

Chapter II

Scope and object

Chapter II

Scope and object

In solutions of paraffin-chain salts the critical concentration for micelle formation (cmc) is determined by a number of factors. It is markedly dependent upon the size and shape of the paraffin chain and on the nature of the polar group. Temperature usually has complex effect on the cmc value [1]. Polar organic additives have been shown to alter it appreciably. In general, factors that increases cmc of a surfactants are (I) carbon-carbon double bonds (II) polar groups within the hydrophobic tail and (III) ionic head groups whereas, the factors that decreases the cmc are (I) increasing number of methylene groups in the alkyl chain (II) introduction of phenyl rings in the alkyl chain (III) fluorocarbons within the hydrophobic tail and (IV) addition of electrolytes to solutions of ionic surfactants. The solutions of these colloidal electrolytes (i.e., soaps, detergents, etc.) change their properties abruptly at critical micelle concentration. The osmotic pressure and the electrical conductivity become much lower than the values predicted by the theory of Debye-Hückel, and viscosity and the turbidity are increased. A considerable number of research works have been devoted recently about the amphiphilic aggregates mainly due to three reasons. First, one can consistently and easily prepare aqueous micellar solutions which have aggregates of colloidal dimensions with, characteristics size, shape and surface properties. Hence micellar systems have been employed as a model system in investigations concerned with understanding colloidal physico-chemical phenomena [2-3]. Second, it has been found that micelles can act as unique reaction media. And finally, the similarities between self-assembled surfactant aggregates, such as micelles and vesicles, and biological lipid membranes prompted researchers to employ micelles and vesicles as model biological systems [4-7]. Bales et al. showed that changing of counterions have great influence on the properties of micelle [8-10]. A complete understanding of the micellization phenomena, its fundamental aspects, use of related studies for technological developments, and understanding molecular behaviour requires a comprehensive knowledge of the forces and factors controlling the process. One approach that is widely being practiced for the said knowledge has been the study of the effect of additives, especially electrolytes and organic solvents, on the micellization characteristics of ionic surfactants. The recent advances in micellar

chemistry have demonstrated the effect of macromolecules in micellar systems and their major applications in the fields of oil recovery, pharmacology, medicine and the food industry [11-13]. They have major applications in surface activity, detergency, wetting, spreading, foaming etc. The effect of different kinds of additives, including various glycols on the micellization of single tail surfactants has also been widely studied [14-16]. Apart from pure water, micelle formation has also been reported in pure non-aqueous solvents such as ethylene glycol, glycerol, formamide and hydrazine [17-22]. All these solvents have high cohesive energies and considerable hydrogen-bonding capability, which favour the aggregation of surfactant monomers to micelles. These aggregates in nonaqueous media are of nanometer size and being almost spherical can solubilize large amount of water, forming water-pool, whose properties have been determined with different techniques [23-25].

The cmc value is usually determined from the abrupt change of a certain physical property over a very small concentration range. It is possible to distinguish between methods examining the behaviour of a bulk solution property such as surface tension, conductivity, light scattering etc. and those using some spectroscopic property. In most cases, the choice of the methods depends on the availability of various techniques or the personal preference of the worker. Usually, the cmc is obtained from the graphical procedures, and often one finds that it is difficult to determine the exact break point providing the cmc value. As a consequence, sometimes the reported value depends, in some measure, on the good judgment of the researcher. A frequent problem arises when the conductance method is used in the cmc determination of surfactants with a small aggregation number. In these cases, it is very difficult to determine the break in the conductance-concentration curves and, consequently, the cmc is affected by a great uncertainty. To solve this problem, the one preferred procedure is to plot differential conductance against concentration of surfactant [26]. Manabe et al. have obtained cmc at the shoulder point of the first derivative versus concentration plots [27]. Sugihara et al. used plots of the first derivative of specific conductivity versus the square root of the surfactant concentration, thus reducing the range of the independent variable where the variation of specific conductivity occurs [28-29]. The other preferred way is to determine cmc of a surfactant with small aggregation number by two or more different methods to solve the above said problem. With this viewpoint, an attempt has been made to correlate most of the cmc value of the surfactants presented here in

two or more different way to avoid the possible errors as these cmc values and systematic information regarding thermodynamics are not as readily available in the literature as sodium dodecyl sulfate, cetyl trimethyl ammonium bromide or Triton X-100 etc.

