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Association of surfactants and polymers studied by luminescence techniques ☆

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Abstract

Light emission spectroscopy has unique possibilities for the study of central issues of surfactants and associating polymers. With the help of luminescent probes, information may be obtained on matters such as molecular association, microstructure, and molecular dynamics; this constitutes an important contribution to the understanding and control of macroscopic properties, as well as biological function and technical applications. Important aspects of these systems considered in this review are: formation of micelles and hydrophobic microdomains; aggregation numbers of surfactants; shape of molecular aggregates; size of droplets in water or in oil in microemulsions; formation and stability of vesicles; intra- vs. intermolecular association in polymers; conformational changes in polymers; polymer–surfactant association; surfactant organization in adsorbed layers; kinetic aspects regarding the formation and disintegration of self-assembly structures; residence times of molecules in microdomains and migration of active molecules.

Keywords: Surfactants; Polymers; Luminescence techniques

Contents

☆ Dedicated to Professor M. Almgren on the occasion of his 60th Birthday.

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1. Introduction

For the study of the aggregation phenomena in solutions of amphiphilic compounds various fluorescence techniques have stood in the foreground for a long time [1–41]. Here we will not focus on the various photophysical techniques themselves but only consider their study in order to obtain information on microstructure, molecular dynamics and solute transport in various amphiphilic systems, in particular aqueous surfactant and lipid solutions, solutions of amphiphilic polymers and mixed polymer–surfactants systems [19,36–41].

A luminescence study can provide information on the energies involved and on the rates of transitions between different states [42–45]. As we will see it is

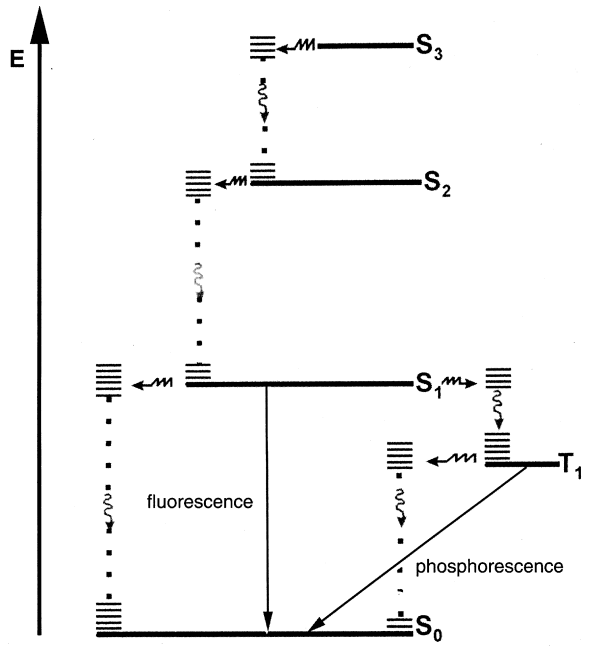


Fig. 1. The Jablonski diagram describes the energy levels and different transitions between states. S and T denotes singlet and triplet states, respectively.

possible, in more or less direct ways, to extract information as diverse as the localization of a molecule in a microstructured system to the dimensionality characterizing the microstructure. While fluorescence techniques have reached broad applications and offer many possibilities the short lifetimes are a frequent limitation; then phosphorescence/luminescence may offer a solution [33,46]. (Fig. 1.)

In many types of studies the luminescent molecule is not an inherent part of the system to be investigated but is added (typically in very small amounts because of the high sensitivity of luminescence techniques) as an extrinsic probe. However, the luminescent molecule can also be intrinsic to the system, like when the hydrophobic grafts of an amphiphilic graft copolymer are aromatic derivatives.

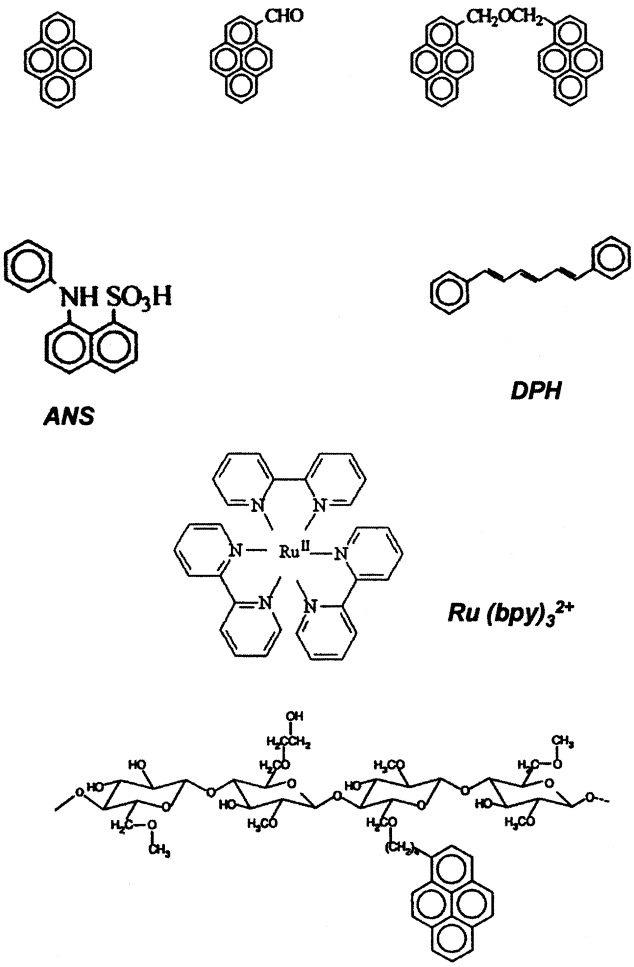


Fig. 2. Examples of fluorescent and luminescent probes commonly used for surfactant and associating polymer systems.

Questions to consider include:

- Formation of microdomains and their aggregation numbers, size and shape.
- Cosolutes in microstructured media with respect to their solubilization,
- localization and migration.
- Transitions between different structures and phases, like from spherical to cylindrical micelles, from micelles to vesicles or from droplet to bicontinuous microemulsions.
- The distinction between intra- and intermolecular association (for polymer solutions)
- The occurrence and nature of conformational transitions.

After excitation of a molecule desactivation can occur in a number of ways, by radiative or non-radiative elimination of the excitation energy, by chemical reactions or by various bimolecular processes, energy transfer, electron transfer and formation of excimers/excited dimers or exciplexes states [42–45].

A large number of luminescence probes have been utilized and we show some examples in Fig. 2 [47].

Luminescence studies of self-assembling systems offer difficult problems of interpretation as can be see from confusion and conflicts between different authors. The one who has most clearly seen the various problems and contributed immensely to the methodological developments is Mats Almgren. In this review of the field, it will not be necessary to particularly point out Mats' contributions.

