

CHAPTER II

LITERATURE SURVEY

2.1 Proposed Mechanisms of Turbulent Drag Reduction

Several theories have been proposed to describe the mechanism of drag reduction.

Toms (1949) proposed the idea of a shear thinning layer at the wall having an extremely low viscosity. This explanation is based on the Oldroyd's theory (Oldroyd, 1948) which considered the slip at the wall.

Virk (1975) proposed that at the onset of turbulent drag reduction the duration of a turbulent burst is of the order of the terminal relaxation time of a macromolecule, and concluded that macromolecular extension is involved in the mechanism of drag reduction.

Hlavacek *et al.*, 1976 proposed that, in turbulent flow, the solvent contains micro disturbances or turbulence precursors. A macromolecule can suppress turbulence by pervading two or more of these micro domains simultaneously and hindering their free movement, growth and interaction.

Lumley, 1969, 1973, 1997 suggested that there is a critical value of wall shear stress, at which macromolecules become expanded due to the fluctuating strain rate. He pointed out that in the laminar sublayer close to the wall, polymer coils are not greatly deformed and viscosity does not increase greatly above that of the solvent alone. In the turbulent zone, the macromolecular expansion yields a dramatic increase in viscosity which damps small dissipative eddies and reduces momentum transport from the buffer layer towards the laminar sublayer, resulting in a thickening of the sublayer and a reduction of the drag.

Ryskin, 1987 developed the yo-yo model, which refers to the proposed mechanism by which polymer molecules unravel in an extensional flow field associated with turbulence. The central portion of the chain straightens, while the end portions remain coiled. When the flow becomes weak, the polymer chain retracts into a fully-coiled state. The taut central portion generates a large stress and facilitates viscous dissipation of turbulent kinetic energy.

De Gennes, 1986, 1990 developed a model based on the Kolmogorov energy cascade theory, and considering the ability of polymer molecules to store elastic energy upon deformation. When this elastic energy is comparable to the kinetic energy of a particular turbulent eddy, the energy cascade is suppressed.

2.2 Turbulent Drag Reduction by Polymer And Surfactant Additives

Rose and Foster, 1989 investigated the drag reduction induced by a cationic surfactant by studying effects of surfactant composition and counter ion concentration. They suggested that the viscoelastic surfactant's critical temperature (the highest temperature in which no drag reduction occurred) and the critical shear stress (the highest shear stress in which no drag reduction occurred) for drag reduction can be significantly increased by the addition of excess viscoelastic surfactant counterion. They found that an addition of excess NaSal in CTASal solutions dramatically increased both the critical temperature and Reynolds number for drag reduction. Longer alkyl chain lengths of cationic surfactants were shown to increase the critical temperature. The degree of drag reduction ability by mixing two different alkyl chain lengths of cationic surfactants was found to be lower than the summation of drag reduction ability of each type of those cationic surfactants. They also found that with increasing temperature, the drag reduction ability is decreased for the solutions of CTASal with and without excess NaSal counterion.

Yi and Kim, 1997 studied the stability of Taylor-Couette flow and drag reduction in Taylor-Couette flow by adding different types of polymers; polyacrylamide, xanthan gum and polyacrylic acid and the solvent was 1:1 mixture by weight of glycerine and distilled water. The result showed that the qualitative characteristics of transition from the stable Couette flow to the turbulent flow were found to be similar to that of Newtonian fluid (pure solvent). In the cases of polyacrylamide and xanthan gum solutions, the critical Taylor number decreased as the polymer concentration increased. In contrast, the critical Taylor number increased as the concentration of polyacrylic acid increased. The Couette flow was stabilized by the added polymer when the solvent viscosity was used in determining the critical Taylor number regardless of polymer type. By using a dilute solution

theory, the second normal stress difference coefficient was estimated. It was found that the ratio of second to first normal stress difference coefficients was negative and in the range of 0.0-0.2, and was closely related to the flexibility of polymer chain. They also found that a very weak shear rate dependency of viscosity could play an important role in determining the stability of Couette flow.