Linear alkyl benzene sulfonates are known as the work horse of the detergent industry and have good foaming property [30-31]. Alkyl benzene sulfonate contains fluorescing group as part of their molecular architecture which exhibit excimer-monomer emission [32]. The alkyl benzene sulfonate is also applied to a typical commercial petroleum sulfonate (TRS 10-80) which is one of a family of surfactants used in chemical flooding oil recovery and is obtained by direct sulfonation of a large variety of aromatic petroleum feed stocks [33]. The surfactant sodium dodecyl benzene sulfonate is also used in chemical, biochemical and industrial works, and it is an effective surface-active compound. It can conveniently interact with neutral and cationic polymers forming solutions of different constituencies. It has antifungal properties and has a low cost of production. So far, the solution properties of this surfactant have not been critically examined although few reports are available in literature [34-36]. These considerations prompted us to make elaborate and critical study of the micellization and interfacial properties of SDBS as a function of counter ion size and hydrophobicity and their interaction with cationic dye. Major advantage of the sulfonate surfactants over the carboxylates is their greater tolerance of divalent metal ions in hard water.

In recent years, attention has been focused on the interactions of surfactants with hydrophobic counter ions and to this effect symmetrical tetraalkyl ammonium cations have been considered in most of the studies. It is also true that SDS is the most well known, and widely used in industry. However, in acidic solutions or at high temperatures, SDS undergoes autocatalytic acid hydrolysis, and dodecanol and sodium hydrogen sulfate are produced. These products are believed to cause skin irritation. In contrast, ammonium dodecyl sulfate is less hydrolyzed in acidic solutions and less skin-irritative than SDS [37]. For this reasons, the use of ammonium dodecyl sulfate in the cosmetic and toiletry industry has been expanding. In view of the growing importance and very limited number of studies on different tetraalkyl ammonium dodecyl benzene sulfonates, viz. tetramethyl ammonium dodecyl benzene sulfonate, tetraethyl ammonium dodecyl benzene sulfonate, tetrapropyl ammonium dodecyl benzene sulfonate and tetrabutyl ammonium dodecyl benzene sulfonate,

investigation on their aggregation behaviour in aqueous solution have been undertaken with the other counter ions of alkali metals.

The cmc and other physico-chemical properties such as surface property, thermodynamic properties etc. change with the change in temperature of the medium. Also the stabilities of surfactant systems with respect to temperature prior to their multifold uses need to be known, especially where elevated temperature prevails. Keeping the above in view, physico-chemical properties of different surfactants are determined with varying temperature to get an overall view of the energetics of the process. Moreover, a series of work done previously in our laboratory to understand the effect of counter ions of the aggregation behaviour of sodium dodecyl sulfate and bis (2-ethylhexyl) sulfosuccinic acid. Therefore, we have undertaken the present study on the characterization of the different properties of dodecyl benzene sulfonate such that we can compare and make a generalized view of the three compounds having different hydrophobic and hydrophilic character.

Linear alkyl benzene sulfonates (ABS) are arguably the most important class of commercial surfactant, used in many industrial applications as described above. Commercial ABS surfactants are generally produced by using a process that results in a mixture of alkyl chain homologues with a range of head group positional isomers. The positional isomers have a molecular structure where the benzene sulfonate head group is attached at different positions along the alkyl chain [3]. For example, the polydispersity of one commercial linear ABS surfactant is illustrated by the numerous peaks in its HPLC chromatogram highlighting the alkyl chain length distribution and the different isomeric components produced for each chain length. Not only are such complex mixtures difficult to characterize, and hence predict functional performance, the situation is even more complex as nominally the same surfactant, manufactured by different suppliers, may contain varying proportions of the individual isomeric components. Dodecyl benzene sulfonates are known to form micelles in dilute solution and display an array of liquid crystalline phases at higher concentrations [38]. In particular, it is already known that a micelle to vesicle aggregate transition can be induced by a change in ionic strength, resulting in a reduction of the air-aqueous solution interfacial tension [39-40]. This behaviour is important from practical perspective, as the ability of surfactants to reduce interfacial tension is often key to their performance. The ability to control the self-assembly aggregate structure and related solution rheology can also be desirable from a formulation and consumer

acceptability perspective. Furthermore, added electrolytes have significant effect on the properties of surfactants with the nature of counter ions, its radius and valence [41-49]. Keeping in view of the above physico-chemical studies of all the surfactant in presence of corresponding bromides have done to understand the changes in properties as mentioned above.

