Chapter Eight

8.1 Conclusions

Water soluble polymeric surfactants have received enormous attention and popularity because of their unique solution behavior and wide usage in variety of applications. A general overview of surfactant science and technology involves a thorough and molecular level understanding of surfactant properties which can be deduced from free-energy phase diagrams. In this thesis, we have focused our investigations mainly on the biodegradable surfactant AOS, though a wide variety of novel polymeric surfactants have drawn significant attention from scientific community recently.

At the same time, amphiphilic polymers containing hydrophobic and hydrophilic moieties have been extensively studied for their surfactant properties [1]. The molecular architectures of these polymers can be tailored to suit a specific application. A wide variety of experiments have been carried out in the past to understand micellization phenomenon. Investigation of polymer -surfactant interactions constitute the next logical step in any such study. The surfactant properties especially the surface activity, self-association and phase behaviors of these copolymers have been extensively measured. The association behavior has been monitored using several experimental methods and the results of such studies are reviewed by Chu and Zhou [2], Almgren et al [3], Alexandridis [4], Booth and Attwood [5]. One of the main disadvantages of above mentioned polymeric surfactants has been that these are less effective or some times fail in organic media. In order to make available polymeric surfactants, which are effective both in aqueous and non-aqueous media, silicone surfactants, a generic name given to molecules consisting of permethylated siloxane group joined with one or more polar groups, have been synthesized. A recent
volume of surfactant science series [6] has reviewed the synthetic methods, surface active and phase behavior studies along with various novel applications areas such as stabilizers for polyurethane foam, de-emulsifiers in oil production and de-foamers in fuels etc. of silicone surfactants. A more recent paper [7] describes the utility of silicone surfactants in other industrial formulations such as inks, paints and coatings, in textiles, agriculture and personal care products. Besides above industrial importance, silicone surfactants are interesting from academic point because by using different synthetic routes, molecular architectures of different types and of wide range of molecular weights can be generated [6-9]. The literature survey cited reveals that in spite of the wide and extensive usage of surfactants little is known about their association behavior in water in general, and the physical and geometrical characteristics of their associates in particular with polyanionpolyciotes. Systematic and detailed investigations on the characterization of the micelles formed by well-defined surfactants and influence of various factors such as temperature, molecular architecture and additives on the micellar structures are highly desirable that will establish a possible correlation between micellar architecture and specific applications.

Gradzielski et al [10] have monitored the association behavior of tri- and polysiloxane surfactants by using static light scattering and small angle neutron scattering (SANS) methods both in dilute and concentrated aqueous solutions. It has been concluded by the authors that both types of silicone surfactants formed globular micelles, whose size hardly changed in the concentration range 1 – 20% (w/v) at 25°C. In a recently reported [11] work systematic investigations on cloud point, surface activity, SANS and viscosity measurements on aqueous solutions of two comb-like polyether
modified poly (dimethylsiloxane)s was discussed. Model fitting of SANS data showed that (i) both the surfactants formed oblate ellipsoidal micelles with a constant size (in the concentration range of 1 – 5 % (w/v)), (ii) the micelles, however registered 30 – 60 % increase in size along the semimajor axis with similar rise in the association number and the other micellar parameter i.e. the number density of micelles changed inversely with the rise in temperature. The changes in the micellar size and other parameters were interpreted mainly in terms of dehydration effects at elevated temperatures as observed from the viscosity data. However, SANS data could not ascertain information on the hydration water within associates, micellar size distribution and inter micellar interactions.