2. Formation of hydrophobic microdomains

A very straight-forward and useful application of fluorescence is to investigate the presence of hydrophobic microdomains and the formation of different aggregates. A simple application is to use a fluorescent probe to establish the concentration where micelles start to form, by means of some observed spectroscopic property, as the emission quantum yield or lifetime. This is illustrated in Fig. 3 for octyl glucoside. In this work it was also shown that the CMC increases with increasing temperature, in contrast to non-ionic oxyethylene surfactants and it was monitored, by energy transfer between fluorescently labeled lipids, the disintegration of lipid vesicles into micelles induced by a hydrophilic surfactant [48].

The emission spectrum of pyrene depends strongly on the solvent; empirically the relative intensity of two peaks has been related to solvent polarity. The relative intensity of the I and III bands (cf. Fig. 4) is 1.87 in water while it is 0.60 in a hydrocarbon [11,39,40]. In line with this there is a huge difference in the intensity ratio between solutions of a water-soluble polymer and the corresponding hydrophobically modified one (Fig. 5); this illustrates clearly the self-association of the latter and the formation of hydrophobic microdomains. The difference persists in the presence of small amounts of a surfactant but is eliminated at higher surfactant concentration where there is a polymer-induced surfactant micellization.

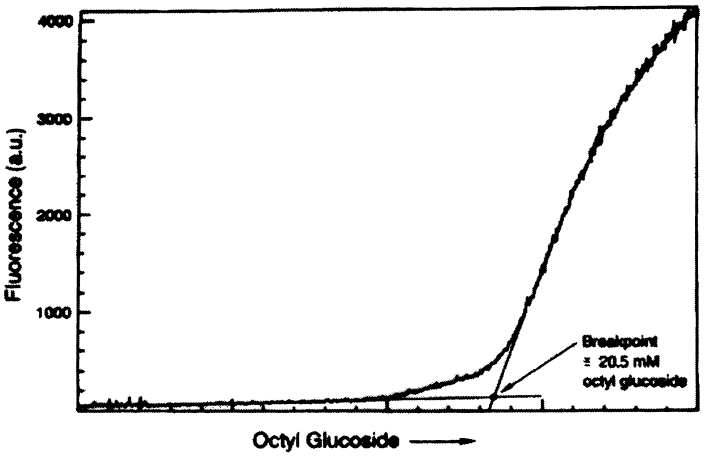


Fig. 3. The fluorescence intensity of anilinonaphthalene sulfonic acid (ANS), in aqueous solutions of octyl glucoside as a function of the surfactant concentration. The intensity starts to increase as micelles start to form (from da G. Miguel et al. [48]).

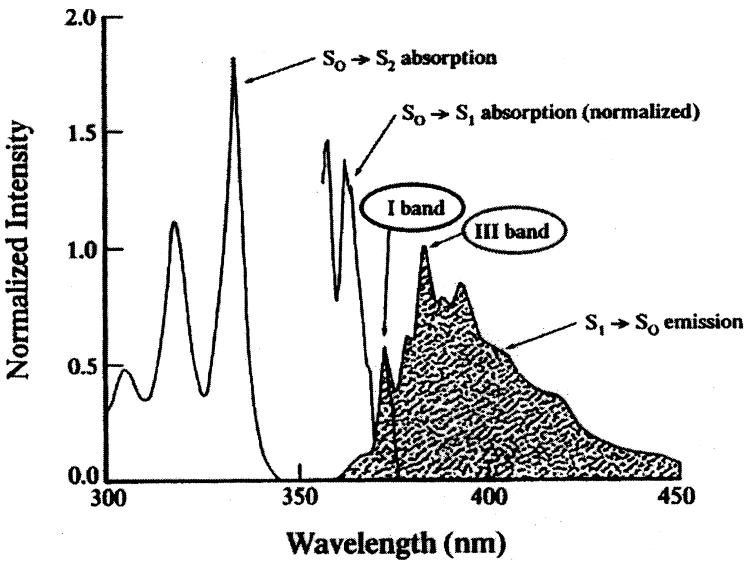


Fig. 4. Fluorescence spectrum of pyrene in a non-polar solvent, cyclohexane. In the emission part there are two prominent bands, I and III, sensitive to the polarity of the environment of the probe. The ratio of the intensities of the two bands are commonly used for probing the formation of hydrophobic microdomains (from Winnik and Regismond [39,40]).

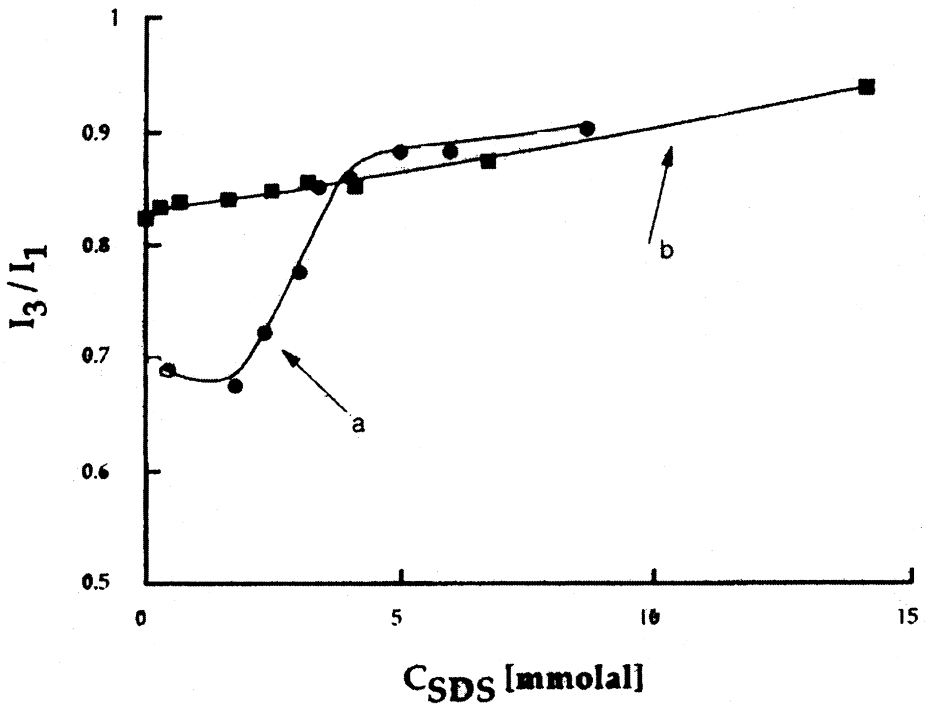


Fig. 5. The intensity ratio of the two pyrene fluorescence bands for aqueous solutions (1% polymer) of two polymers, ethyl hydroxyethyl cellulose (EHEC) and its hydrophobically modified (nonylphenol groups) (HMEHEC). For HMEHEC there are hydrophobic microdomains due to self-association but not for EHEC. On addition of a surfactant, sodium dodecyl sulfate (SDS), there is at a certain concentration (cac), formation of hydrophobic microdomains also with EHEC, due to polymer-induced surfactant micellisation. Reproduced with kind permission of K. Thuresson.