The photochemistry of dyes has contributed to the understanding of the mechanism of electron transfer reactions in photo electrochemical devices [50-55]. Photo induced electron transfer processes in surfactant solutions are potentially important for efficient energy conversion and storage because surfactant micelles help to achieve the separation of the photoproducts by hydrophilic-hydrophobic interactions of the products with the micellar interface [56-59]. Dye-surfactant interactions are generally complex [60]. Molecular complexes having specific and characteristic physicochemical features may be formed. The dyes aggregation phenomena have attracted attention in the past and are nowadays receiving novel consideration [61-63] in view of possible new technical applications such as opto-electronic devices, optical logical elements, sensitizing agents in color photography, photoconductors, electroluminescent devices and electro optically active centers in photogalvanic systems, solar energy conversion, semiconductor photo catalysis, pollutant control, photodynamic therapy, pharmaceutical preparation, besides the more traditional ones. The properties of oxazine dye aggregates at liquid/solid interfaces have been of interest for long time [64]. The solar energy harvesting with wide band gap semiconducting photoconductors may be improved by covering with this dyes to expand the wave length range [65]. The oxazine dyes display surprisingly long wave length absorption and emission maxima given their small sizes and as such have been shown to be important fluorescent probe for biological systems. They can be excited with simple laser sources such as solid state laser diodes. Oxazine dye modified electrodes have been shown to be useful in electrocatalytic oxidation of coenzyme Nicotinamide Adenine Dinucleotide (NADH) in the context of enzyme-based biosensors [66]. A study of the photophysical behaviour of one of the oxazine dye, cresyl fast violet, has been carried out to understand the dye-surfactant interactions present in the system.

Surfactant mixtures are commonly preferred in medicinal and pharmaceutical formulations and industrial preparations due to the purpose of suspension, solubilization and dispersion as compared to single surfactant. The mixed surfactant

exhibits superior interfacial properties such as higher surface activity and lower critical micelle concentration (cmc). Generally, it has been observed that with anions that associate strongly with the surfactant cations, worm-like micellar growth occurs rapidly at low surfactant and salt concentrations. The rheological behaviour exhibited by these systems is viscoelastic and analogous to that observed in solution of flexible polymers. These surfactant solutions undergo similar rheological behaviour whether they are prepared directly from surfactant salts with a strongly associating anion or by addition of strongly associating anions to solutions prepared from surfactant salts with weakly associating anions. The rheological behaviour observed for wormlike micelles in the surfactant solution is similar to that for flexible polymers, and therefore, aqueous solutions of entangled wormlike micelles are often called "living polymer systems". The research of wormlike micelles has drawn considerable interest owing to their superior properties and wide applications [67 - 70].

Main objectives in this present investigation would, therefore, be

1. To investigate the self association behaviour of dodecyl benzene sulfonate with varying counter ion at different temperatures in aqueous solution to know the physico-chemical properties and to compare the same properties with the well investigated anionic surfactants SDS and AOT containing identical counter ions.
2. To extend investigation on the influence of salt or solvent on the micelle formation, especially when a third component was added and to calculate the change in heat content for the process: surfactant molecule in solution \rightarrow surfactant molecule in the micelle using different component in aqueous solution.
3. To know the aggregation number of each of the surfactant in aqueous solution, and also.
4. To know the types of interactions present with the oxazine dye, viz., cresyl fast violet.
5. To investigate the microstructural change of micelle formed in presence of mixed surfactants by using conductance, surface tensiometry and dynamic rheology.

To investigate on the above mentioned objectives, a variety of measurements including conductometry, tensiometry, rheology, spectrophotometry and spectrofluorometry measurements are made.

References:

