Chapter 1

General Introduction

General Introduction

1.1 Surfactants and Micelles

The self association process of surfactant molecules into micelles, vesicles or membranes plays an important role in many fields ranging from biological systems to technical applications. This aggregation, as well as protein and nucleic acid folding and their association, is governed by the intricate balance between hydrophobioc interactions and other types of noncovalent solute-solute and solute-solvent interactions [1-3]. This interest continues to grow because of the flexibility of the properties of these surfactants. A surfactant (a contraction of the term "surface active agent") is a substance that shows ability to adsorb at interfaces. The surfaces (interfaces), at which surfactants adsorb, can be between two immiscible liquids, the liquid-gas (air) surface or between a solid and a liquid. The surfactants are also often called amphiphiles, surface-active agents or "soft-matter". Surfactant molecules have two parts: a hydrophilic (polar) part which likes water, and a hydrophobic (non-polar) part which does not. The amphiphilic nature of these molecules results in many unique phenomena when surfactants are dissolved in aqueous or non-aqueous solutions. In the case of a surfactant dissolved in aqueous medium, the lyophobic (hydrophobic) group distorts the structure of the water by breaking hydrogen bonds between the water molecules and results an orientation of the water in the vicinity of the hydrophobic group. As a result of this distortion some of the surfactant molecules are expelled to the interfaces of the system with their hydrophobic groups oriented so as to minimize contact with the water molecules. The concentration above which aggregate (known as micelle) formation becomes appreciable is termed critical micelle concentration (cmc).

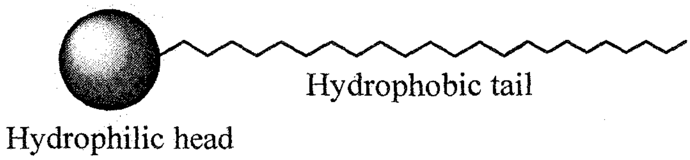


Figure 1.1 Schematic representation of a surfactant molecule

The hydrophobic part of a surfactant is usually a long-chain hydrocarbon residue, and less often halogenated or oxygenated hydrocarbon or siloxane chain. The hydrophilic group on the other hand is an ionic or highly polar group. Depending on the nature of the hydrophilic groups, surfactants are classified as:

(i) *Anionic.* The surface-active portion of the molecule bears a negative charge, e.g. $RCOO^-Na^+$ (soap), $RC_6H_4SO_3^-Na^+$ (alkyl benzene sulfate).

(ii) *Cationic.* The surface-active portion of the molecule bears a posetive charge, e.g. RNH_3^+ (salt of long chain amine), $RN(CH_3)_3^+Br^-$ (quarternary ammonium bromide).

(iii) *Zwitterionic.* Both positive and negative charges may be present in the surface-active portion, e.g. $RN^+(CH_3)_2CH_2CH_2SO_3^-$ (sulfobetaine), $RN^+H_2CH_2COO^-$ (long-chain amino acid).

(iv) *Nonionic.* The surface active portion bears no apparent ionic charge, e.g. $RCOOCH_2CHOHCH_2OH$ (monoglyceride or long chain fatty acid), $RC_6H_4(OC_2H_4)_xOH$ (polyoxyethylenated alkylphenol).

Although surfactants are often present in very small amounts in solution, they do affect the overall properties of the system greatly, such as surface tension, osmotic pressure, solubility, etc., because of their ability to adsorb at surfaces and to form micelles in the solutions. In fact, a large number of experimental observations can be summed up and almost all physicho-chemical properties versus concentration plots for a given surfactant-solvent system will show an abrupt change in slope in a narrow concentration range (the cmc value), that can be illustrated by a classic graph [3], shown in Figure 1.2. The characteristics of surfactants have attracted huge attention from the scientific community. For example, in 1991, de Gennes's Nobel Lecture was on "Soft Matter", i.e. polymers, surfactants and liquid crystals.

The term "micelle" is used for an entity of colloidal dimensions, in dynamic equilibrium with the monomer from which it is formed. As the surfactant concentration increases above the cmc, the addition of fresh monomer results in the formation of new micelles, so the monomer concentration remains essentially constant and approximately equal to the cmc. Water has an open structure because of three dimensional hydrogen bonding, which permits the existence of clusters of water molecules containing cavities of specific sizes which can accommodate non-polar chains [3-5].

