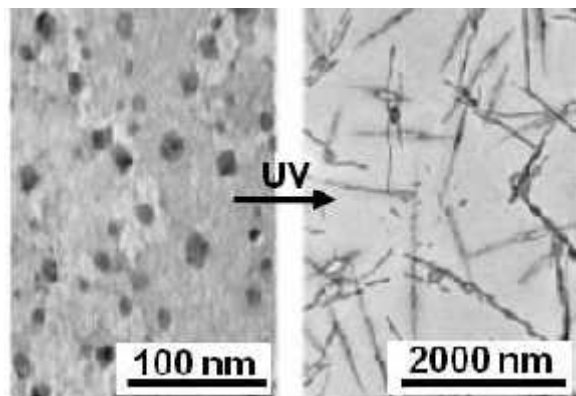


Figure 13. TEM images for 1.4 wt % 1 :3 CTAB / C₆PAS systems in D₂O (a) before and (b) after irradiation (107). Reproduced with permission from (107).

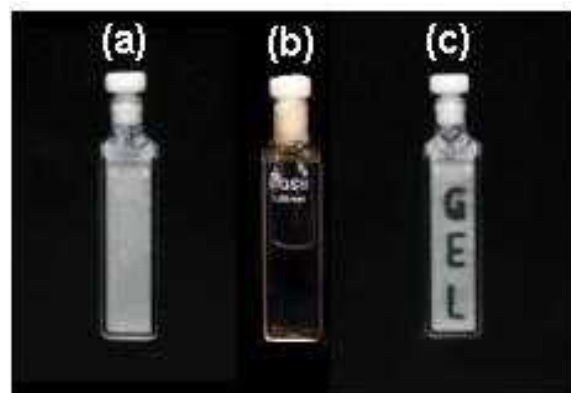


Figure 14. Photo-induced gel-to-sol transition of an 8 % SGP-N,N'-dimethyldodecylamine-toluene-d₈ organogel : initial gel state (a); after irradiation (b) and after irradiation through a mask (c) (109). Reproduced with permission from (109).

CTAB/hexylphenol/hexylbenzene aggregates, where 4-hexylphenol was the dominant product. Vesicles were not present in the post-irradiated samples; instead, TEM showed large needle-like aggregates (Figure 13b). Given the photo-destructible nature of C₆PAS, this transition was irreversible.

Luisi *et al* reported the photo-chemical reaction of water-insoluble precursor didecyl-2-methoxy-5-nitrophenyl phosphate into water-soluble didecylphosphate (96). The latter is a double-chain surfactant and, upon irradiation of the insoluble precursor,

surfactant molecules were generated, which in turn spontaneously self-assembled into 1-10 μm vesicles.

4.3.2. Photo-induced aggregation changes involving viscosity changes: photo-rheological fluids

If a viscous / gel system is doped with photo-active molecules/surfactants, important changes in their rheology can be induced by light. Such systems could be termed as photo-rheological, and their principle follows the path of already existing systems whose rheology is modified by the action of electric (113, 114) or magnetic (114, 115) fields, as well as temperature (116, 117) and pH (116, 117). This kind of rheo-responsive behaviour could form the basis for technologies such as sensors, flow control devices, chemical valves and switches, clutches, delivery systems, actuators, industrial separators, micromachines, mechanical transducers and in the case of gels which present stimuli-induced shape or volumetric changes, artificial muscles.

Several examples of such photo-rheological fluids can be listed. Usually, the change in rheology is accompanied by a change in aggregation. For instance: multilayer stack to small inverse cylindrical micelles plus precipitate (109), ellipsoidal charged micelles to extended sheet like aggregates (118), decreased cross-linking of polymeric chains (119), and re-swelling of microgel particles (120). Shrinkage of micelles (121) and long worms to short cylindrical micelles (122), as well as entangled worm-like micelles into discrete, smaller spherical micelles (123) have also been reported. Some of these examples are mentioned in greater detail below.

Eastoe *et al* reported a photo-responsive organogel made up of *E*-SGP (Figure 9) in toluene (109). Figure 14 shows the gel to sol transition seen for this system upon irradiation with UV light: initially, as the opaque gel (Figure 14a); after around 24 hours of irradiation, a sol with some yellow precipitate (Figure 14b). Interestingly, when the system was irradiated for ~7 hours through a mask, only the illuminated areas were converted to the sol (Figure 14c), demonstrating that some degree of spatial control over the gel-to-sol transition is possible with this system. SANS data of the organogel was best fitted to a multilayer stack model. The irradiated sample was consistent with small inverted rod micelles. This study complements the research on SGP described in Section 6.1 and points out to the versatility of this system, which in addition has been employed to photo-induce the stabilization of water-in-oil microemulsions (110).

The change in viscosity and aggregation of aqueous gelatin doped with photo-destructible C₆PAS has been recently reported by Eastoe *et al* (118). When C₆PAS was added to solutions of aqueous gelatin, large increases in viscosities were obtained. Before irradiation, increases in C₆PAS concentration lead to a sharp increase in viscosity. After UV irradiation, C₆PAS-containing systems displayed a reduction in relative viscosity. This behavior was ascribed to breakdown of the micelle cross-links caused by photolysis of C₆PAS. In the presence of C₆PAS the scattering at low *Q* disappeared, suggesting that the

structure of gelating had been greatly modified. Previous to irradiation, the scattering profile was consistent with charged prolate ellipsoidal micelles. After irradiation, the scattering intensity and profile changed dramatically, and it was indicative of monodisperse, randomly oriented lamellar stacks. The large changes in viscosity and scattering profile were robust indications of a dramatic UV-induced change in aggregation, from charged ellipsoidal prolate micelles to much larger aggregates.