3. Excimer formation

The association of an excited molecule with a non-excited one into an excimer can be reflected in dramatic changes in the emission spectrum as illustrated for pyrene in Fig. 6. The pyrene spectrum in *n*-heptane is dominated by the monomer for low concentration, while at higher concentration the excimer spectrum dominates [43].

A comparison between excimer and monomer emission reflects in a direct way various association processes. In a hydrophobically modified polymer, intra- or interchain hydrophobic association is important and of direct relevance for the function of these compounds in different applications like for rheology control. As illustrated in Fig. 7, with hydrophobically modified poly(*N*-isopropylacrylamide), the excimer peak is strong in water reflecting the importance of hydrophobic associations. Addition of a surfactant, like sodium dodecyl sulfate, efficiently eliminates the excimer bands while the monomer bands increase strongly in

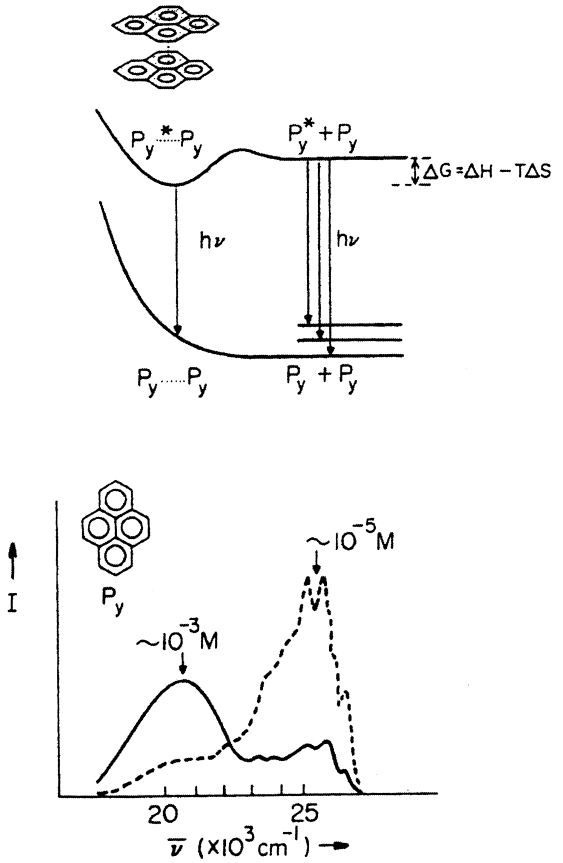


Fig. 6. Complex formation of the fluorescent probe, in this case pyrene, can strongly influence the fluorescence emission spectrum. Association between an excited molecule and a ground-state molecule, excimer formation, leads to a new spectral band. In a non-polar solvent, *n*-heptane, excimer formation is insignificant at low concentrations but very important at high concentrations (from Turro [43]).

intensity [39,40]. This illustrates nicely the (cooperative) self-assembly of the surfactant induced by the polymer chain; micelle formation along the polymer chain leads to a highly charged polymer–surfactant complexe with a high persistence length and an effective repulsion between different parts of a polymer chain and between different polymer molecules.

Hydrophobically modified polyacrylic acid offers a nice illustration to the control of this polymer–polymer association (Fig. 8). At low pH in water when the polymer is predominantly in the non-ionic state and hydrophobic association is strong, the excimer peak has a high intensity. Ionizing the polymer by increasing the pH reduces strongly the excimer peak since the polymer molecules become more extended and more repulsive. Addition of electrolyte screens the electrostatic repulsions and allows association to occur. In another solvent than water hy-

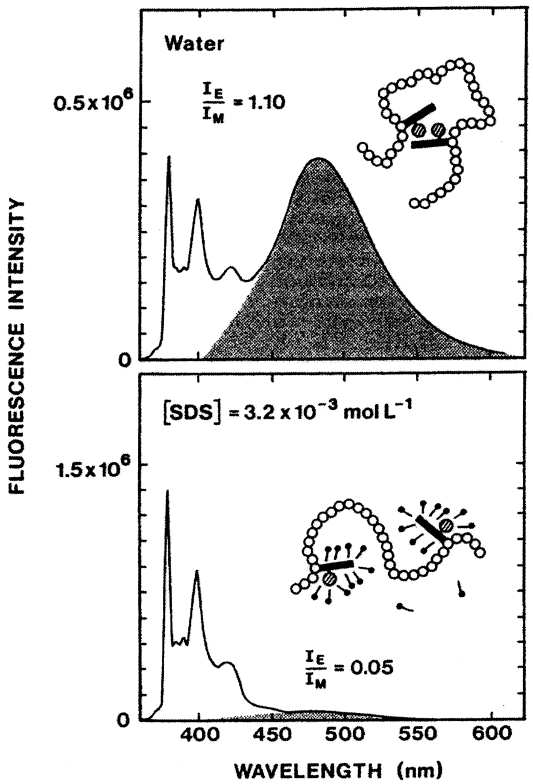


Fig. 7. The pyrene excimer formation, and thus the fluorescent emission spectrum, in solutions of pyrene-labeled poly(*N*-isopropylacrylamide) reports on hydrophobic polymer–polymer association, at low concentrations dominated by intra-chain association. The excimer-to-monomer intensity ratio decreases strongly on binding of an ionic surfactant (here SDS), due to the charging up of the polymer chain and concomitant intra-chain repulsions (from Winnik and Regismond [39,40]).

drophobic association is weak or absent; therefore, as here illustrated for methanol, the excimer peak has very low intensity [49].

4. Aggregation numbers from fluorescence quenching

The quenching of the fluorescence of a probe molecule will be modified if the probe is confined in a microdomain, like a micelle or a microemulsion droplet. From the fluorescence decay the concentration of microdomains can be obtained and indirectly then the aggregation number; fluorescence quenching is a unique and quite generally applicable technique for determining aggregation numbers of micelles. Both static and dynamic fluorescence quenching may be used, the latter being much more reliable and complete in its description [4–7,14,21,33,36].