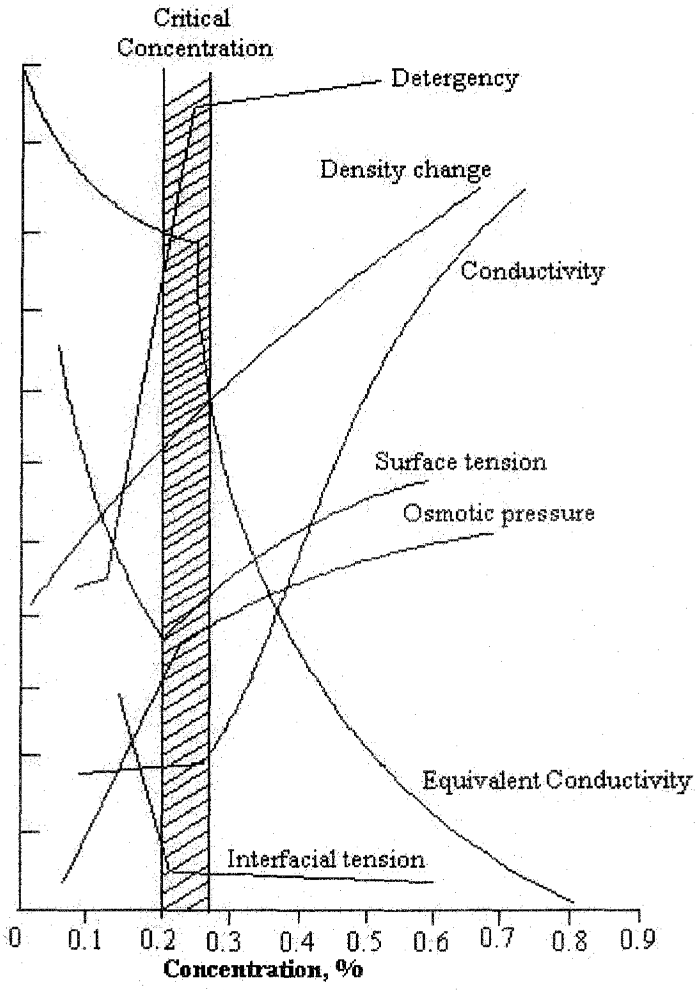


Figure 1.2 Schematic representation of the concentration dependency of some physical properties for solutions of a micelle forming surfactant.

Creation of the cavity restricts the motions of solvent molecules in the hydration shell of a nonpolar solute. This restriction leads to loss of entropy, which is exceptionally large in aqueous solution due to the small size of water molecules [4-9]. For a given surfactant, at a given temperature, only a certain amount of monomer can be accommodated in the cavities and any further addition of surfactant will result in the formation of micelles. In other words, the further addition of surfactant provides a driving force to minimize contact of the monomer hydrocarbon chains with water. Therefore, according to Langmuir's principle of differential solubility, the hydrocarbon chains clusters to form a core (micellar core) while the polar groups interact with the water [2].

Each micelle consists of a certain number of monomer molecules (aggregation number, n) which determines its general size and shape. The exact size and shape of micelles is still uncertain but it is assumed that an ionic micelle in dilute aqueous solution is roughly spherical, though micellar shape transition under dilute salt-free conditions in presence of different hydrotops are also known [6]. The charged (or polar) hydrophilic groups are directed towards aqueous phase (stern layer), while the hydrocarbon chains are directed away from the water (forming the hydrophobic central core). The region adjacent to the stern layer contains a high density of counter- ions of the polar heads (Gouy Chapman double layer) and separates the hydrophobic interior from the bulk aqueous phase [10].

It is interesting to note that although it is usually assumed that there is a fairly well-defined water layers around the micellar surface, there is no agreement on the composition of the micellar core, i.e. whether it consists of pure hydrocarbon or of hydrocarbon mixed with water. However, water penetration in micellar core is still a matter of controversy.

The idea on controversial "water exposure of micelles" is founded mainly on low angle neutron scattering experiments [11]. This modern concept discusses the main characteristics of the molecular conformation in micelles in terms of the predictions of the "phase separation" or "mass action" model [12-14]. Phase separation model predictions are in agreement with experimental data and are particularly consistent with some principal features of micellar structure.

(i) The micellar core is virtually devoid of water, according to Langmuir's original principle of differential solubility.