Long worms to short cylindrical micelles transitions have been recently reported by Raghavan *et al* (122); it was achieved by using a relatively simple system, aqueous mixtures of CTAB with *trans-ortho*-methoxycinnamic acid (OMCA). Aqueous solutions containing CTAB and variable amounts of OMCA were studied before (*trans*-OMCA) and after (*cis*-OMCA) UV-irradiation. The viscosity decreased by a maximum of more than 4 orders of magnitude, which is an outstanding result as compared with other photo-rheological fluids. Flow birefringence and SANS studies of pre-irradiated samples were consistent with the presence of worm-like micelles, whereas the post-irradiated samples indicated a dramatic reduction in aggregation as prolate ellipsoidal micelles were found; the largest dimension of the micelles was reduced by a factor of 10. The first argument to this behaviour was that due to the differences in conformation *trans*-OMCA would associate to CTAB strongly whilst *cis*-OMCA would associate to it weakly. The second argument was related to the hydrophobicity of the different isomers: there is strong evidence demonstrated by previous studies that *trans* isomers are more hydrophobic than *cis* isomers (azobenzene and stilbene derivatives).

Zhao *et al* reported a rheological study involving a novel carboxylate Gemini photosurfactant (C12-azo-C12) (123). As with the SGP work by Eastoe *et al* mentioned above, the Gemini photosurfactant included the photoactive group (azobenzene) in the spacer. The compound formed a photo-responsive fluid in water. Rheology studies were consistent with wormlike micelles behavior prior to irradiation (*trans* isomer). This was confirmed by FFTEM studies which showed a densely entangled network; after UV irradiation FFTEM was consistent with 30 nm micelles. The relatively large micelle size was justified in terms of the stiffness of the spacer. The most remarkable result from this investigation is the large difference in zero shear viscosity obtained before and after UV irradiation, which was as large as 5 orders of magnitude. In addition, such photo-induced viscosity change was reversible after several cycles. In this study, only 30% of the *trans* isomer was converted into the *cis* isomer. The UV irradiation was carried out by a mercury lamp with a 290-400 nm filter. A narrower irradiation wavelength range may have resulted in even more drastic photo-induced changes.

4.3.3 Photo-induced aggregation changes involving liquid crystal phases

Phase transitions in lyotropic liquid crystalline (LLC) surfactant systems are normally achieved with a change in composition or temperature. Wolff *et al* studied a series of LLC systems doped with small amounts of

photosensitive aromatic compounds (124). Irradiation with UV light caused the isothermal phase transition of the systems, from a liquid crystalline phase to an isotropic phase and/or vice versa. Such aggregation change implies the transition from a highly organized structure, with at least one (lamellar), two (hexagonal and rectangular) or three (cubic) dimensional translational order, into a much simpler isotropic (micellar) phase with no directional order. (125-130). Different kinds of phase transitions have been achieved, for example, from micellar isotropic to hexagonal (126-129), nematic (127-131), inverse hexagonal (125, 127), and lamellar phases (125, 130). Another example focuses on transitions between different lamellar phases (132). Some of these examples are described below.

Hexagonal to isotropic micellar phase transition has been also reported in the literature. Potassium octanoate (KO) forms an hexagonal phase in water at concentrations of KO > 43%. For a 43.5 % sample the phase transition temperature T_{HI} (hexagonal liquid crystal \rightarrow isotropic micellar phase) is 37°C. In the work of Nees *et al*, this system was found to be very sensitive to the presence of small amounts of compounds like 4-hydroxystilbene and other substituted stilbenes, depending on whether the *trans* or *cis* isomer was present (130). Solubilization of 1% w/w of *trans*-stilbenes caused a reduction, with $\Delta T_{HI} \sim -12^\circ\text{C}$, whereas isomerization to the *cis* form had the opposite effect and ΔT_{HI} was found to be + 7.5°C. Therefore, phases could be switched from isotropic to hexagonal or vice versa isothermally using UV as a trigger. It could be inferred that the *trans* oblong-shaped solubilizes induced lower phase transitions temperatures than the more spherical-shaped *cis* form.

Wolff *et al* studied the effects of photo-sensitive N-methylhydroxystilbazolium bromide (HSB) in aqueous and non-aqueous lyotropic liquid crystal systems (125). Irradiation of samples in the inverse hexagonal region of the decane/AOT/water system containing 1% of HSB led to increases in the clearing point (inverse hexagonal to isotropic T_{HI}) of 2°C; this increase turned out to be irreversible upon heating, indicating that *trans*-*cis* isomerization was a minor process and hence the main photoreaction taking place was dimerization. On the other hand, larger effects were found in the binary non-aqueous system AOT-glycerol. Irradiation of samples in the lamellar region of this system containing 2% of N-methyl hydroxystilbazolium bromide led to an increase in the clearing point (lamellar to isotropic T_{LI}) by up to 10°C for the AOT-glycerol system (125, 130). The main photoreaction was found to be *trans*-*cis* isomerization. Preferred dimerization was ascribed to the formation of H-aggregates, which were much more abundant in bent interfaces such as microemulsion droplets and inverse hexagonal phases, than in planar interfaces such as found in lamellar phases. In summary, at certain conditions it was possible to isothermally switch between liquid crystalline (lamellar or inverse hexagonal) to isotropic phases simply by the use of UV light.

Transitions between lamellar phases were reported in an investigation by Eastoe *et al* (132), where photo-destructible surfactant C6PAS was used in combination with an inert ABA triblock copolymer, (EO)₁₅-(PDMS)₁₅-(EO)₁₅, dissolved in a glycerol/water

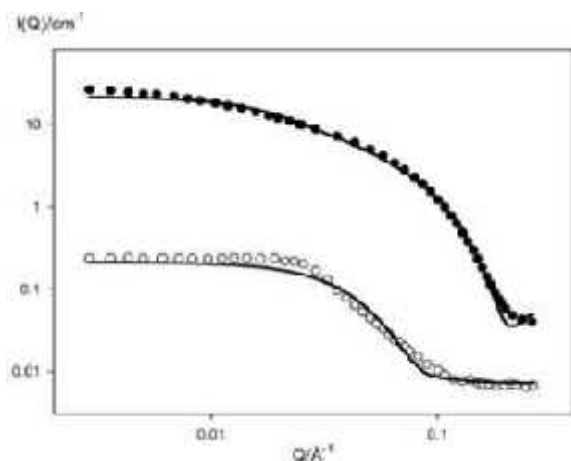


Figure 15. SANS data and fitted functions from D₂O solutions of 85 Mm 50:50 C₆PAS / C₁₂E₆ in 0.5 M NaCl, before irradiation (●) and post-irradiation lower phase (○) (135). Reproduced with permission from (135).

