The present thesis entitled, “Studies on the Micellization Behaviour of Surfactants in Selected Solvent Media”, consists a total of six chapters.

In Chapter 1, a general introduction to the subject is given and the scope of the work is described.

In Chapter 2, a brief description of the experimental techniques used to carry out the work has been given.

Chapter 3 deals with the study on the aggregation and counterion binding characteristics of sodium dioctylsulfosuccinate (AOT) in aqueous sodium chloride medium. Critical micelle concentrations (cmc) of AOT in presence of NaCl and NaSa (sodium salicylate) have been determined from surface tension measurements at 40 °C. The aggregation process in AOT + aqueous NaCl / NaSa is endothermic. The special counterion binding behaviour of AOT has been found to be independent of the temperature. The greater condensation of counterions to AOT micelles has also been confirmed by zeta potential measurements at 40°C for AOT + NaCl, while for NaSa no such observation was made. Small-angle neutron scattering (SANS) profiles of AOT in the presence of NaCl clearly reveal a change in the shape of AOT micelle near the NaCl concentration where a two-fold increase in its $\beta$ value occurs. From the SANS data analysis this shape change has been shown to be from prolate spheroid to rod-like shape. On the other hand, SANS profiles of AOT in the presence of NaSa do not indicate any shape change of AOT micelle and interestingly in NaSa solution no abrupt change in the value of $\beta$
also occurs. Therefore, it is concluded that counterion binding constant of ionic micelle is a micellar shape dependent parameter. From the present study it is proposed that $\beta$ of prolate ellipsoidal shaped micelle is less than that of rod-like shaped micelle. This is consistent with the proposition made by Fujio et al. that the value of $\beta$ follow the order, spherical < oblate ellipsoidal < rod-like micelle. Generally, the counterion binding is thought to be one of the factors determining size and shape of ionic micelles. It emerges from this study that counterion binding controls the size of micelles, but shape change occurs due to geometrical requirement. Since a shift in the value of $\beta$ takes place as the micellar shape changes, surface charge density (ratio of micellar charge to its surface area) rather than surface charge appears to control $\beta$. This concept can be applied to explain why sodium deoxycholate (bile salt) micelle has very low value of $\beta$.

Chapter 4 deals with the study on the aggregation and adsorption characteristics of AOT in aqueous ammonium chloride solutions. Critical micelle concentration of AOT in aqueous medium at 25 °C as a function of $\text{NH}_4\text{Cl}$ concentration has been determined by measuring surface tension and fluorescence emission of pyrene probe. This study revealed that the SCB of AOT exists in the presence of mixed counterions also. The concentration $c^*$ of $\text{NH}_4\text{Cl}$ (0.009 mol kg$^{-1}$) at which the counterion binding constant of AOT changes suddenly is lower than that of $\text{NaCl}$ (0.015 mol kg$^{-1}$). In the presence of added $\text{NH}_4\text{Cl}$, as in the case of added $\text{NaCl}$, the sudden change of counterion binding constant of AOT is attributed to the change in the micellar
shape. Due to binding of NH$_4^+$ the surface area of the AOT micelle increases causing increase in the surface area-to-volume ratio of the micelle, which may be responsible for a transition from prolate to cylindrical shape of AOT micelle at a lower concentration of NH$_4$Cl. In the region of prolate shape (below c*) the amounts of bound sodium and ammonium counterions are almost equal, whereas in the region of cylindrical shape (above c*) bound counterions are predominantly ammonium. It is concluded from this study that (i) cmc depends mostly on the total counterion concentration in the solution and very less on the specific type of the cationic counterions present in the solution and (ii) synergism in the cmc retarding ability of counterions takes place when they are mixed and added to ionic surfactant solutions. In the AOT + NH$_4$Cl system, the plots of Corrin-Harkins (CH) equation and modified CH equation look similar unlike in the case of CPC + NaSa / NaBz system, which implied that when the mixed counterions are inorganic cations CH equation can still be used as an empirical equation. It has been shown that the expression for the surface excess of AOT in the presence of Na$^+$ and NH$_4^+$ counterions becomes similar to the expression for surface excess of AOT in the presence of Na$^+$ counterion alone, provided we consider the mixed counterions to obey Henry’s adsorption isotherm. This approach provides a method to compute the surface excess of ionic surfactants in the presence of mixed counterions.

In Chapter 5 we studied the counterion binding behaviour of AOT and SDS (sodium dodecylsulfate) in aqueous ethylene glycol medium. It has been
confirmed that cmc of AOT in ethylene glycol is more (about 68 times) than that in water and the variation of cmc of AOT in water + EG media as a function of EG content follow the general trend. The special counterion binding behaviour of AOT has a dependence on the solvent and disappears in water + EG media containing ≥ 30 weight % EG. In water + EG medium, the CH equation is not applicable to ionic surfactants for determining the counterion binding constant when the EG content becomes ≥ 40 weight %.

In Chapter 6 we have studied the competitive counterion binding controlled conductivity behaviour of sodium dodecylsulfate in aqueous nitric acid medium. This study has revealed that SDS in aqueous HNO_3 medium can exhibit both the unusual and the normal conductance behaviours. The normal conductance behaviour of SDS in acid medium is observed only if \( \frac{c_0}{c_a} > 3.4 \) (\( c_0 \) and \( c_a \) refer to critical micelle concentration and acid concentration, respectively), which was not reported from the earlier studies in aqueous HCl medium. On the basis of the present results, it is predicted that solutions of ionic surfactant + electrolyte with foreign counterion would exhibit unusual conductance behaviour (i) if the two counterions have large difference in their limiting ionic conductivity and undergo competitive binding to the ionic micelle, and (ii) if \( \frac{c_0}{c_a} < 3.4 \). The mixed-electrolyte model together with the Debye-Huckel-Onsager and the pseudophase-ion exchange models is applied successfully to analyze the conductivity data of ionic surfactant + electrolyte solutions no matter such solutions consist of mixed counterions and show unusual conductance behaviour. The relative values of the binding constants
of the two counterions are controlled by \( c_a, c_s \) (surfactant concentration) and \( c_0 \). The exchange of sodium and hydrogen counterions at the micellar surface has no significant effect on the cmc of SDS implying that these two counterions are not markedly discriminated by the dodecylsulfate micelle. A very useful conclusion of this study is that SDS + aqueous HNO\(_3\) medium with [HNO\(_3\)] ≥ 0.02M can be used as an alternative soft and green medium for nitration of organic molecules.