(ii) Micellar chains are randomly distributed and steric forces determine the final structure.

(iii) Contact of the hydrophobic sections of the micelle with water results from a disordered structure in which the terminal groups or chain ends are near the micellar surface and thus exposed to bulk water [15]

Although the "water penetration" concept of the hydrophobic sections of micelle is now less acceptable than the "water exposure" concept, this controversial topic is still under debate [16,17]. However the phase separation model along with the related thermodynamics of micelle formation is discussed in chapter 3.

Another important characteristic of surfactants is there ability to form microemulsion [18,19]. Microemulsions are compartmentalized liquids having huge application in several physico-chemical and technological processes [20,21]. They are optically isotropic, transparent, normally low viscous and thermodynamically stable solutions (dispersions) having a prolonged life-span [22,23] and can be prepared by mixing appropriate proportion of oil, water and surfactant. In many cases the presence of co-surfactants (polar compounds of intermediate chain length, e.g. medium chain alkanols) may stabilize microemulsions by providing the proper balance between hydrophilic properties for the required oil and water phases under the conditions of use. But cosurfactant free microemulsions are also known [19]. Microemulsions are of two types, based on the nature of the dispersed phase: oil-in water (O/W) and water-in-oil (W/O) having average particle size with in the range of 5-100 nm [18]. Pictorial representations of reverse micelles and microemulsions are shown in Figure 1.3. They are polydispersed in nature and the polydispersity decreases with decreasing particle size. In the formation of microemulsions, one of the two immiscible liquids (viz. oil or water) breaks up into particles that are dispersed in the second liquid. They can be formed with expenditure of a very little energy (can be supplemented by the thermal energy of the system) and are thus thermodynamically stable. A mixture of the right proportion of water, amphiphile and oil may spontaneously homogenize itself forming a microemulsion. In case of W/O microemulsion each water droplet is covered by an oriented monolayer of surfactant molecules.

In recent years microemulsion have been extensively applied to many fields, such as chemical reactions [24,25], nanometerials preparation [26] and drug delivery systems [27]. Reactions performed therein may significantly deviate from the normal courses and are often catalyzed in compartmentalized environments. Recently, attempts have also been made to prepare and study nonaqueous microemulsions for ionic liquids [28-30]. These microemulsions have attracted much interest from both theoretical (thermodynamics, particle interactions, etc.) and practical (potential use as a novel reaction media) view point [30].

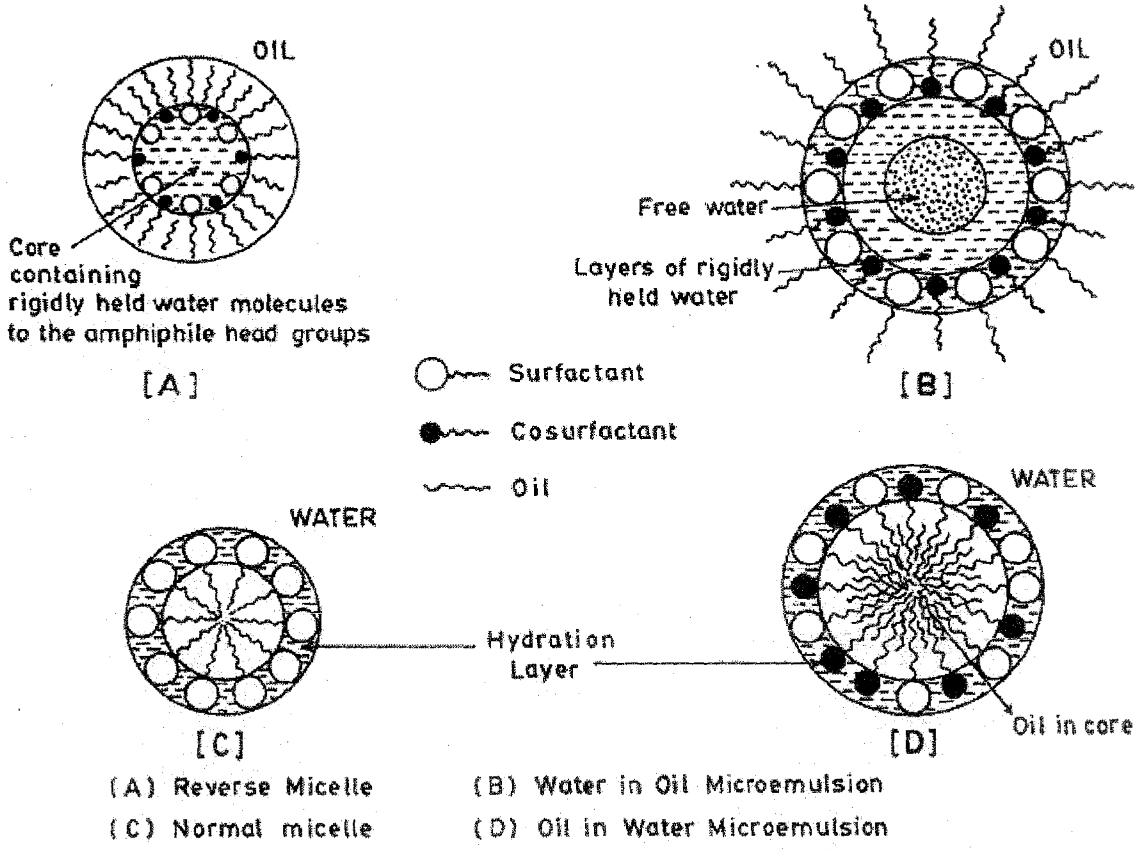
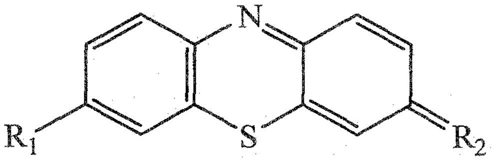