mixture. Rheology, SANS, SAXS and DLS were used to follow the changes in aggregation induced by light. According to SAXS, the ABA triblock copolymer alone formed a weakly structured lamellar phase, whilst the sample with added C₆PAS formed a highly ordered lamellar structure. This difference in aggregation was explained in terms of the electrostatic stabilization added by C₆PAS. The rheological studies were consistent with such aggregation behaviour. Upon UV irradiation, and destruction of C₆PAS, the SAXS spectra as well as the rheology measurements were similar to the system with ABA triblock only, hence, a transition between a viscous, highly ordered lamellar to a weakly structured an undulating lamellar phase with low viscosity took place upon UV irradiation.

4.3.4. Miscellaneous light-induced aggregation changes

The possibility of controlling the formation and disruption of micelles by external triggers such as light in a reversible manner is very attractive for some potential applications, for example in the controlled release of oil-soluble substances, which is used in the fields of cosmetics, pharmacy, perfumes and food industry. The cmc of photosurfactant 4-butylazobenzene-4'-(oxyethyl) trimethylammonium bromide (AZTMA) was found to be 2.7 mM for the *trans* form and 8.2 mM for the *cis* form (133). Solutions with a concentration of 5 mM of the initial *trans*-AZTMA were able to solubilize ethyl benzene, which was almost completely released after irradiation, since at this concentration the *cis* form is below its CMC, and hence a transition from micelles to monomer takes place. The solubilization capacity was clearly isomer-dependent. This phenomenon was ascribed to larger solubilization sites in the hydrophobic part of the *trans* isomer, as compared to the *cis* form, since the hydrophobic moiety is in an extended state in *trans*-AZTMA, whilst it is folded in the *cis* isomer. Additionally, the lower CMC of the *trans* isomer points to a higher hydrophobicity of the micellar core, making oily substances more soluble. Hence, changes in solubilized

amount of oil were found to arise from changes in both the CMC and solubilization capacity of AZTMA induced by photo-isomerization.

An interesting example of photo-induced aggregation change was reported by Sleiman *et al* (134). The compound *trans*-2,2'-Bis (decyloxy)-4,4'-azodibenzoic acid, which resembles the structure of gemini surfactants, was found to self-assemble into dramatically different higher-order structures depending on its conformation. Aggregation is driven by hydrogen bonding; in the *trans* conformation, the two carboxylic groups are expected to be aligned, and thus it aggregates into infinite linear tapes. On the other hand, after irradiation, when the *cis* conformation predominates, the carboxylic acids are expected to be oriented in a perpendicular mode, thus self-assembling into cyclic structures. In a second level of association, these cyclic structures form long, rod-like aggregates through stacking interactions.

Eastoe *et al* reported another outstanding example of photo-induced aggregation change using the photo-destructible surfactant mentioned in previous sections, C₆PAS (135). Mixtures of this photo-surfactant with non-ionic surfactant hexaethylene glycol monododecyl ether (C₁₂E₆) in water were found to aggregate as charged ellipsoidal micelles (SANS). Irradiation of the C₆PAS / C₁₂E₆ mixed micelles resulted in a photo-generated emulsion: C₆PAS breaks down into its oily components (hexylbenzene and 4-hexylphenol), which are emulsified by C₁₂E₆, forming uncharged disk-like aggregates. When instead of pure water, 0.5 M NaCl was used, different behaviour was observed. Prior to irradiation the SANS profile could be fitted to a cylinder form factor. After irradiation, instead of an emulsion, macroscopic phase separation was obtained, due to the electrolyte effect, which reduced the interactions stabilizing the emulsion. SANS of the lower phase showed that the scattering intensity had dropped by approximately two orders of magnitude as compared to the non-irradiated sample (Figure 15), which indicated a significant reduction in aggregation. Analysis was consistent with 4 nm polydisperse spherical C₁₂E₆ micelles partially swollen with oily photo-products.

4.4. Outlook

A broad range of light-induced aggregation transitions has been described. The different research works reviewed here indicate that the most remarkable light-induced effects are obtained with surfactants that undergo a large geometry change (e.g. *E*-SGP to DiSGP, dimerization of anthracene derivatives) at a key position in the molecule (gemini spacer group as in SGP; the middle of a bolaform chain as in BTHA). Similarly, large effects are obtained when photolysis of the surfactant takes place (e.g. C₆PAS), where a switch from a hydrophilic (surfactant based) to a hydrophobic (photoproduct) system occurs. Still, there is room for even more sophisticated photosurfactant molecules in one hand, for example by mimicking the most effective conventional surfactants, e.g. introducing chromophores in surfactants such as AOT, and on the other hand the design of environmentally friendly photosurfactants. A starting point for this could be the

design of photo-labile sugar based surfactants. In addition, it has been demonstrated that large aggregation changes can also be induced in mixed systems where the photoactive molecule has been diluted with conventional, non-photoactive surfactants. The possibility of tailor-made light-induced changes has been demonstrated, since by performing the irradiation with UV or visible light in a controlled fashion, a spatially and timely controlled aggregation transition can be achieved. These findings should encourage thoughtful, clever design of photosurfactants, where the collaboration between surfactant science, organic chemistry, and photochemistry will be key.

