CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Interaction of PEO-HTAC Complex in Dilute Solutions

This investigation concerns the evidence for the existence of complex formations between nonionic polymers and a cationic surfactant.

5.1.1 Effect of Surfactant Concentration

The contraction of PEO chain was observed by adding a small amount of HTAC (below cmc), because of a few adsorptions of HTAC molecules to the PEO chain. An addition of more HTAC to a solution of PEO causes the increases in specific viscosity (η_{sp}) and hydrodynamic radius (R_h), indicating a chain expansion due to electrostatic repulsions between bound micelles. On further addition of surfactant, η_{sp} and R_h reach their maximum values as the polymer chains are saturated with HTAC micelles. Beyond the binding saturation, both η_{sp} and R_h decrease because of contraction of the PEO-HTAC complex due to electrostatic screening from the accumulation of free micelles and counterions in the solution.

5.1.2 Effect of Polymer Concentration

The maximum binding condition depends on the polymer concentration, which shifts to the higher surfactant concentration with increasing polymer concentration; the great number of PEO chain in the solution the more surfactants are required to bind polymer to obtain a maximum binding. The average concentration ratio at the maximum binding point was found to be at $c_s/c_p = 1.75$. The higher PEO concentration corresponds to the lower degree of counterion binding and therefore the larger hydrodynamic radius R_h was also observed.

5.1.3 Effect of Temperature

The critical aggregation concentration (cac) gradually decreases with increasing temperature above 25°C, suggesting the interaction between PEO and

HTAC. The magnitude of the chain expansion increases with increase of temperature, consistent with the idea that the loss of hydrophilicity of the polymer leads to a stronger binding interaction with surfactant and hence an increase in micellar ionization at higher temperature. However, the location of the maximum in viscosity and R_h is independent of temperature, suggesting that the saturation concentration of binding is independent of temperature. It means that the saturation of surfactant binding to a polymer does not depend on the polymer hydrophobicity.

5.1.4 Effect of Molecular Weight

The interactions between HTAC and PEO with different molecular weights are quite similar. Therefore, the molecular weight of PEO has no influence on PEO-HTAC interaction. However, the locations of the peak maximum in both specific viscosity and R_h are weakly dependent on the PEO molecular weight. The slight decrease in the saturation ratio is possible to the fact that the probability of a micelle having multiple attachment sites to the PEO chains increases with increasing molecular weight.

5.1.5 Effect of Salt

The polymer conformation was changed by adding 0.1 M KNO_3 solution. The salt effect was attributed to the contraction of PEO chain due to the breakdown of intermolecular hydrogen bonding between polymer and the solvent water. The critical micelle concentration (cmc) and the critical aggregation concentration (cac) of HTAC in the absence and the presence of PEO in 0.1 M KNO_3 solution are lower than those in water due to the stabilization of HTAC micelles in salt solution, which promoted the interaction between polymer and surfactant by increasing charge density of HTAC micelles from the reduction of electrostatic repulsion between bound micelles.

5.2 The Structure of PEO-HTAC Complex in Dilute Solutions

The structure of PEO-HTAC complex in dilute aqueous solution was determined by the measurements of molecular weight of complex ($M_{w,com}$) and

radius of gyration (R_g). The binding of HTAC to PEO is evidenced by increases in $M_{w,com}$ and R_g, which level off at the HTAC/PEO concentration ratio where the viscosity and R_h maxima occur. The preferential binding of HTAC to PEO indicated that 0.874 g of surfactant is bound per g of PEO at the maximum. It was further observed that on average 2.0 ± 0.3 PEO chains are involved in the formation of the complex. The chain expansion is enhanced by the electrostatic repulsions between bound micelles, and formation of interpolymer complexes. At the maximum binding, only 50% of the HTAC molecules are bound to the PEO chain, and therefore the complex coexists with free surfactant micelles. The weak binding affinity of HTAC to PEO may be the driving force for PEO chains to share micelles when the formation of complex. The proposed model for the complex in aqueous solution is shown in Figure 5.1.
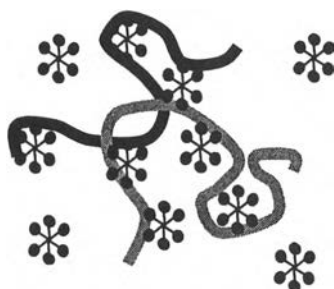

Figure 5.1 The proposed model for PEO-HTAC complex in aqueous solution at maximum binding.

5.2.1 Effect of Ionic Strength

The structure of complex formed between PEO and HTAC, in 0.1 M KNO_3 was investigated near the maximum binding point. The amount of bound HTAC to PEO indicated that on average 1.18 ± 0.06 PEO chains are incorporated in the complex in 0.1M KNO_3 salt solution. Moreover, 0.23 mole HTAC are bound per mole of EO in the presence of salt, compared to 0.12 mole HTAC per mole of EO in salt free aqueous solution, corresponding to a salt-induced increase in the number of HTAC bound per PEO chain from 50% to 94% of the total HTAC available in the solution. Again, radius of gyration (R_g) and hydrodynamic radius (R_h) of the PEO-HTAC complex in 0.1 M KNO_3 are significantly smaller than in water, due to the

twin effects of chain contraction via electrostatic screening, and dissociation of multichain complexes. The proposed model for the PEO-HTAC complex in 0.1 M KNO$_3$ solution is pictured in Figure 5.2.

Figure 5.2 The proposed model for PEO-HTAC complex in 0.1 M KNO$_3$ solution at maximum binding.