Myska and Zakin, 1997 investigated differences in the flow behaviors of polymeric and cationic surfactant drag-reducing additives by studying rheological behaviors of cationic surfactant, Habon G (Hexadecyldimethylammonium 3 hydroxy 2 naphthoate). They demonstrated that while polymer solutions are generally of shear thinning behavior, cationic surfactants show increases in viscosity when sheared, indicating the formation of a shear-induced structure (SIS). Polymer solutions degrade irreversibly when sheared and lose their drag-reduction behavior. Cationic surfactants degrade under high shear, but their structures are repairable and surfactant molecules regain their drag-reducing ability when shear is reduced. Dilute polymer solutions become drag reducing when a critical shear rate is exceeded. Surfactant solutions generally show a gradual departure from laminar flow curve and are drag reducing until a critical shear rate is reached. A thread-like network formed in surfactant solutions may cause a different drag reduction mechanism from that for high-polymer solutions.

Lu *et al.*, 1998 performed cryo-TEM, rheology and drag reduction experiments on cationic surfactant, Arquad 16-50 (cetyltrimethylammonium chloride) and Ethoquad O/12 (oleyl-methyldihydroxyethylammonium chloride) surfactant systems at different counterion (NaSal) to surfactant ratios. The surfactant concentration was fixed at low concentration, 5 mM, appropriate for drag reduction and mole ratio of counterion to surfactant was varied from 0.6 to 2.5. The results showed that the viscoelasticity and the drag reducing effectiveness increase with counterions/surfactant ratio because of the more stable micelle networks formed after increased neutralization of positive charges on the surfactant headgroups by the negative charges of the counterion molecules. When counterions/surfactant ratio is above unity, cryo-TEM images confirmed the existence of thread-like micelles. However, no micellar network formed when the counterions/surfactant ratio is 0.6 or

below 1. The thread-like micelles formed in this case may form networks under shear, but they are apparently easily broken up in regions of high shear.

Choi *et al.*, 1999 examined turbulent drag reduction by using rotating disk apparatus. They investigated drag reduction, DR for a homologous series of polyisobutylene (PIB) with two different solvent systems, cyclohexane and xylene and found that the polymer concentration, c dependence on DR obeys an empirical universal equation; $c/DR = K[c]/DR_{max} + c/DR_{max}$, where c is polymer concentration, DR is a percent drag reduction, K is a characteristic value which depend on solvent system, $[c]$ is an intrinsic concentration of polymer, DR_{max} is a maximum percent drag reduction for a given polymer solution.

Kim *et al.*, 1999 reported a drag reduction behavior and mechanical degradation of poly(ethylene oxide) (PEO) in solutions comparing between distilled water and synthetic seawater by using a rotating disk apparatus. They found that maximum drag reduction in seawater system occurs at the same concentration of PEO irrespective of the PEO molecular weight whereas the PEO concentration giving the maximum drag reduction in the pure distilled water is shifted to a lower value as the molecular weight of PEO increases. They explained that the alkaline metal ions in seawater possibly make a chelate complex with PEO molecules and alters the conformation of the polymer and drag reducing ability. By considering effect of mechanical degradation, they found that the polymer degradation occurs more rapidly with decreasing polymer concentration. This behavior is consistent with the fact that at low concentration of polymer solution, the number average molecular weight decreases more rapidly.

Kim *et al.*, 2000, 2001 investigated effects of turbulent flow and solvent quality on polymer degradation of high molecular weight polystyrene, PS in three solvent systems, benzene, chloroform and toluene by using rotating disk apparatus. They found that the percentage of drag reduction efficiency depends on degree of polymer-solvent interaction. The higher in solubility parameter leads to the more expanded polymer conformations in solvent which results in an increasing of drag reduction effectiveness.

Lin *et al.*, 2000 studied effects of counterion, sodium salicylate (NaSal) on drag reduction behaviors of a cationic surfactant drag reducer, Arquad S-50 (Soya-