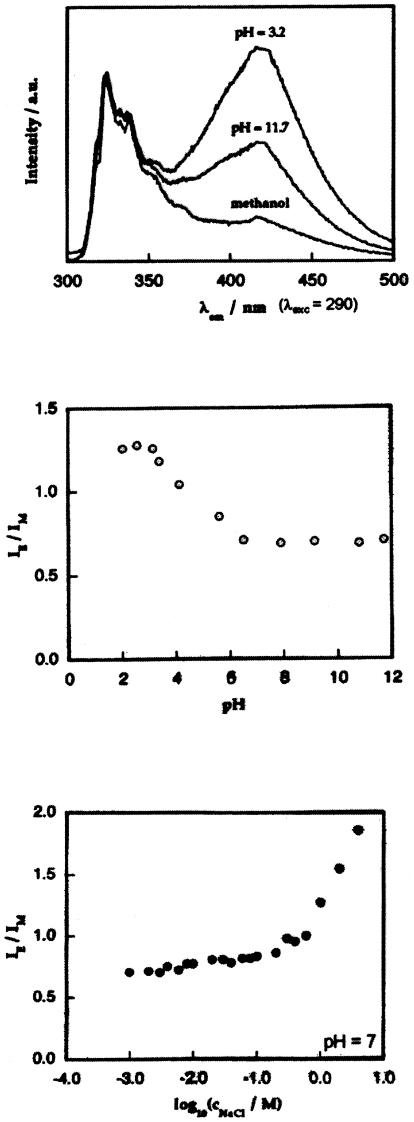


Fig. 8. Here is offered another illustration of conformational changes in solutions of pyrene-labeled polyacrylate using the excimer and monomer band intensities. The upper figure shows that intra-chain association is strong at low pH when the polymer has a low charge density but weaker at high pH when the polymer is charged and has an extended conformation. In methanol, hydrophobic association is insignificant and excimer formation inhibited. The middle figure illustrates the reduction in excimer formation on charging up the polymer and the lower figure the screening of the electrostatic repulsion on adding salt (from Schillén et al. [49]).

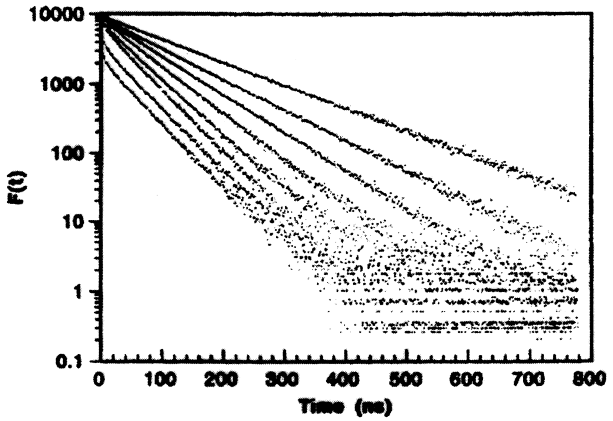


Fig. 9. Time-dependent fluorescence intensity of pyrene in solutions of a cationic surfactant, *N*-(1,1,2,2-tetrahydroperfluorodecyl pyridinium chloride, which is also an efficient quencher. As the concentration of surfactant increases, the fluorescence decay becomes non-exponential and the quenching more efficient (from Almgren et al. [50]).

Many studies are performed with pyrene as fluorescence probe and a suitably selected extrinsic quencher. Fig. 9 describes a cleverly designed experiment with pyrene as probe and with an intrinsic cationic surfactant as quencher [50]. Without surfactant, fluorescence decay is monoexponential since there is no confinement. In the presence of micelles, decay is non-exponential and from the decay curves at different quencher concentrations the number of micelles is obtained.

In a general case of a micellar solution containing low concentrations of a luminescence probe and of a quencher, there are 'empty' micelles, micelles with either luminescent probe or quencher and micelles with both probe and quencher (Fig. 10). The luminescence intensity can be under certain conditions be assumed to be proportional to the concentration of probe molecules in micelles, which contain no quencher. The determination of aggregation number is straightforward in the simplest version of the approach where the micelles are small and monodisperse, the probe and quencher distribution follows a Poisson distribution, the probe and quencher are stationary and do not migrate between micelles on the time-scale of the experiment and there is a total quenching in micelles with quencher [33].

The study represented in Fig. 11 illustrates the experimental decay curves and the evaluation for the case of sodium dodecyl sulfate micelles [50]. The probe is again pyrene and the quencher a cationic surfactant in low concentration. From the non-exponential decay parameters, which include the rate constant and fractional intensity corresponding to quenching in micelles, the concentration of hydrophobic microdomains and thus the aggregation number is obtained.

The fluorescence quenching technique has been instrumental in advancing our understanding of micellar systems and aggregation numbers have been determined

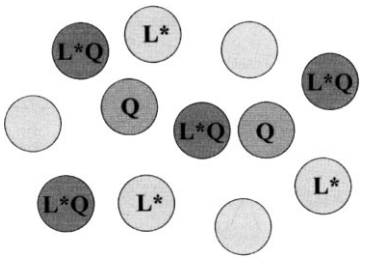
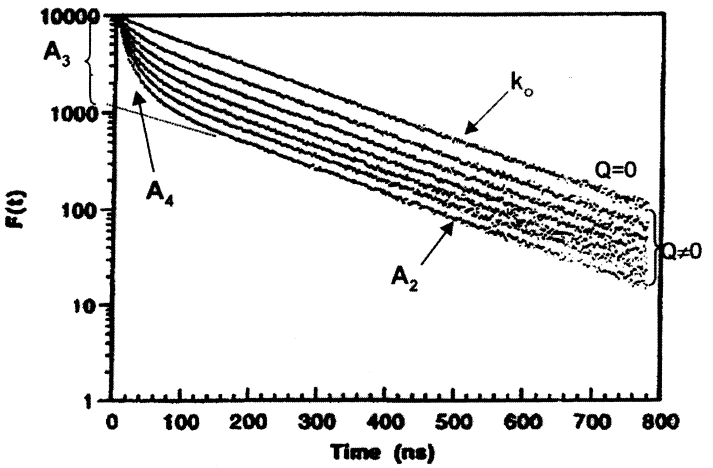


Fig. 10. In luminescence quenching experiment to determine aggregation numbers, there are micelles/microdomains which are 'empty', contain only luminescence probe, only quencher or contain both probe and quencher. To a first approximation, i.e. in the absence of probe or quencher migration, the degree of quenching is related only to the concentration of micelles containing both probe and quencher.

for a very large number of surfactants. Even more important has been the information furnished on more complex systems. A simple example is the effect of various cosolutes — electrolytes, hydrophobes and cosurfactants — on aggregation numbers. Very significant are the studies of surfactant aggregation in solutions of



$$\ln (F(t)/F(o)) = - A_2 t + A_3 (\exp (- A_4 t) - 1)$$

Fig. 11. Time-dependent fluorescence intensity of pyrene in solutions of sodium dodecyl sulfate with different concentrations of a cationic surfactant, *N*-(1,1,2,2-tetrahydroperfluorodecyl pyridinium chloride, which is also an efficient quencher. With increasing concentration of quencher the intensity decreases, which allows the determination of the micellar aggregation number (from Almgren et al. [50]).

polymers and on interfaces. Mixed polymer–surfactant solutions — originally commonly described in terms of a cooperative binding of surfactant to the polymer — were shown to be characterized by polymer-induced surfactant self-assembly into aggregates of finite size and with aggregation numbers similar to those formed in the absence of polymer: the 'pearl-necklace' model [51–53]. Surfactant adsorption on polar surfaces was in the literature generally described in terms of formation of monolayers and bilayers but fluorescence quenching studies by Levitz [54] gave the first conclusive evidence for the picture of surfactant adsorption in terms of surface-induced micelle formation into discrete aggregates. Recent studies from Almgren's laboratory [55,56] verify the general applicability of this picture and illustrate that surface — self-assembly sizes vary in qualitatively the same way as bulk aggregates.