5. REFERENCES

1. JN Israelachvili, DJ Mitchell, BW Ninham: Theory of self-assembly of hydrocarbon amphiphiles into micelles and bilayers. *J Chem Soc Faraday Trans 2* 72, 1525-1568 (1976)
2. R Nagarajan: Molecular Packing Parameter and Surfactant Self-Assembly. The Neglected Role of the Surfactant Tail. *Langmuir* 18, 31-38 (2002)
3. PGD Gennes: *Scaling concepts in polymer science*. Cornell University Press, Ithaca, New York (1978)
4. ME Cates, SJ Candau: Statics and dynamics of worm-like surfactant micelles. *J Phys: Condens Matter* 2, 6869-6892 (1990)
5. T Imae, S Ikeda: Sphere-rod transition of micelles of tetradecyltrimethylammonium halides in aqueous sodium halide solutions and flexibility and entanglement of long rodlike micelles. *J Phys Chem* 90, 5216-5223 (1986)
6. M Swanson-Vethamuthu, E Feitosa, W Brown: Salt-induced sphere-to-disk transition of octadecyltrimethylammonium bromide micelles. *Langmuir* 14, 1590-1596 (1998)
7. M Pisarcik, F Devinsky, E Svajdenka: Spherical dodecyltrimethylammonium bromide micelles in the limit region of transition to rod-like micelles. A light scattering study. *Colloids Surfaces A* 119, 115-122 (1996)
8. R Zielinski: Sphere-Rod Transition of Micelles in Aqueous NaBr Solutions of Hexadecyltrimethylammonium Bromide. *Pol J Chem* 73, 1819-1826 (1999)
9. D Nguyen, GL Bertrand: Calorimetric observations of the sphere-rod transition of tetradecyltrimethylammonium bromide and sodium dodecyl sulfate: Effects of electrolytes and non electrolytes at 25 and 45°C. *J Colloid Interface Sci* 150, 143-157 (1992)
10. GM Forland, J Samseth, MI Gjerde, H Hoiland, AO Jensen, K Mortensen. Influence of Alcohol on the Behavior of Sodium Dodecylsulfate Micelles. *J Colloid Interface Sci* 203, 328-334 (1998)
11. A Gonzalez-Perez, JM Ruso, G Prieto, F Sarmiento: The self-aggregation of sodium perfluorooctanoate in aqueous solution at different temperatures. *J Surfactants Deterg* 7, 387-395 (2004)
12. K Panchal, A Desai, T Nagar: Sphere-to-Rod Transitions in Cationic Micelles: Quaternary Ammonium Halides+Phenol+Water Systems. *J Disp Sci Technol* 27, 963-970 (2006)
13. G Stainsby, AE Alexander: Studies of soap solutions. Part II.—Factors influencing aggregation in soap solutions. *Trans Faraday Soc* 46, 587-597 (1950)
14. RC Murray, GS Hartley: Equilibrium between micelles and simple ions, with particular reference to the solubility of long-chain salts. *Trans Faraday Soc* 31, 183-188 (1935)
15. WM Gelbart, A Ben-Shaul, D Roux: *Micelles, Membranes, Microemulsions, and Monolayers*. Springer-Verlag, New York, New York (1994)
16. MJ Rosen: *Surfactants and Interfacial Phenomena*. John Wiley & Sons, Inc., Hoboken, New Jersey (2004)
17. Y. Moroi: *Micelles Theoretical and Applied Aspects*. Plenum Press, New York, New York (1992)
18. JB Hayter, J Penfold: Self-consistent structural and dynamic study of concentrated micelle solutions. *J Chem Soc-Faraday Trans I* 77, 1851-1863 (1981)
19. KS Birdi: The size, shape and hydration of micelles in aqueous medium. *Prog Colloid Polym Sci* 70, 23-29 (1985)
20. JW McBain, ME Laing, AF Titley: CXIX.—Colloidal electrolytes: soap solutions as a type. *J Chem Soc* 115, 1279-1300 (1919)
21. K Hess, W Philippoff, H Kiessig: Viskositätsbestimmungen, Dichtemessungen und Röntgenuntersuchungen an Seifenlösungen. *Kolloid-Zeitschrift* 88, 40-51 (1939)
22. J Stauff: Die Mizellenarten wässriger Seifenlösungen. *Kolloid-Zeitschrift* 89, 224-233 (1939)
23. P Ekwall, H Eikrem, L Mandell: The Properties and Structures of Aqueous Sodium Caprylate Solutions. I. The Densities and Partial Specific Volumes. *Acta Chemica Scandinavica* 17, 111-122 (1963)
24. P Ekwall, P Holmberg: The Properties and Structures of Aqueous Sodium Caprylate Solutions. II. The Viscosities of Sodium Caprylate Solutions at 20 degrees C Measured with Capillary Viscometers. *Acta Chemica Scandinavica* 19, 455-468 (1965)
25. P Ekwall, P Holmberg: The Properties and Structure of Aqueous Sodium Caprylate Solutions. III. The Viscosities at Temperatures between 20 degrees and 40 degrees C. *Acta Chemica Scandinavica* 19, 573-583 (1965)