Figure 1.3 Schematic representations of reverse micelles and microemulsions.

1.2 Thiazine Dyes

Continuously tunable lasers can now be produced to cover the entire visible spectrum using organic dyes as lasing medium. The visible absorption spectra of organic dyes exhibit strong dependence on concentration in aqueous solution because of self aggregation [31]. Aggregation affects colour, solubility, photophysical and photo chemical behaviour of dyes. A systematic study of the aggregation characteristics of dyes from spectrophotometric data has become a useful field of research because of its possible application in understanding such phenomena on energy transfer in biological systems, metachromatia, hypochromism and confirmation of polypeptides, and staining properties of dyes for biological specimens etc. The force responsible for holding the component molecules in the dimer or on polymer is not yet well understood. Nevertheless, it is clear that for ionic dyes, aggregation would be possible if there exists some very strong attractive interaction, which first of all overcomes the coulombic repulsion and then brings the component molecules to a reasonable distance to form dimers and subsequently high polymer. Photochemical systems for photoreduction of water and photoinduced electron transfer reaction in surfactant solutions are of considerable interest as models for understanding of photobiology [32,33] and the conversion of solar energy [34,35]. Compared with inorganic complexes, organic dyes have been investigated only rarely as sensitizers for the photo reduction of water [36-38]. Because of their photophysical properties, thiazine dyes (Figure 1.4) are used as photosensitizer in light-induced reactions. These studies are important particularly from the standpoint of the possibility of their utilization in photodynamic therapy (PDT) [39], photodegradation of environmental contaminants [40-42], molecular recognition and photo sensitized modification of DNA [43]. It has been found that the thiazine dyes designed as azures (Figure 1.4c, 1.4d and 1.4e) are promising photosensitizers for PDT [44]. Structures of different thiazine dyes are shown in Figure 1.4.



a) **Th**$^+$ R_1 :NH_2 R_2 : $\overset{+}{N}H_2$

b) **MB**$^+$ R_1 : $N(CH_3)_2$ R_2 : $\overset{+}{N}(CH_3)_2$

c) **AzA**$^+$ R_1 : $N(CH_3)_2$ R_2 : $\overset{+}{N}H_2$

d) **AzB**$^+$ R_1 : $N(CH_3)_2$ R_2 : $\overset{+}{N}H(CH_3)$

e) **AzC**$^+$ R_1 : $NH(CH_3)$ R_2 : $\overset{+}{N}H_2$

Figure 1.4 Structures of thiazine dyes: (a) thionine, (b) methylene blue, (c) azure A, (d) azure B and (e) azure C.

The course of the photosensitized reactions can be significantly affected when they occur in organized systems, i.e. thin films, microemulsions, vesicles and micelles [45,46]. These systems can simulate the environment in biological systems and are thus frequently used as relatively simple models [47]. The choice of a suitable micellar system is very important, as the electrostatic interactions between the studied substances and the surface charge of the micelles can have a favourable or unfavourable effect on the properties of interest.