$\text{N}(\text{CH}_3)_3\text{Cl}$). They found that by increasing the mole ratio of NaSal to cationic surfactant from $\xi = 1$ to $\xi = 2.5$, the maximum percent drag reduction and the critical temperature for effective drag reduction increased. Microstructure observed by cryo-TEM showed that thread-like micellar network existed in the cationic solutions containing counterion of $\xi = 1$ and 2.5. Lower counterion concentration has a lower critical temperature because its microstructure changes from thread-like micelles to spherical micelles at a lower critical temperature ($\sim 60^\circ\text{C}$). Higher counterion concentration extends the thread-like micellar structure to a higher critical temperature ($\sim 80^\circ\text{C}$). They explained that the counterion affects the strength of the micellar network. Thread-like micellar network microstructures are broken up by shear, leading to loss of drag reduction effectiveness. The excess counterion concentration imparts greater strength to the thread-like microstructure, as well as extending its upper temperature drag reducing effectiveness. They also found that excess counterion causes the solution change from viscoelastic to non-viscoelastic without any apparent change in the thread-like micellar microstructure.

Lin *et al.*, 2000 studied drag reduction in mixed cationic surfactants, alkyl trimethyl quaternary ammonium surfactants with different alkyl chain lengths of C_{12} and C_{22} and NaSal was used as a counterion. They suggested that mixing cationic surfactants is an effective way of tuning the drag reduction temperature range. By adding 10% by mol of C_{12} , the effective temperature range for drag reduction expanded to $4\text{--}120^\circ\text{C}$, compared with $80\text{--}130^\circ\text{C}$ with only C_{22} surfactant. Cryo-TEM micrographs revealed thread-like micellar networks for surfactant solutions in the drag reducing temperature range, while at non-drag reducing temperatures, the vesicles microstructures were observed.

Nakken *et al.*, 2001 studied the rheological behaviors in laminar and Taylor flows of 1-50 ppm poly α -olefins in Varsol 80. The measurements were carried out using a commercial rheometer equipped with a standard double-gap sample holder with axial symmetry. They found that in Taylor flow, all poly α -olefins displayed polymer induced drag reduction and polymer scission. Plots of friction factor versus Reynolds number of water and Varsol 80 showed the slope to be -1.00 in the region corresponding to laminar flow, and -0.6 in the region with established Taylor

vortices. They suggested that the employed rheometer with axial symmetric double-gap geometry exhibits a reproducibility and accuracy, when used to characterize flow containing well-developed Taylor vortices.

Myska *et al.*, 2001 studied influence of counterion on dynamic properties of drag reducing surfactants. Two different types of surfactant were studied; i.e., a cationic surfactant, cetyltrimethylammonium chloride (CTAC) and a zwitterionic surfactant, SPE 98330 (C₁₆-betain). The experiment has been carried out in a 40mm tube. They found that the zwitterionic surfactant and a mixture of cationic CTAC with NaSal are excellent drag reducers with the ability to decrease friction losses by more than 90%. The presence of calcium cations changes the drag reducing effectiveness of the zwitterionic surfactant substantially because the decrease in hydrodynamic radius, R_h whereas the same cations increase the R_h of CTAC/NaSal micelles. Extensional viscosities of both types of surfactants at their effective drag reduction concentrations are up to several hundred times greater than shear viscosities.

Koeltzsch *et al.*, 2003 reported drag reduction experiment of cationic surfactant solution Arquad S-50 (5 mM) + NaSal (12.5 mM) in turbulent Couette flow by using rotating cylinder geometry. From this study, this surfactant solution can reduce the drag up to 70% (for Reynolds number of about 70,000 – 150,000). They summarized that Couette flow is an alternative method for drag reduction investigations that has an important advantage. The geometry of Couette is much smaller in comparison to conventional test facilities like wind, water or oil channels, as well as pipe flows. In Couette flow, the flow is homogeneous and has a parallel in the cyclic boundary conditions used in computational fluid dynamics. Cyclic boundary conditions set the outgoing flow as the incoming flow. The Couette can be used as a powerful instrument for studying the effect of drag reducing surfaces or fluids.

Nakken *et al.*, 2004 investigated drag reduction in Taylor flow of polystyrene, PS in Toluene solutions by using a commercial rheometer equipped with a standard double-gap sample holder with axial symmetry. They found that drag reduction of PS in toluene is affected by concentration and molar mass of polymer. High molar mass and concentration up to overlap concentration promote drag reduction. Furthermore,

they found that the drag reduction behavior of solutions depends on hydrodynamic volume fraction and thermodynamic conditions of the system. The most of drag reduction effect occurs at volume fractions below 0.2. The flow induced chain extension was suppressed or drag reduction effectiveness decreased as the thermodynamic conditions become poorer. They summarized that both the flow induced extension of the polymer chains and the magnitude of the hydrodynamic volume fraction of the polymer damp the Taylor vortices.