26. P Ekwall, KE Lemstrom, H Eikrem, P Holmberg: The Properties and Structures of Aqueous Sodium Caprylate Solutions. IV. Vapour Pressure of the Solutions and the Osmotic Coefficient of the Sodium Caprylate. *Acta Chemica Scandinavica* 21, 1401-1407 (1967)
27. P Stenius, P Ekwall: The Properties and Structures of Aqueous Sodium Caprylate Solutions. VI. Measurements of the Activity of Sodium Ions. *Acta Chemica Scandinavica* 21, 1643-1646 (1967)
28. P Ekwall, P Stenius: The Properties and Structures of Aqueous Sodium Caprylate Solutions. VII. Activities of Caprylate Anions, and Counter Ion Binding to the Micelles. *Acta Chemica Scandinavica* 21, 1767-1772 (1967)
29. Y Kubota, M Kodama, M Miura: The Second CMC of an Aqueous Solution of Sodium Dodecyl Sulfate. IV. Fluorescence Depolarization. *Bulletin of the Chemical Society of Japan* 46, 100-103 (1973)
30. M Miura, M Kodama: The Second CMC of the Aqueous Solution of Sodium Dodecyl Sulfate. I. Conductivity. *Bulletin of the Chemical Society of Japan* 45, 428-431 (1972)
31. M Kodama, M Miura: The Second CMC of the Aqueous Solution of Sodium Dodecyl Sulfate. II. Viscosity and Density. *Bulletin of the Chemical Society of Japan* 45, 2265-2269 (1972)
32. M Kodama, Y Kubota, M Miura: The Second CMC of the Aqueous Solution of Sodium Dodecyl Sulfate. III. Light-scattering. *Bulletin of the Chemical Society of Japan* 45, 2953-2955 (1972)
33. YS Lee, KW Woo: Micellization of aqueous cationic surfactant solutions at the micellar structure transition concentration—based upon the concept of the pseudophase separation. *J Colloid Interface Sci* 169, 34-38 (1995)
34. A Gonzalez-Perez, J Czapkiewicz, G Prieto, JR Rodriguez: Second critical micelle concentration of dodecyltrimethylammonium chloride in aqueous solution at 25 °C. *Colloid Polym Sci* 281, 1191-1195 (2003)
35. D Attwood, PH Elworthy, SB Kaye: Membrane osmometry of aqueous micellar solutions of pure nonionic and ionic surfactants. *J Phys Chem* 74, 3529-3534 (1970)
36. U Menge, P Lang, GH Findenegg: From oil-swollen wormlike micelles to microemulsion droplets: A static light scattering study of the L-1 phase of the system water plus C12E5 plus decane. *J Phys Chem B* 103, 5768-5774 (1999)
37. WH Richtering, W Burchard, E Jahns, H Finkelmann: Light scattering from aqueous solutions of a nonionic surfactant (C14E8) in a wide concentration range. *J Phys Chem* 92, 6032-6040 (1988)
38. O Glatter, G Fritz, H Lindner, J Brunner-Popela, R Mittelbach, R Strey, SU Egelhaaf: Non-ionic Micelles near the Critical Point: Micellar Growth and Attractive Interaction *Langmuir* 16, 8692-8701 (2000)
39. JH Mu, GZ Li, WC Zhang, ZW Wang: Determination of the second CMCs of dodecyl polyoxyethylene polyoxypropylene ether by the methods of cloud point, fluorescence, and viscosity. *Colloids Surfaces A* 194, 1-6 (2001)
40. G Ilgenfritz, R Schneider, E Grell, E Lewitzki, H Ruf: Thermodynamic and kinetic study of the sphere-to-rod transition in nonionic micelles: Aggregation and stress relaxation in C₁₄E₈ and C₁₆E/H₂O systems. *Langmuir* 20, 1620-1630 (2004)
41. A Gonzalez-Perez, LM Varela, M Garcia, JR Rodriguez: Sphere to rod transitions in homologous alkylpyridinium salts: a Stauff-Klevens-type equation for the second critical micelle concentration. *J Colloid Interface Sci* 293, 213-221 (2006)
42. A Bernheim-Groswasser, R Zana, Y Talmon: Sphere-to-Cylinder Transition in Aqueous Micellar Solution of a Dimeric (Gemini) Surfactant. *J Phys Chem B* 104, 4005-4009 (2000)
43. A Bernheim-Groswasser, E Wachtel, Y Talmon: Micellar Growth, Network Formation, and Criticality in Aqueous Solutions of the Nonionic Surfactant C₁₂E₅. *Langmuir* 16, 4131-4140 (2000)
44. ED Goddard, GC Benson: Conductivity of aqueous solutions of some paraffin chain salts. *Can J Chem* 35, 986-991 (1957)
45. JE Adderson, H Taylor: The temperature dependence of the critical micelle concentrations of cationic surface-active agents. *J Pharm Pharmacol* 23, 311-312 (1971)
46. R Zielinski, S Ikeda, H Nomura, S Kato: Effect of temperature on micelle formation in aqueous solutions of alkyltrimethylammonium bromides. *J Colloid Interface Sci*, 129, 175-184 (1989)
47. EH Crook, GF Trebbi, DB Fordyce: Thermodynamic Properties of Solutions of Homogeneous p,t-Octylphenoxy ethoxyethanols (OPE₁₋₁₀) *J Phys Chem* 68, 3592-3599 (1964)
48. LJ Chen, SY Lin, CC Huang, EM Chen: Temperature dependence of critical micelle concentration of polyoxyethylenated non-ionic surfactants. *Colloids Surfaces A* 135, 175-181 (1998)
49. LJ Chen, SY Lin, CC Huang: Effect of Hydrophobic Chain Length of Surfactants on Enthalpy-Entropy Compensation of Micellization. *J Phys Chem B* 102, 4350-4356 (1998)
50. M Grubic, R Strey, M Teubner: On the application of a laser T-jump apparatus for perturbation of ionic micellar solutions. *J Colloid Interface Sci* 80, 453-458 (1981)