1.3 Dye – Surfactant Interactions

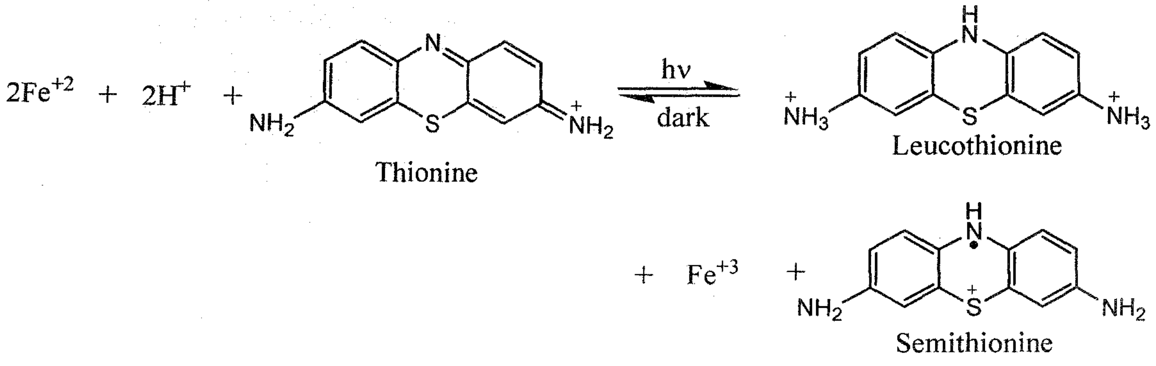
Although from early time the changes in the colour of ionic dyes in the presence of oppositely charged ionic surfactants in aqueous solution have led many workers [48-50] to propose dimer and multimer formation of dye molecules in the surfactant micelle, this area are still important and interesting for the theoretical, ecological and technological point of view. The enhanced energy transfer between dyes in dye-surfactant systems made them good model membrane systems of chloroplast [51,52]. The peculiar behaviour in both absorption [53] and fluorescence [54] spectra of dyes in the presence of surfactants of opposite charge were attributed to the formation of a continuum of dye-surfactant aggregates or mixed micelles depending on the surfactant: dye ratio (S/D). Among other things, the investigations into the behaviour of different dyes in surfactant aqueous solutions, give useful information about the mechanisms according to which surfactants operate as leveling agents and provide information on the influence of dye–surfactant interactions on the thermodynamics and kinetics of dyeing process. This may directly affect the quality of dyeing, which is one of the goals of textile finishing. Surfactants are also used as solubilizers for water insoluble dyes, to break down dye aggregates in order to accelerate adsorption process on fiber, as auxiliaries for improving dye adsorption and as leveling or dispersing agents [55-57]. According to the structures of dye and substrate, surfactants used as levelling agents operate by different mechanisms. Consequently, a great deal of research work focused on dye–surfactant interactions in binary mixtures including the interactions between ionic dyes and ionic surfactants of the opposite and the same charges [58–61], ionic dyes and nonionic surfactants [58,62,63] as well as between nonionic dyes and ionic or nonionic surfactants [64] in the submicellar and micellar concentration ranges of surfactants. It seems probable that once the electrostatic forces have brought together the oppositely charged molecules, hydrophobic interactions take place, dramatically changing the microenvironment experienced by the chromophore. Knowledge of dye surfactant interaction should also be of great value on understanding the chemical equilibria, mechanism and kinetics of surfactant sensitized colour reactions.

The results of spectral studies on phenosafranin, a cationic phenazine dye, in aqueous solution containing three different types of surfactants such as cetyltrimetylammonium bromide (CTAB), sodium lauryl sulfate (SLS) and Triton X-

100 have been reported [65]. The dye forms 1:1 molecular complexes with Triton X-100 and SLS, but there is no interaction of phenosafranin with CTAB. The thermodynamic and spectrophotometric properties of these complexes suggest that phenosafranin forms a strong charge-transfer (CT) or electrondonor-acceptor (EDA) complex with Triton X-100, whereas the interaction with SLS is coulombic in nature. This conclusion is confirmed by photovoltage and photoconductivity measurement of phenosafranin in these surfactants. The same studies confirm the CT interaction of Triton X-100 with other cationic dyes such as crystal violet, fuchsin and rhodamin B [66]. Thiazine dyes are structurally very similar to phenosafranin and we have chosen some thiazine dyes such as thionine, methylene blue, azure A, azure B and azure C for our consideration.