5. Micelle aggregation numbers in mixed-polymer surfactant solutions

We will dwell a little more on aggregation numbers in mixed polymer–surfactant solutions since they have shown to be significant in understanding and controlling the rheology of industrial formulations. Hydrophobically modified polymers in aqueous solution gives a very important increase in viscosity; for a 1% solution the viscosity increase obtained on grafting one or a few percent of hydrophobes on the polymer monomer units typically is one order of magnitude. A surfactant in low concentration can produce further increases in viscosity by orders of magnitude and for many systems induce gelation. However, as illustrated in Fig. 12 the viscosity increase is typically limited to a quite narrow range of concentrations; at higher surfactant concentrations it decreases to quite low levels. The explanation to this behavior was offered in studies by Piculell [57,58] relating the rheology to the surfactant binding isotherm and the surfactant to polymer hydrophobe stoichiometry. For the system of Fig. 12 the concentration of hydrophobic aggregation microdomains was determined by the fluorescence quenching method [59]. The number of polymer hydrophobes per hydrophobic microdomain is roughly 10 in the absence of surfactant. A very important observation is that on surfactant addition there is virtually no change in the concentration of hydrophobic microdomains; as surfactant is binding it enters existing aggregates and increase their aggregation numbers. However, for a hydrophilic surfactant like sodium dodecyl sulfate there is maximum in the micellar size due to strong repulsion between hydrophilic headgroups. As this maximum is obtained addition of surfactant leads to an increase in the number of micelles. As the number of micelles increases there is a dilution of polymer hydrophobes in the micelles; this leads clearly to a viscosity decrease and as the number of hydrophobes per micelle is reduced to ca. one all cross-linking between polymer chains and formation of a three-dimensional network is lost. Then the viscosity drops to low values.

While for some applications this strong dependence of viscosity on formulation composition may be useful it is normally a problem and makes properties strongly dependent on a very accurate control of composition and purity of components.

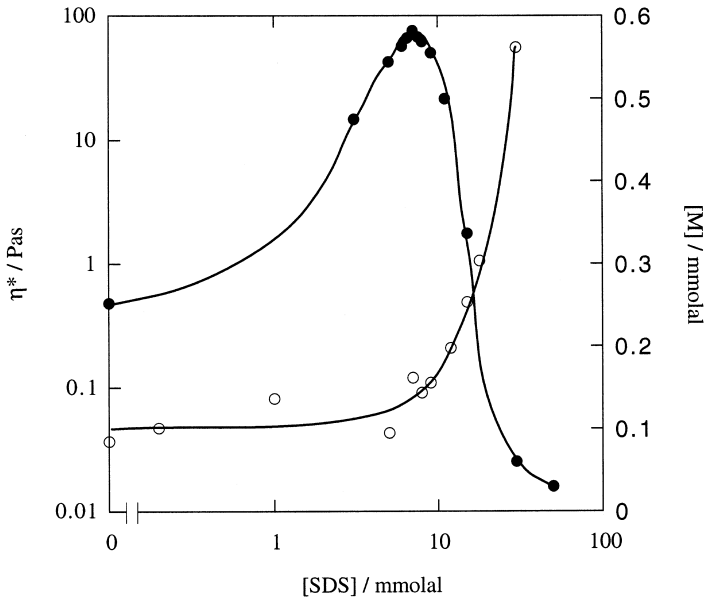


Fig. 12. The fluorescence quenching technique has considerably helped in understanding surfactant self-assembly in the presence of water-soluble polymers. In solutions of a non-ionic hydrophobically modified cellulose ether (HM-EHEC), the concentration of micelles/hydrophobic microdomains stays constant on addition of an anionic surfactant (SDS) over a wide concentration and then increases. As surfactant binds into the micelles there is at first a very important viscosity increase due to the re-enforcement of the interpolymer crosslinks. As the micelle concentration increases, and the number of polymer hydrophobes per micelle decreases, the crosslinking is progressively eliminated and the viscosity decreases (from Nilsson et al. [59]).

Apparently we would be able to eliminate the drop in viscosity at high surfactant concentrations if surfactant addition would lead to aggregate growth rather than to an increased number of aggregates. Ionic surfactant micelles are know to grow on addition of electrolyte, oppositely charged surfactant, a polar or polarizable solubilizate, etc. Fig. 13 demonstrates that the addition of a cationic surfactant to sodium dodecyl sulfate leads to micellar growth and a reduced number of micelles and, consequently, to a viscosity increase [59].

6. Solute migration

Complications in the determination of aggregation numbers occur when the above-mentioned simple conditions do not apply. In particular we have to consider changes in micelle size and shape, phase transitions, and polydispersity [5–7,33,36]. However, one problem that deserves special attention is the possibility that a probe or quencher is not stationary in an aggregate but migrates on the time scale of the

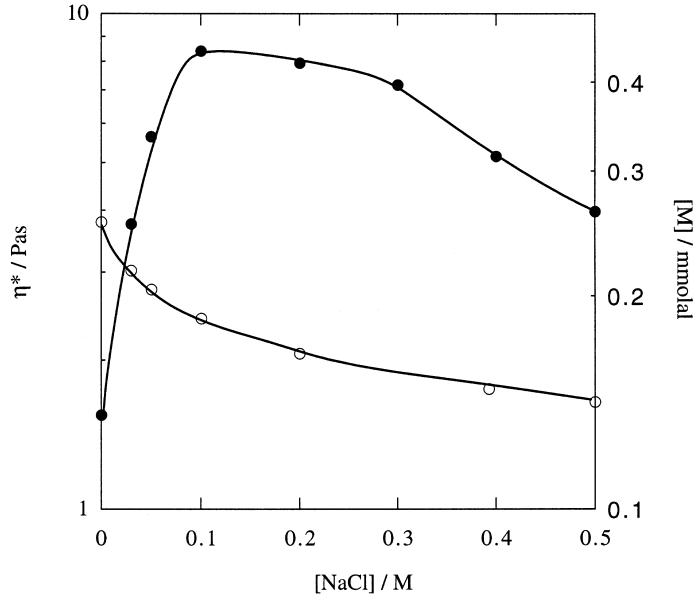


Fig. 13. On addition of an oppositely charged surfactant to the system of Fig. 12, there is a micellar growth and a decrease in the micellar concentration. This results to an increased number of polymer hydrophobes per micelle and an enhanced crosslinking (from Nilsson [59]).

experiment [60]. This problem has been addressed both for micellar solutions and for microemulsions. Migration can result from a number of processes and literature discusses deviations from a simple behavior in terms such as collisions, sticky collisions, 'clusters', coagulation–fragmentation, fusion–fission and molecular 'jumps'. The situation is clearly confused and analyses often in conflict with independent evidence or even what is physically possible.