51. W Binana-Limbele, R Zana: Effect of temperature on the aggregation behavior of the nonionic surfactant C₁₂E₈ in H₂O and D₂O solutions. *J Colloid Interface Sci* 121, 81-84 (1988)
52. JR Rodriguez, A Gonzalez-Perez, JL Del Castillo, J Czapkiewicz: Thermodynamics of Micellization of Alkyldimethylbenzyl ammonium Chlorides in Aqueous Solutions. *J Colloid Interface Sci* 250, 438-443 (2002)
53. N Mazer, N. G Olofsson: Calorimetric studies of micelle formation and micellar growth in sodium dodecyl sulfate solutions. *J Phys Chem* 86, 4584-4593 (1982)
54. E Grell, E Lewitzki, R Schneider, G Ilgenfritz, I Grillo, M von Raumer: Phase Transitions in Non-ionic Detergent Micelles. *J Therm Anal Calorim* 68, 469-478 (2002)
55. A Gonzalez-Perez, J Czapkiewicz, J Ruso, JR Rodriguez: Temperature dependence of second critical micelle concentration of dodecylmethylbenzylammonium bromide in aqueous solution. *Colloid Polym Sci* 282, 1169-1173 (2004)
56. A Gonzalez-Perez, JM Ruso, G Prieto, F Sarmiento: Temperature-Sensitive Critical Micelle Transition of Sodium Octanoate. *Langmuir* 20, 2512-2514 (2004)
57. P Garidel, A Hildebrand: Thermodynamic properties of association colloids. *J Therm Anal Calorim* 82, 483-489 (2005)
58. A Sein, JAFN Engberts, E van der Linden, JC van de Pas: Salt-induced transition from a micellar to a lamellar liquid crystalline phase in dilute mixtures of anionic and nonionic surfactants in aqueous solution. *Langmuir* 9, 1714-1720 (1993)
59. R Ranganathan, L Tran, BL Bales: Surfactant- and Salt-Induced Growth of Normal Sodium Alkyl Sulfate Micelles Well above Their Critical Micelle Concentrations. *J Phys Chem B* 104, 2260-2264 (2000)
60. WJ Chen, GZ Li, GW Zhou, LM Zhai, ZM Li: pH-induced spontaneous vesicle formation from NaDEHP. *Chem Phys Lett* 374, 482-486 (2003)
61. M Bergsma, ML Fielden, JBFN Engberts: pH-Dependent Aggregation Behavior of a Sugar-Amine Gemini Surfactant in Water: Vesicles, Micelles, and Monolayers of Hexane-1,6-bis(hexadecyl-1-deoxyglucitylamine) *J Colloid Interface Sci* 243, 491-495 (2001)
62. H Fukuda, A Goto, H Yoshioka, R Goto, K Morigaki, P Walde, P. Electron Spin Resonance Study of the pH-Induced Transformation of Micelles to Vesicles in an Aqueous Oleic Acid/Oleate System. *Langmuir* 17, 4223-4231 (2001)
63. JR McElhanon, T Zifer, SR Kline, DR Wheeler, DA Loy, GM Jamison, TM Long, K Rahimian, BA Simmons: Thermally cleavable surfactants based on furan-maleimide Diels-Alder adducts. *Langmuir* 21, 3259-3266 (2005)
64. H Yin, Z Zhou, J Huang, R Zheng, Y Zhang: Temperature-Induced Micelle to Vesicle Transition in the Sodium Dodecylsulfate/Dodecyltriethylammonium Bromide System. *Angew Chem Int Ed* 42, 2188-2191 (2003)
65. H Sakai, H Imamura, Y Kakizawa, M Abe, Y Kondo, N Yoshino, JH Harwell: Active control of vesicle formation using redox-active surfactant. *Denki Kagaku oyobi Kogyo Butsuri Kagaku* 65, 669-672 (1997)
66. K Tsuchiya, H Sakai, T Saji, M Abe: Electrochemical Reaction in an Aqueous Solution of a Ferrocene-Modified Cationic Surfactant Mixed with an Anionic Surfactant. *Langmuir* 19, 9343-9350 (2003)
67. N Aydogan, NL Abbot: Comparison of the Surface Activity and Bulk Aggregation of Ferrocenyl Surfactants with Cationic and Anionic Headgroups. *Langmuir* 17, 5703-5706 (2001)
68. M Sanchez-Dominguez, J Eastoe, P Wyatt: Photosurfactants New and Old, in: *Self-Assembly*, IOS Press Ohmsha, Amsterdam, The Netherlands, Editor: Brian Robinson; Section II, pgs. 132-143 (2003)
69. J Eastoe, A Vesperinas: Self-assembly of light-sensitive surfactants. *Soft Matter* 1, 338-347 (2005)
70. X Liu, NL Abbott: Spatial and temporal control of surfactant systems. *J Colloid Interface Sci* 339, 1-18 (2009)
71. O Myakonkaya, J Eastoe: Low energy methods of phase separation in colloidal dispersions and microemulsions. *Adv Colloid Interface Sci* 149, 39-46 (2009)
72. N Katsonis, M Lubomska, MM Pollard, BL Feringa, P Rudolph: Synthetic light-activated molecular switches and motors on surfaces. *Prog Surface Sci* 82, 407-434 (2007)
73. H Meier: The Photochemistry of Stilbenoid Compounds and Their Role in Materials Technology. *Angew Chem Int Ed Eng* 31, 1399-1420 (1992)
74. JM Hicks, MT Vandersall, EV Sitzmann, KB Eisenthal: Polarity-dependent barriers and the photoisomerization dynamics of molecules in solution. *Chem Phys Lett* 135, 413-420 (1987)
75. J Schröder, D Schwarzer, J Troe, FJ Voss: Cluster and barrier effects in the temperature and pressure dependence of the photoisomerization of trans stilbene. *J Chem Phys* 93, 2393-2404 (1990)
76. YP Sun, J Saltiel: Application of the Kramers equation to stilbene photoisomerization in n-alkanes using translational diffusion coefficients to define microviscosity. *J Phys Chem* 93, 8310-8316 (1989)
77. V Sundström, T Gillbro: Dynamics of Trans-Cis Photoisomerization of Stilbene in Hydrocarbon Solutions. *Ber Bunsenges Phys Chem* 89, 222-226 (1985)