Yu *et al.*, 2004 showed that addition of drag reducing additives such as cationic surfactant, cetyltrimethylammonium chloride (CTAC) induced several changes in turbulent flow characteristics: (1) In the viscous sublayer, the mean velocity gradient becomes gentler due to the viscoelastic forces introduced by the additives. The buffer layer becomes expanded and the slope of the velocity profile in the logarithmic layer increases. (2) The locations where the streamwise velocity fluctuation and Reynolds shear stress attain their maximum value shifted from the wall region to the bulk flow region. (3) The root-mean-square velocity fluctuation in the wall normal direction decreases for the drag-reducing flow. (4) The Reynolds shear stress decreases dramatically and the deficit of the Reynolds shear stress is mainly compensated by the viscoelastic shear stress. (5) The turbulent production becomes much smaller and its peak-value position moves toward the bulk flow region. Moreover, they have demonstrated that surfactant additives have dual effects on drag reduction: (1) introduces a viscoelastic shear stress, which increases frictional drag, and (2) dampens the turbulent vertical structures, decreases the turbulent shear stress, and then decreases the frictional drag. The second effect is a major effect and thereby causes drag reduction.

2.3 Various Effects on Formation of Complex between PEO and HTAC

Khine *et al.*, 2000, 2001, 2003 studied effects of temperature, molecular weight and ionic strength on the formation of a polymer, PEO and cationic surfactant, HTAC complexes in the aqueous solutions with and without salt added. Effects of temperature and PEO molecular weight were observed by the changes in the conductivity, specific viscosity (η_{sp}), and hydrodynamic radius (R_h). Their results

showed that an interaction between PEO and HTAC occurs at a temperature above 25 °C, as indicated by a decrease in the critical association concentration (CAC) in the presence of PEO relative to the critical micelle concentration (CMC) of a surfactant in the absence of PEO. Increasing temperature induces a stronger interaction between PEO and HTAC because hydrophilicity of PEO is diminished. The maximum in η_{sp} and R_h occurred at maximum binding concentration (MBC). The η_{sp} and R_h at MBC increase with increasing temperature and PEO molecular weight. The amount of surfactant molecules per PEO chain varies with molecular weight, but it is independent of temperature. The structure of macromolecular complexes formed between PEO and HTAC was observed by light scattering. This investigation reported that binding of HTAC micelles on PEO chain is accompanied by an increase in radius of gyration (R_g), up to the maximum binding point. From measurements of the molecular weight of the PEO-HTAC complex, accounting for preferential binding of surfactant, they deduced that, at the maximum binding condition, 0.12 mol of HTAC is bound per mol of EO. When HTAC concentration is above MBC, an electrostatic screening induces the PEO chain to contract, evidenced by a reduction in η_{sp} , R_h and R_g . They also studied influence of ionic strength on the interaction between HTAC and PEO and found that the height of the maximum in η_{sp} is diminished in the presence of salt (0.1 M KNO_3) because of the screening of electrostatic repulsions. Conductivity and differential refractometry measurements indicate that added salt stabilizes the binding of HTAC micelles to the polymer. Static light scattering (SLS) studies in the absence of salt revealed the formation of multipolymer PEO-HTAC complexes at the maximum binding point, whereas in salt solution, unipolymer complexation occurred. Dynamic light scattering (DLS) analysis indicated, for the complex in water, a broad size distribution that corresponds to a widely polydisperse mixture of multichain clusters. In contrast, in salt solution, the size distribution of the complex is similar to that of the pure PEO.