However, an important step forward was taken in classical studies by Mats Almgren [33]. In considering the time-scale problem he realized the need of probes with longer lifetimes than pyrene and developed further oriented studies with phosphorescent probes [46], some used before by others [9,12,15,18]. Fig. 14 offers a nice example and an illustration of difficulties [60]. The probe of this water-in-oil microemulsion system has a lifetime of approximately 25 μs and, as can be seen, three different processes can be distinguished if the system is followed over long enough times. The first, on a nanosecond time-scale, is attributed to intradroplet quenching, the second to intracluster quenching, while the third one relates to intercluster quenching.

These problems of transfer of probe and quencher between aggregates still await a complete analysis but a recent summary of Mats Almgren (cf. Fig. 15) identifies different mechanisms and gives a good starting-point for an important issue [61]. In the present author's opinion there is in literature frequently a neglect of a possible microdomain growth.

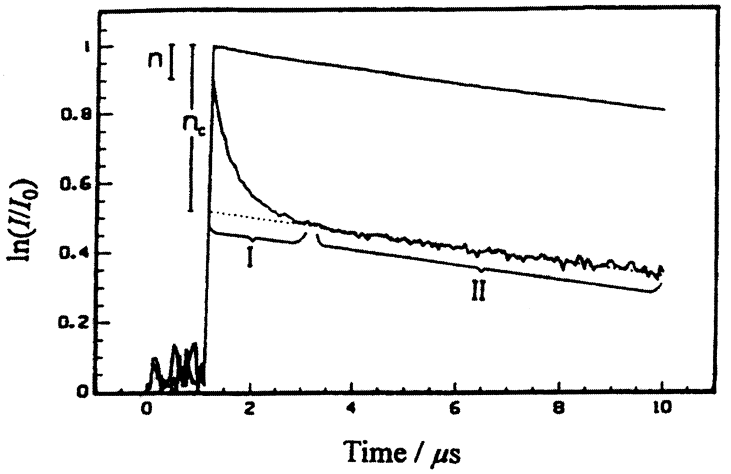


Fig. 14. Aerosol OT forms W/O microemulsions in mixtures with water and a hydrocarbon. The luminescence intensity of a probe, Cr(bpy)33 + , in the presence of quencher, I-, shows a complex time dependence, indicating distinct quenching processes (from Jóhannsson et al. [60]).

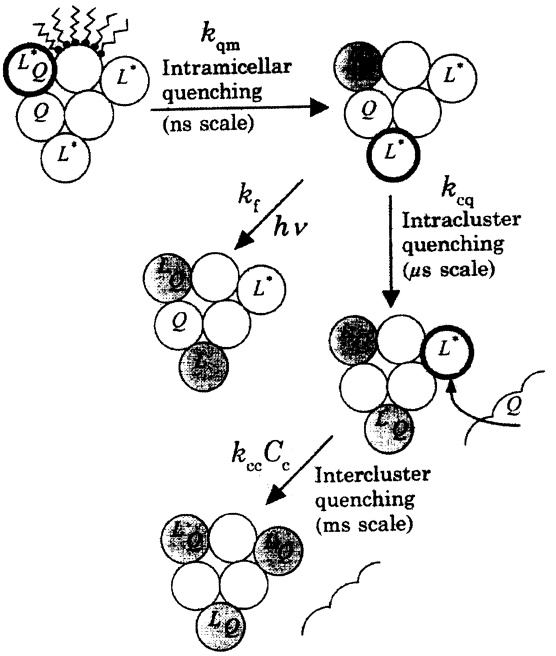


Fig. 15. In their analysis of luminescence decays curves of microemulsions, the authors onsidered quencher migration and droplet clustering, and analyzed the results in terms of intramicellar, intracluster and intercluster quenching (from Almgren and Mays [61]).

7. Dimensionality of aggregates

Luminescence studies of surfactant self-assembly systems have often taken a very restricted view in assuming that all systems are built up of discrete aggregates of a spherical. This has not only lead to some serious misinterpretation [33,36] and considerable confusion, but has also excluded work on many of the more interesting and intriguing problems. Mats Almgren, with his broad understanding and perception of surfactant self-assembly, has been rather unique in the field of discussing other than spherical self-assemblies and connected structures [62,63]. However, a consideration of other than spherical droplets has not yet been extensively discussed in the field of microemulsions.

A simple classical example is given in Fig. 16. In solutions of hexadecyl trimethylammonium chloride and sodium chlorate the decay curves differ from the normal behavior and a more gradual change in curvature is seen. The behavior gives direct evidence for a growth of micelles from small spherical to elongated thread-like or cylindrical micelles as chlorate is added [62].

Unidimensional growth is but one possibility. Mats Almgren clearly identified that luminescence techniques would be uniquely adapted to clarify the dimensionality of aggregates. We can distinguish between the following cases:

- 0 D — Spherical micelles, or microemulsion droplets.
- 1 D — Cylindrical micelles or microemulsion droplets.
- 2 D — Bilayers in lamellar liquid crystalline phase.
- 3 D — Neat liquid surfactant or bicontinuous structures.

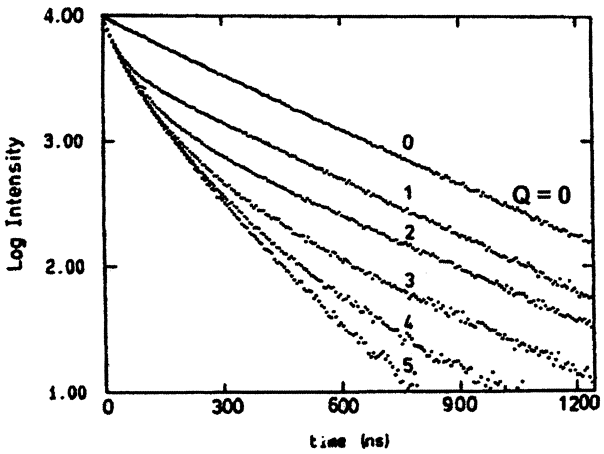


Fig. 16. The transition from spherical micelles to cylindrical ones can be efficiently monitored in fluorescence quenching experiments. This study illustrates the growth of micelles of hexadecyl trimethyl ammonium chloride on addition of sodium chlorate as followed in dynamic fluorescence quenching experiments using pyrene as a probe and benzophenone as a quencher (from Almgren et al. [62]).