78. J Schröder, J Troe: Rates of photoisomerization of trans-stilbene in isolated and solvated molecules. *J. Phys. Chem* 1986, 90, 4215-4216.
79. H Rau, E Lueddecke: On the rotation-inversion controversy on photoisomerization of azobenzenes. Experimental proof of inversion. *J Am Chem Soc* 104, 1616-1620 (1982)
80. K Ishihara, N Hamada, S Kato, I Shinohara: Photoinduced swelling control of amphiphilic azoaromatic polymer membrane. *J Polym Sci Polym Chem Ed* 22, 121-128 (1984)
81. Y Okahata, S Fujita, N Iizuka: Bilayer-Immobilized Films Containing Mesogenic Azobenzene Amphiphiles-Electrically Controllable Permeability. *Angew Chem Intl Ed Engl* 25, 751-752 (1986)
82. P Bortolus, S Monti: cis - trans Photoisomerization of azobenzene-cyclodextrin inclusion complexes. *J Phys Chem* 91, 5046-5050 (1987)
83. X Song, J Perlstein, DG Whitten: Supramolecular Aggregates of Azobenzene Phospholipids and Related Compounds in Bilayer Assemblies and Other Microheterogeneous Media. Structure, Properties, and Photoreactivity. *J Am Chem Soc* 119, 9144-9159 (1997)
84. G Hammond, J Saltiel, AA Lamola, NJ Turro, GS Bradshaw, DO Cowan, RS Counsell, V Vogt, C Dalton: Mechanisms of Photochemical Reactions in Solution. XXII. Photochemical *cis-trans* Isomerization. *J Am Chem Soc* 86, 3197-3217 (1964)
85. LB Jones, GS Hammond: Mechanisms of Photochemical Reactions in Solution. XXX. Photosensitized Isomerization of Azobenzene. *J Am Chem Soc* 87, 4219-4220 (1965)
86. E Fisher, M Frankel, RJ Wolovsky: Wavelength Dependence of Photoisomerization Equilibria in Azocompounds. *J Chem Phys* 23, 1367 (1955)
87. GC Hampson, JM Robertson: Bond lengths and resonance in the *cis*-azobenzene molecule. *J Chem Soc*, 409-413 (1941)
88. J Griffiths: II. Photochemistry of azobenzene and its derivatives. *Chem Soc Rev* 1, 481-493 (1972)
89. IR Dunkin, A Gittinger, DC Sherrington, P Wittaker: Synthesis, characterization and applications of azo-containing photodestructible surfactants. *J Chem Soc, Perkin Trans 2*, 1837-1842 (1996)
90. T Mezger, O Nuyken, K Meindl, A Wokaun: Light decomposable emulsifiers: application of alkyl-substituted aromatic azosulfonates in emulsion polymerization. *Progr Org Coat* 29, 147-157 (1996)
91. T Arndt, L Häußling, H Ringsdorf, G Wegner: Photosensitive polymeric amphiphiles: Irradiation-induced structural changes in Langmuir-Blodgett multilayer. *Adv Materials* 3, 58-63 (1991)
92. M Haubs, H Ringsdorf: Photosensitive monolayers, bilayer membranes and polymers. *New J Chem* 11, 151-156 (1987)
93. T Nagasaki, A Taniguchi, S Tamagaki: Photoenhancement of Transfection Efficiency Using Novel Cationic Lipids Having a Photocleavable Spacer. *Bioconjugate Chem* 14, 513-516 (2003)
94. O Nuyken, B Voit: The photoactive diazosulfonate group and its role in polymer chemistry. *Macromol Chem Phys* 198, 2337-2372 (1997)
95. DA Holden, H Ringsdorf, V Deblauwe, G Smets: Photosensitive monolayers. Studies of surface-active spiropyran at the air-water interface. *J Phys Chem* 88, 716-720 (1984)
96. A Veronese, N Berclaz, PL Luisi: Photoinduced Formation of Bilayer Vesicles. *J Phys Chem B* 102, 7078-7080 (1998)
97. M Haubs, H Ringsdorf: Photoreactions of *N*-(1-Pyridinio)amides in Monolayers and Liposomes. *Angew Chem Intl Ed Engl* 24, 882-883 (1985)
98. LD Taylor, HS Kolesinski, B Edwards, M Haubs, H Ringsdorf: The photochemical rearrangement of polymeric *N*-(1-pyridinio) amides. A novel, aqueous photoresist system. *J Polym Sci: Part C: Polym Letters* 26, 177-180 (1988)
99. T Wolff, H Hegewald: Light induced switching of conductivity in AOT-isooctane-water microemulsions via photoreactions of solubilizates. *Colloids and Surfaces A* 164, 279-285 (2000)
100. T Wolff, CS Emming, G von Büнау: Photoreological effects in cationic and nonionic micellar solutions containing methyldiphenylamine. *J Phys Chem* 95, 3731-3735 (1991)
101. HH Hub, B Hupfer, H Koch, H Ringsdorf: Polymerizable Phospholipid Analogues-New Stable Biomembrane and Cell Models. *Angew Chem Intl Ed Engl* 19, 938-940 (1980)
102. X Tong, G Wang, A Soldera, Y Zhao: How Can Azobenzene Block Copolymer Vesicles Be Dissociated and Reformed by Light? *J Phys Chem B* 109, 20281-20287 (2005)
103. J Eastoe, M Sanchez-Dominguez, P Wyatt, A Beeby, RK Heenan: Properties of a Stilbene-Containing Gemini Photosurfactant. Light-Triggered Changes in Surface Tension and Aggregation. *Langmuir* 18, 7837-7844 (2002)

