ABSTRACT


Chapter 1 consists of general introduction and the scope of the work. In Chapter 2 the experimental techniques employed have been described.

In Chapter 3, the measured surface tension and conductance values of cetylpyridinium chloride (CPC) in aqueous lithium chloride, sodium chloride and potassium chloride are presented and from these data critical micelle concentration (cmc) of CPC has been determined as a function of salt concentration at 295, 298 and 303 K. The co-ions are found to have no influence on the cmc of CPC. Cmc of CPC passes through a minimum at around 298 K. The surface density of CPC calculated at the cmc indicates that temperature and co-ion do not have any significant effect on the surface excess of CPC. The surface area covered per CPC molecule at the air – water interface is about 63 % higher than that of sodium dodecyl sulfate molecule indicating location of pyridine ring of the adsorbed CPC molecule at the interface. The values of the counter ion binding constant (β) have been determined from the Corrin – Harkin (CH) plots and the slope – ratio method. The CH plot provides an overall value of β, whereas β obtained from the slope - ratio method is dependent on electrolyte concentration. The co-ion effect on the counter ion binding constant is found to be negligible. The standard Gibbs free energy of micellization for CPC was computed and found to have almost same value at a particular electrolyte concentration in the case of all the three electrolytes. Mixed electrolyte model was applied for analyzing the conductance data in order to
estimate the aggregation number of CPC in the presence of electrolytes. For more than $5.2 \times 10^{-4}$ mol kg$^{-1}$ electrolyte concentration, aggregation number of CPC is found to be higher in NaCl than in the presence of LiCl and KCl thereby envisaging a likely effect of the co-ion on aggregation number.

In chapter 4, the measured surface tension and conductance values of CPC in aqueous sodium salicylate and sodium benzoate are presented and from these data the cmc values for CPC in aqueous sodium salicylate and sodium benzoate have been determined at 298 K. Salicylate counter ion has significantly larger tendency to decrease the cmc of CPC. The ortho hydroxyl group in sodium salicylate has a favouring influence on the aggregation of CPC to the extent of 3.5 kJ mol$^{-1}$. A modified Corrin – Harkins equation has been derived and it accounts successfully for the change in cmc of CPC with concentrations of sodium salicylate and sodium benzoate. The slope of the modified CH equation does not provide the value of the total counter ion binding constant, but gives the information about the lower limit to the value of $\beta$. Salicylate and benzoate ions bind predominantly to the CPC micelle suppressing the binding of chloride. Salicylate and benzoate ions bind almost equally to the CPC micelle and consequently the amount of counter ion binding is not responsible for the viscoelasticity observed for CPC + sodium salicylate. An adsorption isotherm was derived to estimate the surface excess of CPC in the presence of mixed counter ions by taking into account the adsorption of counter ions at the air – solution interface. Using this adsorption isotherm and choosing arbitrary values for the constant of binding of chloride ion at the adsorption layer ($\beta_{\text{lad}}$), surface excess of CPC was evaluated in the presence of salicylate and
benzoate ions. The results show that the ortho hydroxyl group in sodium salicylate has profound influence on the adsorption behaviour of CPC. Thus, this study provides a new approach to explain the influence of mixed counter ions on the adsorption and micellization behaviours of ionic surfactants.

In chapter 5, surface tension and conductance measurements of aqueous solutions of CPC at 30 °C in the presence of different pairs of coions and counter ions were made. The systems studied are CPC + sodium bromide and CPC + tetrabutylammonium bromide (TBAB). The bromide counter ion is found to decrease the cmc of CPC more than chloride counter ion. The modified Corrin-Harkins equation was used to describe the variation of cmc with added electrolyte concentration in the presence of mixed counter ions. From the slope of this equation the lower limit to the value of β was obtained. It is demonstrated that the mixed – electrolyte – model (MEM) can be applied to analyze the conductance data of surfactant solution containing chloride and bromide as mixed counter ions. The value of β obtained from the MEM was then used to determine the binding constants of the individual counter ions (β₁ and β₂). By this treatment we could show that (i) bromide preferentially binds to CPC micelle by replacing chloride counter ion, (ii) bromide binding is more than chloride and (iii) aggregation number of CPC is higher in the presence of bromide. Na⁺ and tetrabutylammonium (TBA⁺) coions do not have any effect on the cmc of CPC, but TBA⁺ affects the adsorption of CPC. In TBAB solution, adsorption of CPC takes place on a surface that already contains adsorbed TBA⁺ coions and above 0.02 mol kg⁻¹ TBAB the adsorbed TBA⁺ hinders the adsorption of CPC due to electrostatic and steric effects.
In chapter 6, the cmc of CPC in water + glycerol media as functions of glycerol and NaCl concentrations were determined at 25 °C from the experimental data of surface tension and specific conductance. Variation in cmc follows the normal trend, i.e., increases with increase in glycerol content and decreases on adding NaCl. Empirical analysis of the exponential increase in cmc of CPC with weight per cent of glycerol is indicative of cmc having two components; one component being dependent while the other independent of glycerol amount. Counter ion binding constant determined from both slope – ratio and Corrin-Harkins methods showed no dependence on glycerol amount, thus confirming the unusual trend in the behaviour of β. This anomalous behaviour of β is viewed as due to existence of a water-like environment around micellar surfaces in water + glycerol medium. In water + glycerol medium the ratio of solvent surface tension to limiting surface tension at cmc is also independent of glycerol amount, whereas Gordon Parameter decreases with increase in glycerol content as in other aqueous organic solvents and represents solvophobicity of the medium. The air – solution interface becomes saturated by the adsorption of CPC when the concentration of added NaCl is about 0.02 mol kg\(^{-1}\) irrespective of the glycerol amount.