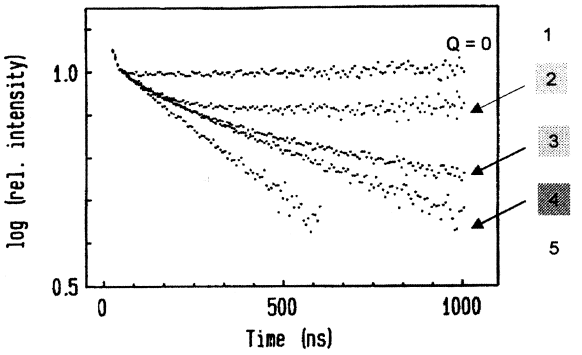


Fig. 17. The shapes of the time-resolved luminescence decay curves are directly related to the dimensionality of a surfactant self-assembly. This is illustrated here for a non-ionic surfactant (C12E6) with pyrene as probe and hexylbenzophenone as quencher. Curves 1–5 exemplify, respectively: no quencher; O D — spherical micelles; 1 D — cylindrical micelles; 2 D — lamellar phase; 3 D — neat surfactant (from Almgren and Alsins [63]).

The case of non-ionic surfactants proved to nicely illustrate the relation between decay curves and aggregate dimensionality and is taken as an example in Fig. 17 [63]. Fig. 18 provides a simulation of the same problem [34,64].

8. Fluorescence microscopy of polymer–surfactant association

From these examples the breadth of luminescence techniques with respect to problems addressed should emerge. As the final example, let us consider a case of

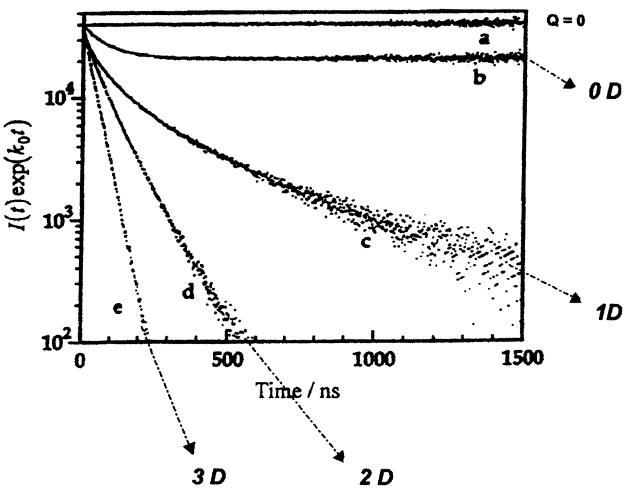


Fig. 18. Illustrates a numerical simulation related to Fig. 17 of the effect of dimensionality of the aggregates on the fluorescence decay curves (from Medhage and Almgren [64]).

direct visualization of conformational changes resulting from polymer–surfactant interactions. Using fluorescence microscopy we can directly image the distribution of added fluorescent molecules in the system. If the fluorescing molecules are associated to polymer molecules we can probe the location of the polymer

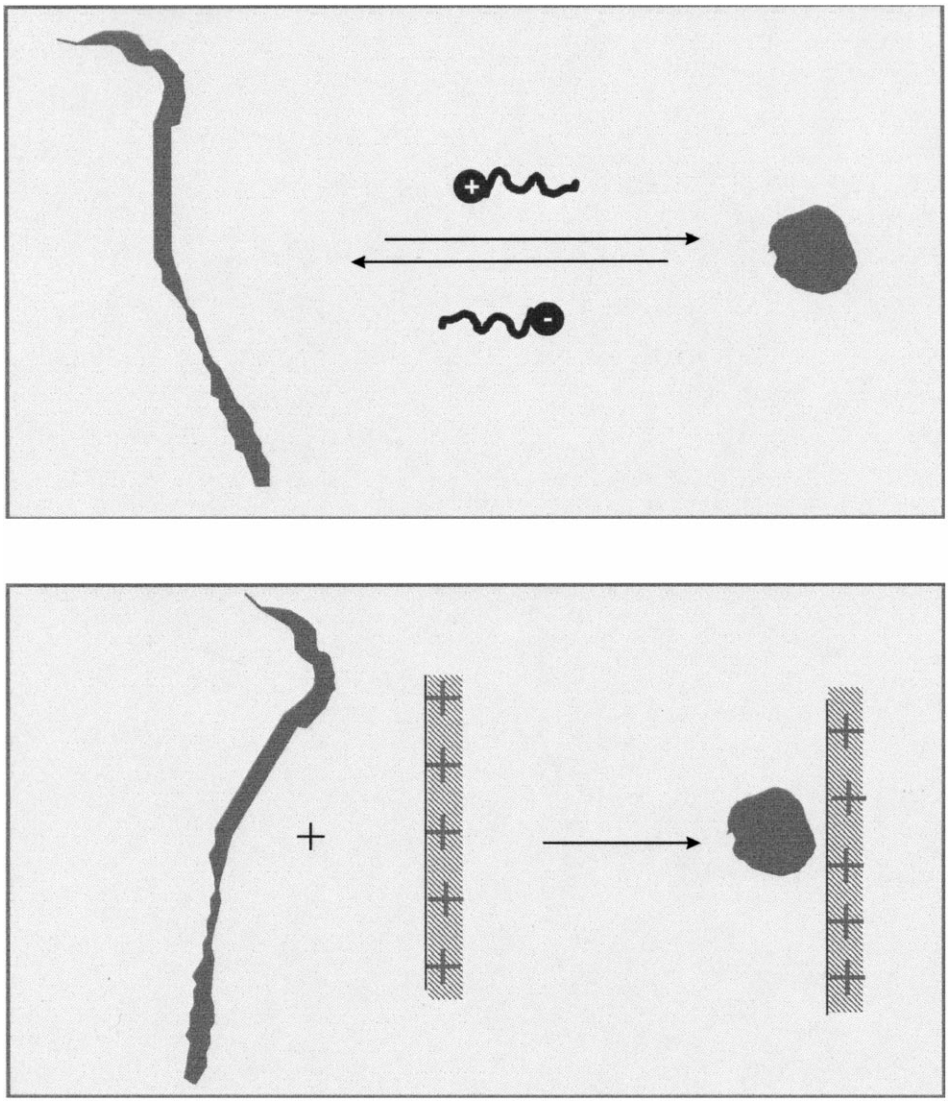


Fig. 19. DNA has due to its high charge density as well as a considerable stiffness an extended conformation, 'coil', in aqueous solution. Binding of a cationic surfactant (in a self-assemblied state) induces DNA compaction into 'globules'; this can be reversed by an anionic surfactant. DNA compaction can also occur on a positively charged surface.

molecules. For a high molecular weight polymer like DNA we can go a step further and map the location of different parts of the molecule and get an image of its shape [65,66].