5.3 Viscoelastic Properties of PEO in Water

The storage modulus (G'), the loss modulus (G"), and the complex viscosity (η^*) are the most widely measured material functions to determine the viscoelastic properties of polymer. At low shear rates, the viscosity was observed to be a constant (η_0), so called the Newtonian plateau region, but at high shear rates the viscosity decreases, exhibiting the shear-thinning behavior. This behavior is more pronounced at higher PEO concentrations.

G" is always greater than the G' over the entire frequency range, indicating that the viscous behavior of PEO solution is predominant. The complex viscosity and both G' and G" of PEO solution slightly decrease as salt is added due to the effect of electrostatic shielding on the PEO chain, and thus reduces the size of the polymer chain. In the terminal region at low frequencies, the polymer shows the scaling behavior of G' $\propto \omega^2$, G" $\propto \omega$ which are characteristic of a linear homopolymer.

5.4 Viscoelastic Properties of HTAC Micelles

Cationic surfactants can self-assemble into long, flexible wormlike micelles in aqueous solution. The solution with lower HTAC concentration (c$_{HTAC}$ < 5 M) did not show the dynamic behavior due to the existence of spherical micelles. At low

frequencies, G' and G" follow the simple Maxwell behavior (G' $\propto \omega^2$, G" $\propto \omega$). The viscosity of micellar solution decreases as increasing temperature, suggesting that the micellar contour length gradually decreases with increasing temperature. Therefore, the relaxation time (τ_R) would be expected to decrease according to the equation: $\eta_0 = G_0\tau_R$. However, our results show the contrary. The longer relaxation time was observed as increasing temperature. We found that the decrease in plateau modulus (G_0) exceeds the increase of relaxation time and therefore, the relaxation time increases with increasing temperature.

A progressive deviation from Maxwell fluid behavior was found in a Cole-Cole plot, the plot of G"(ω) on the loss modulus versus the storage modulus G'(ω), with decreasing temperature at higher frequencies. The Cole-Cole plots were found to vary from the semicircular shapes, characteristic of a single exponential stress relaxation, to non-semicircular shapes. The changes in micellar structure strongly depend on the electrostatic interaction between surfactant micelles. At present, our system cannot be explained by Cates' theory which is only applicable for the highly concentrated systems in the presence of high ionic salt.

5.5 Viscoelastic Properties of PEO-HTAC Complexes

Rheological measurement indicates that the storage modulus (G') and the loss modulus (G") of the PEO-HTAC complex solution give rise to a largest value at mass concentration ratio of 1.5, which is near the maximum binding point of HTAC to PEO in dilute aqueous solution. It is confirmed that the progressive increase in the polymer-surfactant aggregates induces a cross-linking between PEO and HTAC, leading to an increase in the modulus. The viscosity data shows that the enormous increase in viscosity of PEO on addition of HTAC is obvious at 50°C and lack of zero-shear viscosity was observed. It is evident that binding of HTAC micelles to the PEO induces the non-Newtonian behavior at 50°C. The decreases in both G' and G", and viscosity were observed beyond the maximum binding point due to the breakdown of the PEO-HTAC aggregates, which leads to the reduction of the stiffness of PEO-HTAC complex.

The storage and loss moduli of PEO-HTAC complex slightly decrease with added salt (0.1 M KNO_3) due to the screening of electrostatic repulsions between the bound micelles and because of the effect of the disentanglement of the polymer chains in the complex. The viscosity reduces on an addition of salt is due to the decrease in persistence length of the polymer chain. The summary for the formation of PEO-HTAC complex is shown in Table 5.1.

Table 5.1 Summary for the formation of PEO-HTAC complex

	Complex in dilute aqueous solution	Complex in 0.1 M KNO_3 solution	Complex in concentrated solution
Temperature	$> 25^{\circ}C$	-	$> 20^{\circ}C$
Maximum concentration ratio (c_s/c_p)	1.5	1.75	1.5
Preferential binding (D')	0.87	1.64	-
$N_{s,b}/N_p$	50%	94%	-
Complex	Multichain complex	Unipolymer complex	-

5.6 Interaction of HPC-CADG Complex in Dilute Solutions

The surface tension measurement indicates that the critical micelle concentration (cmc) of CADG reaches a minimum at pH = 9, which is known as the isoelectric point. The surfactant has the same cmc in the presence of HPC as it does in water. This is similar to the situation encountered with the complex formation between a neutral polymer with a nonionic surfactant.

The viscosity measurement shows that a maximum and a minimum viscosity occur at c_s/c_p = 0.026 and 0.43, respectively. The maximum viscosity is correlated with the point at which the surfactant molecules start to form micelles, as indicated in conductivity measurement. On the other hand, the minimum viscosity is observed due to the electrostatic attractions between positive charge and negative charge within the polymer chain. This would induce a strong reduction in hydrodynamic volume of the HPC chain, and therefore reduces the viscosity.

From Zimm plot analysis, the molecular weights of HPC-CADG complex at c_s/c_p = 0.026 (maximum point) and c_s/c_p = 0.43 (minimum point) are determined by static light scattering. At the maximum point, the molecular weight of complex is approximately equal to the molecular weight of pure HPC solution, which indicates that there is no interaction between HPC and CADG at c_s/c_p = 0.026. However, at c_s/c_p = 0.43, the increases in both molecular weight of the complex and the preferential binding of CADG to HPC are observed due to the binding between polymer and surfactant. The amount of bound CADG to HPC indicated that one HPC chain is incorporated in the HPC-CADG complex solution.

5.7 Recommendations

1. It will be interesting to measure the dynamic properties of cationic worm-like micelles in terms of the effect of concentration and ionic strength.

2. The stress relaxation measurement should be studied in order to determine the terminal relaxation time and regime.

3. At present, the cationic surfactant in the salt free aqueous system cannot be explained by the existing theories. It is interesting to introduce the new theory for the system in the absence of salt.