1. Clint, J. H.; *Surfactant Aggregation*, Blackie Chapman and Hall, New York, 1992.
2. Nilsson, S.; Thuresson, K.; Hansson, P.; Lindman, B. *J. Phys. Chem. B*, **1998**, 102, 7099.
3. Rosen, M. J. *Surfactants and Interfacial Phenomena*, Wiley-Interscience, USA, 2004.
4. Saha, S. K.; Jha, M.; Ali, M.; Chakraborty, A.; Bit, G.; Das, S. K. *J. Phys. Chem. B*. **2008**, 112, 4642.
5. Yin, H.; Lei, S.; Zhu, S.; Huang, J.; Ye, J. *Chem. Eur. J.* **2006**, 12, 2825.
6. Hedin, N.; Sitnikov, R.; Furo, I.; Henriksson, U.; Regev, O. *J. Phys. Chem. B*. **1999**, 103, 9631.
7. Lindemuth, P. M.; Bertrand, G. L. *J. Phys. Chem.* **1993**, 97, 7769.
8. Benrraou, M.; Bales, B. L.; Zana, R. *J. Phys. Chem. B* **2003**, 107, 13432.
9. Bales, B. L. *J. Phys. Chem. B* **2001**, 105, 6798.
10. Pisărcăik, K.; Devinsky, F.; Lacko, I. *Acta. Facult. Pharm. Univ. Comenianac*, **2003**, 50, 119.
11. Karlström, G.; Carlsson, A.; Lindman, B. *J. Phys. Chem.*, **1990**, 94, 5005.
12. Goddard, E. D. *Colloid Surf.*, **1986**, 19, 255.
13. Hoffmann, H.; Ulbricht, W. *Curr. Opin. Colloid. Interface Sci.*, **1996**, 1, 726.
14. Jha, R.; Ahluwalia, J. C. *J. Phys. Chem.*, **1991**, 95, 7782.
15. Bakshi, M. S.; *J. Chem. Soc., Faraday Trans.*, **1993**, 89, 4323.
16. Collaghan, A.; Doyle, R.; Alexander, E.; Palepu, R. *Langmuir*, **1993**, 9, 3422.
17. Ray, A. *Nature (London)*, **1971**, 231, 313.
18. Evans, D. F.; Yamauchi, A.; Wei, G. J.; Bloomfield, V. A. *J. Phys. Chem.*, **1983**, 87, 3537.
19. Sjöberg, M.; Henriksson, U.; Warnheim, T. *Langmuir*, **1990**, 6, 1205.
20. Lattea, A.; Rico, I. *Colloids Surf.*, **1989**, 35, 221.
21. Ramadan, M.; Evans, D. F.; Lumry, R. *J. Phys. Chem.*, **1983**, 87, 4538.
22. Ramadan, M.; Evans, D. F.; Lumry, R.; Pillion, S. *J. Phys. Chem.*, **1985**, 89, 3405.
23. Tatikolov, A. S.; Costa, M. B. *Photochem. Photobiol. Sci.* **2002**, 1, 211.
24. Mittal, K. L. *Micellization, Solubilization and Microemulsion*, Vol. 2, USA, 1977.
25. Forley, M. S. C.; Beebay, A.; Parker, A. W.; Bishop, S. M.; Phillips, D. *J. Photochem. Photobiol. B: Bio.* **1977**, 38, 18.
26. Carpena, P.; Aguiar, J.; Bernal-Galván, P.; Ruiz, C. C. *Langmuir*, **2002**, 18, 6054.
27. Manabe, M.; Kawamura, H.; Yamashita, A.; Tokunaga, S. *J. Colloid Interface Sci.* **1987**, 115, 147.