2.4 Rheological Behaviors on Isotropic Wormlike Micelle Solution

Cates and Candau, 1990 developed a model to explain various relaxation processes in micellar network of living polymers. The model consists of (1) the reptation of long polymer-like chains, (2) another related to the breaking and fusing of the constitutive units, and (3) Breathing and Rouse motions of the chains. This model considers that at low frequencies the behavior is Maxwellian as ascertained by the semicircular shape of the Cole-Cole plots. A deviation from the semicircle occurs at a frequency corresponding to the inverse of the breaking time of the micelles, τ_{br} . At higher frequencies, there is an upturn associated with the presence of rouse modes with time scales corresponding to that of molecular motions between entanglements. The characteristic time in this region (τ_c) is shorter than τ_{br} . This model revealed a parameter, $\zeta = \tau_{br}/\tau_{rep}$, where τ_{rep} is the reptation time of micelle. In the fast breaking limit ($\tau_{br}/\tau_{rep} \ll 1$), the long time behavior of the stress relaxation can be described by a single exponential decay with a relaxation time given by $\tau_R = (\tau_{br} \cdot \tau_{rep})^{1/2}$, where τ_R is the reciprocal of the cross over frequency between G' and G'' . In the slow breaking limit, τ_{br} is approximately equal to τ_{rep} .

Soltero and Puig, 1996 studied rheological properties of a cationic surfactant, cetyltrimethylammonium tosilate-water system by considering in linear viscoelastic regime. This experiment was made in the absence of additional electrolytes and the concentration of surfactant was high enough to form cylindrical micelle solutions. Analysis of the data with the Cates theory indicated that the dynamic behavior of the micellar system deviates from that of a single relaxation time mechanism, corresponding to a kinetic process of breakage and re-formation of the structural units. This system was in the slow breaking limit, and it exhibited constant entanglement density in the whole concentration range where micelle formed.

Hartmann and Cressely, 1997 investigated influence of sodium salicylate (NaSal) on the rheological behavior of an aqueous cetyltrimethylammonium chloride (CTAB) solution. In this work, they fixed the CTAB concentration, C_D at 0.1 M and NaSal concentration, C_S varied between 0.015 and 0.1 M. They observed two different kinds of rheological behaviors. Shear thickening was obtained at low C_S

concentration ($C_S < 0.025$ M) whereas shear thinning was observed at $C_S > 0.025$ M. At low C_S concentration, the critical shear rate at which we observed shear thickening effect was found to be a function of temperature and C_S . The Cole-Cole plots were also studied as a function of C_S concentration. They found that the Cole-Cole plot was close to a semi-circle at low frequencies but with departures in the high frequency range. These departures decrease with the increase in C_S .

Hartmann and Cressely, 1998 investigated the influence of some organic counterions: sodium salicylate (NaSal), sodium tosylate (NaTos) and sodium benzoate (NaBz) on the rheological properties of two aqueous solutions (0.1 and 0.05 M) of CTAB. The counterion concentration was varied between 0.01 – 0.02 M. From this observation, only NaBz showed a shear thinning behavior. For the two other salts, they found a shear thickening effect corresponding to some shear induced structures (SIS) found.

Kim *et al.*, 1997 observed effects of additives on the microstructure evolution in hexadecyltrimethylammonium bromide (HTAB) solution and its rheological properties. The studied additives are primary, secondary, and tertiary heptanols and sodium salicylate (NaSal). The results show that addition of the solubilized additives enhances the microstructure transitions (spherical micelles to rod-like micelles), which are affected by the additive concentration and its chemical structure. In these experiments, the HTAB concentration was fixed at 50 mM and NaSal was varied from 5 to 500 mM. The results showed that the micellar solution containing NaSal exhibited shear thinning behavior when the molar ratio of NaSal to CTAB was above 0.5. The shear viscosity increased with increasing the molar ratio of NaSal to CTAB until the molar ratio reached around unity. The shear viscosity decreased as the molar ratio exceeded the equimolar ratio. They explained that the scission of the micelle network junctions occurred at higher concentration of NaSal owing to the hindrance effect of the excess salicylate ions. From dynamic frequency sweep test (G' and G'' versus ω), they found a deviation from the linear viscoelastic Maxwell model which shows that the micellar solution containing CTAB and NaSal have the multiple relaxation time scales. The dynamic behaviors for the micellar solutions of molar ratio 1.0 and 10.0 are totally different. Specifically, the dynamic behaviors of the equimolar solution are quite similar to those of a concentrated

polymer solution and the loss modulus has its minimum value. Meanwhile, for the solution containing excess salicylate ions the dynamic behaviors belong to those of dilute entangled polymer solution.