1.4 Electrochemical Behaviour of Dyes

The search for renewable sources of energy has led to an increasing interest in photochemical cells because of their possible role as transducers of solar to electrical energy. It has been observed that photo effects in electrochemical systems are enhanced if the electrodes are coated with dye stuff, wherein their redox chemistry playes an important role [67,68]. There have been reports in the past that use of dyes as sensitizers in photo-electrochemical devices for solar energy conversion suffer from very poor power conversion efficiency [69,70]. This drawback has been variously attributed to slow discharge of photo-produced intermediate dye radicals (viz., semi reduced 'leuco' dyes) at the cell electrode as compared to radical - radical recombination reaction in the bulk of the solution. The reaction with thionine can be stated as follows:



To make the discharge process favorable, it is necessary to arrest the recombination reaction in the bulk homogeneous phase. Attempts have been made in the past to slow down the bulk reactions in a suitable micellar medium [71]. In this connection some oxazine dyes have been considered sensitizers in photogalvanic devices in the past. The dye surfactant interactions have been the subject of interest also because they mimic many biological processes taking place between the large organic molecules and biomembranes and can act as a model redox system [72,73]. Further such interactions between ionic dyes and charged surfaces are of interest in numerous applications ranging from the design of electronic devices to the characterization of drug-delivery system. It has been reported that pure metal electrodes becomes sensitive to light when coated with a dye or immersed in a dye solution [74]. Phenothiazine and substituted-phenothiazine dyes are thought to be important in the direct conversion of solar energy to electricity [75,76]. For example, the photochemical redox reaction between thionine and Fe^{2+} has been used advantageously to devise and understand the mechanism of the photogalvanic cell. Early workers have extensively examined the photogalvanic activity of various dyes with reversible and irreversible reducing agents [77,78]. In order to understand the mechanism of photogalvanic action it is essential to investigate the electrochemical behaviour of these dyes.

References

1. Schramm L. L., *Surfactants: Fundamentals and Applications in the Petroleum Industry,* Cambridge University Press, 2000.

2. Tanford, C. *The Hydrophobic Effect: Formation of Micelles and Biological Membranes,* 2nd Ed., Wiley - Interscience, New York 1980.

3. Lindman, B.; Wennerström, H. Topics in Current Chemistry, Vol. 87, Springer-Verlag, Berlin, 1980.

4. Lindman, B.; Marie-Claude, P.; Kamenka, N.; Rymdén, R.; Stilbs, P. *J. Phys. Chem.* **1984**, *88*, 5048.

5. Blokzijl, W.; Engberts, J.B.F.N. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1545.

6. Mancera, R.L. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2547.

7. Saha, S. K.; Jha, M.; Ali, M.; Chakraborty, A.; Bit, G.; Das, S. K. *J. Phys. Chem. B* **2008**, *112*, 4642.

8. Graziano, G.; Barone, G. *J. Am. Chem. Soc.* **1996**, *118*, 1831

9. Graziano, G. *Phys. Chem. Chem. Phys.* **1999**, *1*, 1877.

10. Fendler, J.H. and Fendler, E.J. *Catalysis in Micellar and Macromolecular Systems,* Academic Press, New York, 1975.

11. Dill, K.A.; Koppel, D.E.; Cantor, R.S.; Dill, J.D.; Bendedouch, D.; Sow. H. *Nature Chem.*, **1984**, *42*, 309.

12. Myers, D., *Surfactant Science And Technology,* VCH: New York, 1992.

13. Suarez, M.J.; Lopez-Fontan, J.L.; Sarmiento, F.; Mosquera, V. *Langmuir* **1999** *15*, 5265.

14. González-Pérez, A.; Czapkiewicz, J.; Del Castillo, J.L.; Rodríguez, J.R. *Colloid Polym. Sci.* **2004**, *282*, 1359.