These substances are amphipathic in nature and consist of hydrophilic and hydrophobic moieties in the same molecule. The hydrophilic part of the molecules is invariably based on poly(oxyethylene) (POE), E because of its excellent water solubility even up to the temperature close to 100 °C and the Flory theta temperature of POE chains is around 100 °C [1]. The hydrophobic part of the molecules offer a wider choice because it can be chosen from water insoluble long alkyl chains, poly(oxypropylene) PPO, (P), poly(oxybutylene) PBO, (B), polydimethylsiloxane, PDMS and polystyrene, PS etc. The multiple possibilities in variation of initiator functionality and order of addition of respective oxide monomers lead to the synthesis of several well defined hydrophobic – hydrophilic copolymers based on EP, EB diblock and EPE, EBE, PEP and BEB triblocks. Some of these copolymers are now commercially available. The graft or comb like copolymers based on PDMS with a branch of a grid containing E or E – P units are relatively new entrants in the market.
Besides their ability to associate into micellar self assemblies, the architectural variation for a given composition or variable compositions within a given architecture enables the polymeric surfactants to possess unique surface active, phase and gelation behavior. These special features have been the subject of extensive academic investigations especially on dilute as well as concentrated solutions of EPE, EP and PEP copolymers and the published work has been reviewed by Chu and Zhou [2], Alexandridis [3], Booth and Attwood [4]. However, from the academic interpretation point of view, it has been noted that EPE triblock copolymers are compositionally heterogeneous and contain significant proportion of diblock PE copolymers and also homopoly(oxypropylene) because of an inherent transfer reaction (hydrogen abstraction) involving propylene oxide monomer. To over come this problem Heatley et al [6] and Mai et al. [7] have selected 1, 2-butylene oxide and styrene oxide as precursor monomers for the hydrophobe and found that the transfer reaction is absent when these monomers are copolymerized together with oxyethylene chains. Dow chemical company has made available series of EB and EBE copolymers commercially [8]. Inverse gas chromatographic measurements indicated that EB diblock copolymers are less hydrophobic than nonyl phenol and fatty alcohol ethoxylates but more hydrophobic than EP copolymers. This intermediate hydrophobicity and ease of synthesizing copolymers with homogeneous compositions has lead to the increasing interest in EB di- and EBE or BEB triblock copolymer solutions. Nace et al. [9] have reported that EB diblock copolymers have improved the surfactant performance over their EP analogues. Within the comparable block lengths and compositions for two molecular architectures of EB and EBE copolymers, it has been reported [9-13] that (i) diblock copolymers have lower critical micelle
concentration (CMC), and (ii) the micelles of diblock copolymers have larger size and association number.

From the literature available on the CMC's and surface active parameters of EB and EBE copolymers, it is found that with the lengthening of E block with fixed B part, the CMC values showed large decrease in diblock EB copolymers [14-16] and while the same increased in triblock EBE copolymers [4,12,16]. Kelarakis et al. [15-16] have observed that the area adsorbed per copolymer molecule at the air / water interface becomes 1.6 times more when E block length is almost doubled. A common feature was generally noted on the dependence of the micellar association number, $n$ on the overall E block length for the micelles of the di- and triblock copolymers. The association number at a fixed temperature always decreased drastically when E block is lengthened [4, 11, 12, 14, 16-19]. There are interesting observations as far as the change in hydrodynamic radius, $R_h$ of the copolymer micelles with the variation in hydrophilic chain length is concerned. It has been found that, the micelles of diblock EB copolymers have bigger size when the parent copolymer has a longer (> $E_{38}$) E block [14, 16-19] and the micellar size diminished under the same conditions among $E_{18}B_{10}$ and $E_{24}B_{10}$ copolymers [12, 14]. No definite trend was however noted in $R_h$ dependence on E block length for triblock EBE copolymer micelles [4, 12].

The effect of temperature on $R_h$ and aggregation number of di- and triblock copolymer micelles has been monitored by Booth and coworkers [11,12,14,16-22] The rise in temperature did not produce significant changes in the $R_h$ values but at the same time the micellar associates could accommodate more copolymer molecules. In all these studies, the authors treated the data assuming spherical shape for the micelles. The question, whether the micelles of EB copolymers retain the same shape? has been addressed using Small Angle Neutron Scattering (SANS) measurements on
E$_{90}$B$_{10}$, E$_{40}$B$_{10}$ and E$_{18}$B$_{10}$ micelles in dilute aqueous solutions by Derici et al.[18] and Hamley et al.[23] Derici et al.[18] noted that E$_{90}$B$_{10}$ copolymer micelles are spherical in shape with homogeneous core attached with Gaussian chains in the temperature range of 20 – 70 °C. Similar conclusion was drawn for the micelles of E$_{40}$B$_{10}$ [23]. However Hamley et al.[23] reported that the micelles of the short chain containing E$_{18}$B$_{10}$ copolymer turn into worm-like in the temperature range of 40 – 50 °C from initial spherical geometry at 20 °C.

A range of new biomaterials can be produced from micelles. Living polymers, as they are called, of long micellar structures can be crosslinked to produce soft and fragile gels. Micelles can be used as colloidal particles to charge neutralize polyelectrolytes and generate coacervate material. Gels can be suitably tailored to yield user defined visco-elastic properties, a feature, which can be extended to include elastomers, thermoplastics and melts. There is also a considerable debate on whether micelles can be used as soft fillers in rubber. Thus the application potential of micelles, in particular of biodegradable one's, is boundless. The present study attempts to highlight a small portion of the same.

8.2 References

8. B - Series Polyglycols, Butylene Oxide/Ethylene Oxide Block Copolymers, technical literature; Dow Chemical Co., Freeport, TX, (1994).
Mazin Ahmed Abed

M.Sc. Physics Department, College of Science, Mosul University, Iraq

List of Publications


4- Mazin Ahmad Abed and H. B. Bohidar, Effect of temperature on Surfactant induced softening in gelatin hydrogels, European Polymer Journal. (Communicated).