For some of the most promising developments in gene delivery, compaction of DNA molecules is considered to be critical. Compaction, i.e. a change over from an

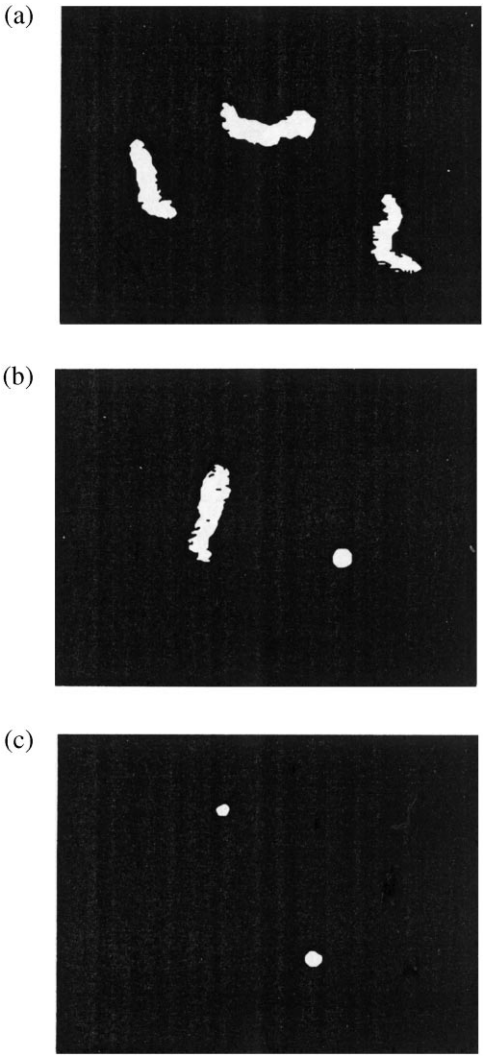


Fig. 20. Due its high molecular weight, DNA compaction can be imaged by fluorescence microscopy if a fluorescent probe is bound to DNA. In the absence of cationic surfactant (upper photo), DNA has an extended coil conformation, while it occurs as compact coils at high concentrations of cationic surfactant (lower photo). At intermediate concentrations of surfactant there is coexistence between coils and globules (middle) (from Mel'nikov et al. [65,66]).

extended state, 'coil', to a compact state, 'globule', can be effected in a number of ways [67,68]. Here we will consider two of the more intriguing ones, that due to the binding to DNA of a cationic surfactant and that due to a positively charged surface, for example of a vesicle (Fig. 19).

The compaction of DNA due to the association of cationic surfactants can easily be monitored as a function of time and surfactant concentration by fluorescence microscopy [69]. One notable feature of the compaction is the coexistence at

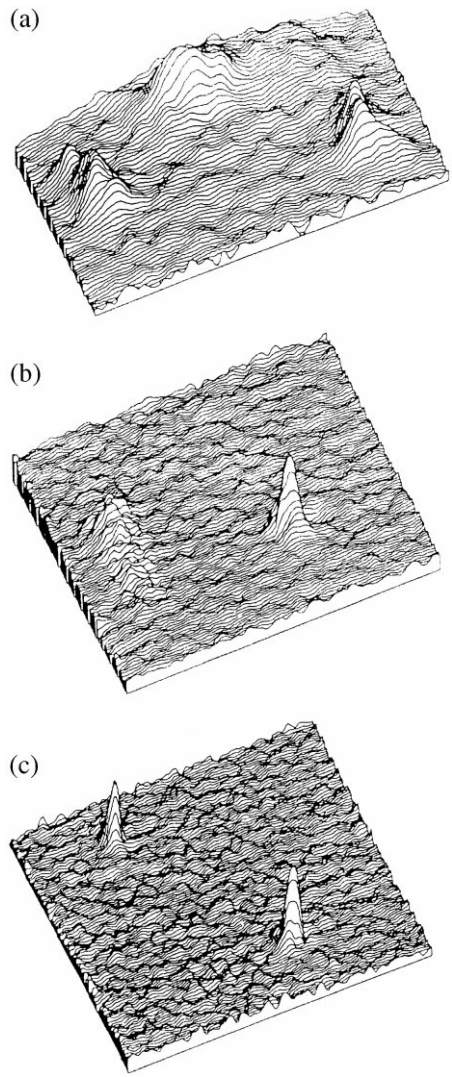


Fig. 21. Gives an alternative visualization of the DNA compaction imaged by fluorescence microscope (from Takahashi et al. [67] and Mel'nikov et al. [68]).

intermediate surfactant concentrations of coils and globules (Figs. 20 and 21). This coexistence is by no means trivial and points, in addition to a well understood cooperative surfactant binding to DNA, to the significance of attractive interactions between different segments of a DNA molecule; these attractions appear to involve electrostatic correlation effects.

Further features of DNA compaction that have been visualized by fluorescence microscopy include the decompaction effected by an anionic surfactant and the compaction induced by cationic polymers. In the presence of thermodynamically stable vesicles composed of cationic and anionic surfactant, but with a net positive charge, we can observe the compaction of DNA on the surface of the vesicle (Fig. 22) [70].

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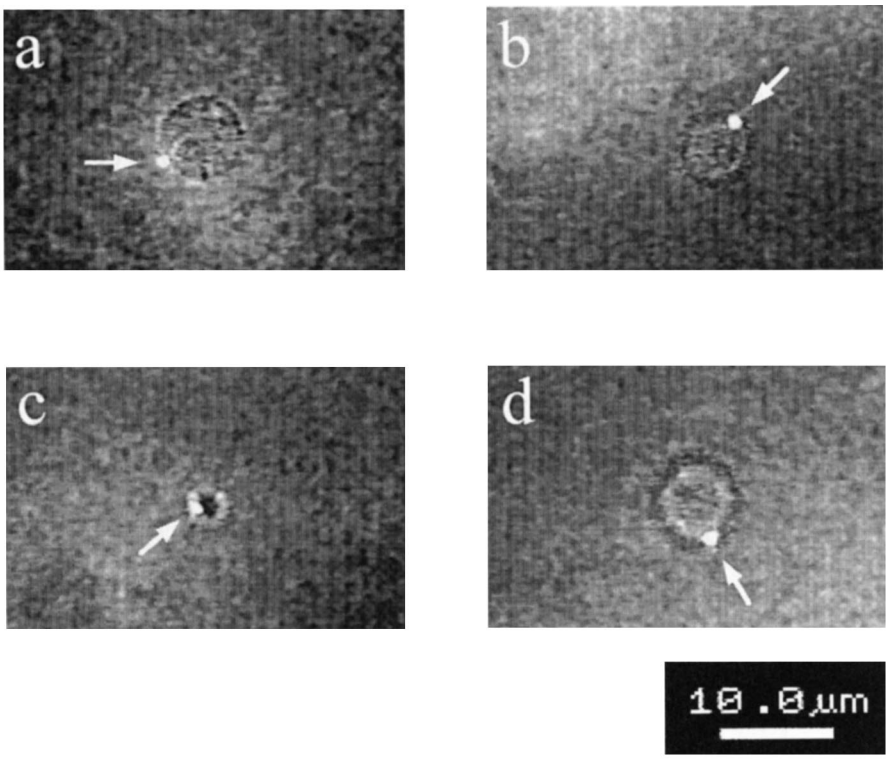

Fig. 22. DNA compaction occurs on surfactant (in this case mixed cationic and anionic) vesicles with a net positive charge (from Mel'nikov et al. [70]).

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