15. Dill, K.A.; Flory, P.J., *Proc. Natt. Acad. Sci.* USA, 1980, **77**, 3115; **78**, 676, 1981.

16. Menger, F.M. *Nature*, **1985**, *313*, 603.

17. Cabane, B. *Nature*, **1985**, *314*, 385.

18. Moulik, S.P.; Paul, B.K.; *Adv. Colloid Interface Sci.* **1998**, *78*, 99.

19. Holmberg, K.; Osterberg, E. *J. Dispersion Sci. Technol.* **1986**, *7*, 299.

20. Schwuger, M.-J.; Stickdorn, K.; Schomacker, R. *Chem. Rev.* **1995**, *95*, 849.

21. Velazquez, M.M.; Valero, M.; Ortega, F. *J. Phys. Chem. B* **2001**, *105*, 10163.

22. Holt, S.L.; *J. Dispersion Sci. Technol.* **1986**, *1*, 423.

23. Kahlweit, M. *Science* **1988**, *240*, 617.

24. Oh, S.; Kizling, J.; Holmberg, K. *Colloid Surf. A* **1995**, *97*, 169.

25. Spiro, M.; de Jesus, D.M. *Langmuir* **2000**, *16*, 2464.

26. Bonini, M.; Bardi, U.; Berti, D.; Neto, C.; Baglioni, P. *J. Phys. Chem. B* **2002**, *106*, 6178.

27. Lv, F.F.; Zheng, L.Q.; Tung, C. *Int. J. Pharm.* **2005**, *301*, 237.

28. Ray, S.; Moulik, S.P. *Langmuir* **1994**, *10*, 2511.

29. Peng, S.; An, X.; Shen, W. *J. Colloid Interface Sci.* **2005**, *287*, 141.

30. Falcone, R.D.; Correa, N.M.; Biasutti, M.A.; Silber, J.J. *langmuir* **2000**, *16*, 3070.

31. Horng, M ; Quitevis, E.L. *J. Chem. Edu.* **2000**, *77*, 637.

32. Buryak, A.; Severin, K. *Chem. Comm.*, **2007**, 2366.

33. Kwon, J.Y.; Singh, N.J.; Kim, H.N.; Kim, S.K.; Kim, K.S.; Yoon, J. *J. Am. Chem. Soc.* **2004**, *126*, 8892.

34. De Groot, M.S.; Hendriks, P.A.J.M. ; Brokken-Zijp, J.C.M. *Chem. Phys. Lett.* **1983**, *97*, 521.

35. Lal, C. *J. Power Sources*, **2007**, *164*, 926.

36. Kalyanasundaram, K.; Dung, D.; *J. Phys. Chem.* **1980**, *84*, 2551.

37. Chan, M.S.; Bolton, J.R.; *Photochem. Photobiol.* **1981**, *34*, 537.

38. Hashimoto, K.; Kawai, T.; Sakata, T. *Chem. Lett.* **1983**, *5*, 709.

39. Wainwright, M. *Chem. Soc. Rev.* **1996**, *25*, 351.

40. Gak, V.Y.; Nadtochenko, V.A.; Kiwi, J. *J. Photochem. Photobiol. A* **1998**, *116*, 57.

41. Tanielian, C.; Mechin, R.; Sakinullah, M. *J. Photochem. Photobiol. A* **1992**, 64,191.

42. Lang, K.; Luňák, S.; Sedlák, P.; Brodilová, J. *Zeit. Phys. Chem.* **1995**, *190*, 203.

43. Fujimoto, B.S.; Clendenic, J.B.; Delrow, J.J.; Heath, P.J.; Schurr, M. *J. Phys. Chem.* **1994**, *99*, 6633.

44. Jirsa, M.; Jirsaa, Jr. M.; Kubát, P. *J. Photochem. Photobiol. B* **1996**, *36*, 99.

45. Barra, M.; Redmond, R.W.; Allen, M.T.; Colabrese, S.S.; Sinta, R.; Scaina, J.C. *Macromolecules* **1991**, *24*, 4972.