28. Sugihara, G.; Era, Y.; Funatsu, M.; Kunitake, T.; Lee, S.; Sasaki, Y. *J. Colloid Interface Sci.* **1997**, 187, 435.
29. Fujiwara, M.; Okano, T.; Nakashima, T. -H.; Nakamura, A. A.; Sugihara, G. *Colloid Polym. Sci.* **1997**, 275, 474.
30. Berth, P.; Jeschke, P. *Tenside Deterg.* **1989**, 26, 75.
31. Richtler H. J. in *World prospects for surfactants. Proceedings of the 2nd World Surfactant Congress (CESIO), Paris, 1988.*
32. Aoudia, M.; Rodgers, M. A. J.; *J. Am. Chem. Soc.*, **1979**, 101, 6777.
33. Linfield, W. M. (Ed.), "Anionic Surfactants", Vol. 2., Dekker, New York, **1976.**
34. Bi, Z. C.; Yu, Z. Y. *Chin. Sci. Bull.* **2001**, 46 (5), 372.
35. Bahdur, P.; Chand, M.; *Tenside, Surfactants, Deterg.* **1998**, 35 (2), 134.
36. Hait, S. K.; Majhi, P. R.; Blume, A.; Moulik, S. P. *J. Phys. Chem. B.* **2003**, 107, 3650-3658.
37. Porter, M. R. *Handbook of Surfactants*; Chapman and Hall: New York, **1991**, p 73.
38. Težak, D.; Hertal, G.; Hoffmann, H. *Liq. Cryst.* **1991**, 10, 15.
39. Farquhar, K. D.; Misran, M.; Robinson, B. H.; Steytler, D. C.; Morini, P.; Garrett, P. R.; Holzwarth, J. F. *J. Phys.: Condens. Matter*, **1996**, 8, 9397-9404.
40. Brinkmann, U.; Neumann, E.; Robinson, B. H. *J. Chem. Soc.* **1998**, 94.
41. Ropers, M. H.; Czichocki, G.; Brezesinski, G. *J. Phys. Chem. B.* **2003**, 107, 5281.
42. Gaillon, L.; Lelievre, J.; Gaboriaud, R. *J. Colloid Interface Sci.* **1999**, 213, 287.
43. Zana, R.; Benraou, M.; Bales, B. L. *J. Phys. Chem. B.* **2004**, 108, 18195.
44. Bales, B. L.; Tiguída, K.; Zana, R. *J. Phys. Chem. B.* **2004**, 108, 14984.
45. Vasilescu, M.; Angelescu, D.; Caldararu, H.; Almgren, M.; Khan, A. *Colloid Surf. A.* **2004**, 235, 57.
46. Paul, A.; Griffiths, P. C.; Petersson, E.; Stilbs, P.; Bales, B. L.; Zana, R.; Heenan, R. H. *J. Phys. Chem. B.*, **2005**, 109, 15775.
47. Chatterjee, A.; Moulik, S. P.; Sanyal, S. K.; Mishra, B. K.; Puri, P. M. *J. Phys. Chem. B.* **2001**, 105, 12823.
48. Molina-Bolivar, J. A.; Aguiar, J.; Ruiz, C. C. *J. Phys. Chem. B.* **2002**, 106, 870.
49. Singh, O. G.; Ismail, K. *J. Surf. Deterg.* **2008**, 11, 89.
50. Rohatgi-Mukherjee, K. K.; Bagchi, M.; Bhowmik, B. B. *Electrochem. Acta.* **1983**, 28, 293.
51. Rohatgi-Mukherjee, K. K.; Roy, M.; Bhowmik, B. B. *Sol. Energy.* **1983**, 31, 417.
52. Bhowmik, B. B.; Roy, S.; Rohatgi-Mukherjee, K. K. *Indian. J. Chem.* **1986**, 25A, 714.

53. Calvin, M. *Photochem. Photobiol.* **1983**, 37, 349.
54. Kalyansundaram, K.; Gratzel, M. *Photochem. Photobiol.* **1984**, 40, 807.
55. Tsubomura, H.; Shimoura, Y.; Fujiwara, S. *J. Phys. Chem.* **1979**, 83, 2103.
56. Kalyansundaram, K.; *Chem. Soc. Rev.*, **1978**, 7, 453.
57. Matsuo, T. K.; Kano, K.; Nagamura, T.; *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **1979**, 20, 1087.
58. Moroi, Y.; Braun, A. M.; Gratzel, M.; *J. Am. Chem. Soc.* **1979**, 101, 567.
59. Moroi, Y.; Infelta, P. P.; Gratzel, M.; *J. Am. Chem. Soc.* **1979**, 101, 573.
60. Shinoda, K. et al., *Colloidal Surfactants*, Academic Press, New York, **1963**, 155.
61. Ohline, S. M.; Lee, S.; William, S.; Chang, C. *Chem. Phys. Lett.* **2001**, 46, 9.
62. Vostiar, I.; Tkac, J.; Sturdik, E.; Gemeiner, P. *Bioelectrochemistry*, **2000**, 56, 113.
63. Usacheva, M. N.; Teichert, M. C.; Biel, M. A.; *J. Photochem. Photobiol. B: Biol.* **2003**, 71, 87.
64. Adhikari, R.; Saha, S. K. *Z. Phys. Chem.* **2005**, 219, 1373-1384.
65. Steinhurst, D. A.; Owrutsky, J. C. *J. Phys. Chem. B.* **2001**, 105, 3062.
66. Malinausks, A.; Ruzgas, T.; Gorton, L. *J. Electroanal. Chem.* **2000**, 484, 55.
67. L. M. Walker, *Curr. Opin. Colloid Interface Sci.*, **2001**, 6, 451.
68. G. C. Maitland, *Curr. Opin. Colloid Interface Sci.*, **2000**, 5, 301.
69. J. Yang, *Curr. Opin. Colloid Interface Sci.*, **2002**, 7, 276.
70. J. L. Zakin and H. W. Bewersdorff, *Rev. Chem. Eng.*, **1998**, 14, 2533.