104. J Eastoe, M Sanchez-Dominguez, P Wyatt, AJ Orr-Ewing, RK Heenan: UV Causes Dramatic Changes in Aggregation with Mixtures of Photoactive and Inert Surfactants. *Langmuir* 20, 6120-6126 (2004)
105. (a) FP Hubbard, G Santonicola, EW Kaler, NL Abbott: Small-Angle Neutron Scattering from Mixtures of Sodium Dodecyl Sulfate and a Cationic, Bolaform Surfactant Containing Azobenzene. *Langmuir* 21, 6131-6136 (2005) (b) Hubbard, F. P.; Abbott, N. L. Effect of Light on Self-Assembly of Aqueous Mixtures of Sodium Dodecyl Sulfate and a Cationic, Bolaform Surfactant Containing Azobenzene. *Langmuir* 23, 4819-4829 (2007)
106. T Kunitake, N Nakashima, M Shimomura, Y Okahata, K Kano, T Ogawa: Unique properties of chromophore-containing bilayer aggregates: enhanced chirality and photochemically induced morphological change. *J Am Chem Soc* 102, 6642-6644 (1980)
107. J Eastoe, A Vesperinas, AC Donnewirth, P Wyatt, I Grillo, RK Heenan, S Davis: Photodestructible Vesicles. *Langmuir* 22, 851-853 (2006)
108. H Sakai, A Matsumura, S Yokoyama, T Saji, M Abe: Photochemical Switching of Vesicle Formation Using an Azobenzene-Modified Surfactant. *J Phys Chem B* 103, 10737-10740 (1999)
109. J Eastoe, M Sanchez-Dominguez, P Wyatt, RK Heenan: A photo-responsive organogel. *Chem. Commun.*, 2608-2609 (2004)
110. J Eastoe, P Wyatt, M Sanchez-Dominguez, A Vesperinas, A Paul, RK Heenan, I Grillo: Photo-stabilised microemulsions. *Chem. Commun.*, 2785-2786 (2005)
111. JY Shin, NL Abbott, N. L. Using Light to Control Dynamic Surface Tensions of Aqueous Solutions of Water Soluble Surfactants. *Langmuir* 15, 4404-4410 (1999)
112. M Bonini, D Berti, JM Di Meglio, M Almgren, J Teixeira, P Baglioni: Surfactant aggregates hosting a photoresponsive amphiphile: structure and photoinduced conformational changes. *Soft Matter* 1, 444-454 (2005)
113. T Tanaka, I Nishio, S Sun, S Ueno-Nishio: Collapse of Gels in an Electric Field. *Science* 218, 467-469 (1982)
114. K Minagawa, K Koyama: Electro- and Magneto-Rheological Materials: Stimuli-Induced Rheological Functions. *Curr Org Chem* 9, 1643-1663 (2005)
115. M Zrínyi: Intelligent polymer gels controlled by magnetic fields. *Colloid Polym Sci* 278, 98-103 (2000)
116. ES Gil, SM Hudson: Stimuli-responsive polymers and their bioconjugates. *Prog Polym Sci* 29, 1173-1222 (2004)
117. D Schmaljohann: Thermo- and pH-responsive polymers in drug delivery. *Adv Drug Delivery Rev* 58, 1655-1670 (2006)
118. Vesperinas, A.; Eastoe, J.; Wyatt, P.; Grillo, I.; Heenan, R. K. Photosensitive gelatin. *Chem. Commun.*, 4407-4409 (2006)
119. CT Lee, KA Smith, TH Hatton: Photoreversible Viscosity Changes and Gelation in Mixtures of Hydrophobically Modified Polyelectrolytes and Photosensitive Surfactants. *Macromolecules* 37, 5397-5405 (2004)
120. M Bradley, B Vincent, N Warren, J Eastoe, A Vesperinas: Photoresponsive Surfactants in Microgel Dispersions. *Langmuir* 22, 101-105 (2006)
121. T Wolff, CS Emming, TA Suck, G von Büнау: Photorheological effects in micellar solutions containing anthracene derivatives: a rheological and static low angle light scattering study. *J Phys Chem* 93, 4894-4898 (1989)
122. AM Ketner, R Kumar, TS Davies, PW Elder, SR Raghavan: A Simple Class of Photorheological Fluids. Surfactant Solutions with Viscosity Tunable by Light. *J Am Chem Soc* 129, 1553-1559 (2007)
123. B Song, Y Hu, J Zhao: A single-component photo-responsive fluid based on a gemini surfactant with an azobenzene spacer. *J Colloid Interface Sci* 333, 820-822 (2009)
124. T Wolff, B Klaussner: Overlap of colloid chemistry and photochemistry in surfactant systems. *Adv. Colloid Interface Sci.* 59, 31-94 (1995)
125. D Nees, T Wolff: Interactions of AOT Lyotropic Liquid Crystals and Photochemical Reactions of Hydroxystilbazolium Bromides. Steering Reactions and Switching Phases. *Langmuir* 12, 4960-4965 (1996)
126. D Nees, T Wolff: Influence of solubilized stilbene derivatives in trans and cis configuration on the phase equilibrium hexagonal - isotropic in potassium octanoate - water systems : Light-induced isothermal switching of clearing point. *Colloid Polym Sci* 274, 904-907 (1996)
127. T Wolff, B Klaussner, D Nees: Isothermal Switching of Phases in Lyotropic Liquid Crystalline Surfactant Systems via Photoreactions of Solubilized Molecules. *Ber Bunsen-Ges Phys Chem* 97, 1407-1427 (1993)
128. T Wolff, B Klaussner, D Nees: Photochemically induced phase transitions in lyotropic liquid crystalline surfactant systems. *Progr Colloid Polym Sci* 93, 369-370 (1993)

Temp., conc. And light-induced aggregation changes

129. B Klaussner, D Nees, F Schmidt, T Wolff: Photochemically triggered isothermal phase transitions in lyotropic liquid crystalline systems of anionic and cationic surfactants. *J Colloid Interface Sci* 162, 481-486 (1994)
130. D Nees, M Blenkle, A Koschade, T Wolff, P Baglioni, L Dei: Switching flow and phase behavior in surfactant systems via photochemical reactions. *Progr Colloid Polym Sci* 101, 75-85 (1996)
131. O Tsutsumi, A Kanazawa, T Shiono, T Ikeda, LS Park: Photoinduced phase transition of nematic liquid crystals with donor-acceptor azobenzenes: mechanism of the thermal recovery of the nematic phase. *Phys Chem Chem Phys* 1, 4219-4224 (1999)
132. A Zou, J Eastoe, K Mutch, P Wyatt, G Scherf, O Glatter, I Grillo: Light-sensitive lamellar phases. *J Colloid Interface Sci* 322, 611-616 (2008)
133. Y Orihara, A Matsumura, Y Saito, N Ogawa, T Saji, A Yamaguchi, H Sakai, M Abe: Reversible Release Control of an Oily Substance Using Photoresponsive Micelles. *Langmuir* 17, 6072-6076 (2001)
134. F Rakotondradany, MA Whitehead, AM Lehuis, HF Sleiman: Photoresponsive supramolecular systems: self-assembly of azodibenzoic acid linear tapes and cyclic tetramers. *Chem Eur J* 9, 4771-4780 (2003)
135. A Vesperinas, J Eastoe, P Wyatt, I Grillo, RK Heenan, JM Richards, GA Bell: Photoinduced Phase Separation. *J Am Chem Soc* 128, 1468-1469 (2006)

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