46. El-Torki, F.M.; Schmehl, R.M.; Reed, W.F. *J. Chem. Soc. Faraday Trans. 1* **1989**, *85*, 349.

47. Barbes, J., *Photosynthesis in relation to model systems*, Elsevier, New York, 1979.

48. Mukerjee, P.; Mysels, K.J. **1955** *J. Am. Chem. Soc.* *77*, 2937.

49. Hiskey, C.P.; Downery, T.A. **1954** *J. Phys. Chem.* *58*, 835.

50. Cockbain, E.G. *Trans. Faraday Soc.* **1954**, *49*, 104.

51. Sato, H.; Kusumoto, Y.; Nakashima, N.; Yoshihara, K. *Chem. Phys. Lett.* **1980**, *71*, 326.

52. Usui, Y.; Saga, K.; *Bull. Chem. Soc. Japan* **1982**, *55*, 3302.

53. Reeves, R.L.; Harkaway, S.A. *Micellization, Solubilization and Microemulsion*, Mittal, K. (Ed.), Vol. 2, Plenum Press, New York, 1979.

54. Vaidyanathan, S.; Patterson, L.K.; Möbius, D.; Gruniger, H.-R. *J. Phys. Chem.* **1985**, *89*, 491.

55. Akbaş, H.; İşcan, M. *Turk. J. Chem.* **1994**, *18*, 80.

56. Sudbeck, E.A.; Dubin, P.L.; Curran, M.E.; Skelton, J. *J. Colloid Interface Sci.* **1991**, *142*, 512.

57. Missclyn-Bavduin, A.M.; Thibaut, A.; Grandjean, J.; Broze, G.; Jerome, R. *Langmuir* **2000**, *16*, 4430.

58. Gou, L.N.; Arnaud, I.; Petit-Ramel, M.; Gauthier, R.; Monnet, C.; Le Perchec, P., Chevalier, Y. *J. Colloid Interface Sci.* **1994**, *163*, 334.

59. Simončič B, Špan J. *Dyes and Pigments* **2000**, *46*, 1.

60. Bračko, S.; Špan, J. *Dyes and Pigments* **2001**, *50*, 77.

61. Moulik, S.P.; Ghosh, S.; Das, A.R.; *Colloid Polym. Sci.* **1979**, *257*, 645.

62. Tanaka, F.; Harada, Y.; Ikeda, N.; Aratono, M.; Motomura, K. *Bull. Chem. Soc. Japan* **1994**, *67*, 2378.

63. Bhattacharya, S.C.; Das, H.; Moulik, S.P. *J. of Photochem. Photobio. A* **1993**, *74*, 239.

64. Ogino, K.; Kasuya, T.; Abe, M. *Colloid Polym. Sci.* **1988**, *266*, 539.

65. Rohatgi-Mukherjee, K.K.; Chaudhuri, R.; Bhowmik, B.B. *J. Colloid Interface Sci.* **1985**,106, 45.

66. Bhowmik, B.B.; Chaudhuri, R.; Rohatgi-Mukherjee, K.K. *Indian J. Chem.* **1987**, 26A, 95.

67. Perkinson, B.A.; Spitler, M.T. *Electrochem. Acta* **1992**, *37*, 943.

68. Das, S.; Thomas, K.G.; Kamat P.V.; George, M.V. *Proc. Ind. Acad. Sci. (Chem. Sci.)* **1993**, *105*, 513.

69. Kamat, P.V.; Karkhanavala, M.D.; Moorthy, P.N. *Ind. J. Chem. A.* **1977**, *15*, 342.

70. Kamat, P.V.; Karkhanavala, M.D.; Moorthy, P.N. *Solar Energy* **1978**, *20*, 171.

71. Kiwi, J.; Kalyan Sunderam, K.; Gratzel, M.; *Struct Bonding* **1982**, *49*, 37.

72. Shah S.S.; Ahmed, R.S.W.H.; Asif, K.M.; Naeem, K. *Colloid Surf. A.* **1998**, *137*, 301.
73. Chibisov, A.K.; Prokhorenko, V.I.; Gomer, H. *Chem. Phys.* **1999**, *250*, 47.

74. Jana, A.K. *J. Photo Chem. Photo Biol. A : Chem.* **2000**, *132*, 1.

75. W. J. Albery, Photovoltaic and Photoelectrochemical Solar Energy Conversion, ed. F. Cardon, W. P. Gomes and W. DeKeyser, NATO Advanced Study Institute Series Plenum Press: New York, 1980

76. Petritsch, Dipl.Ing. K., *Ph.D. Thesis*, Technische Universität Graz, Austria, 2000.

77. Ahmed, S.; Saha, S.K. *Can. J. Chem.* **1996**, *74*, 1896.

78. Murthy, A.S.N.; Reddy, K.S. *Electrochim. Acta*, **1983**, *28*, 473.