

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Materials and Sample Preparation

Poly (ethylene oxide) (PEO) of various quoted molecular weights  $1.00 \times 10^5$ ,  $3.00 \times 10^5$ ,  $6.00 \times 10^5$ ,  $9.00 \times 10^5$  and  $40.0 \times 10^5$  g/mol, designated as PEO1, PEO3, PEO6, PEO9 and PEO20 were purchased from Aldrich Chemical Co. and used without further purification. The cationic surfactant was Hexadecyltrimethylammonium Chloride, (HTAC,  $C_{16}H_{33}N(CH_3)_3Cl$ ), a commercial product donated by Unilever Holding Inc., was used as received. The surfactant solution contains 50 %HTAC, 36 %  $H_2O$  and 14 % isopropanol. Analytical grade sodium chloride (NaCl), at 99.5 % minimum assay (Carlo Erba Reagenti Co.) was used to vary the ionic strength of the complex solutions. Distilled water was used as our solvent after two times filtration through  $0.22 \mu m$  Millipore membrane filters were used to remove dust particles. PEO stock solutions of 0.5 % (w/v) were prepared and stirred gently at room temperature for 4 to 30 days, depending on polymer molecular weight. The polymer-surfactant complex solutions were prepared as %w/v in distilled water at room temperature by dissolving PEO stock solutions in distilled water and by gentle stirring for 24 h at room temperature. Surfactant and polymer-surfactant complex solutions were prepared by adding appropriate amounts of HTAC and NaCl into mixtures of distilled water and polymer stock solutions and by gentle stirring for 24 h at room temperature. For light scattering measurements, the polymer-surfactant complex solutions were centrifuged at 10,000 rpm for 15 min and then filtered through  $0.45 \mu m$  Millipore membranes. All measurements were carried out at the temperature of  $30^\circ C$ .

#### 3.2 Procedure

Kinematic viscosity measurements were carried out using a Cannon-Ubbelohde viscometer (size no. 50, with  $\pm 0.2\%$  precision) at  $30^\circ C$ . Measured efflux

times were converted to the reduced viscosity and the specific viscosity, neglecting the density difference between the solution and the solvent ( $\rho_{\text{water } 30^{\circ}\text{C}} = 0.9957 \text{ g/cm}^3$ ). The intrinsic viscosity was determined using the Huggins and Kramer plots, and the viscosity-average molecular weight was computed via the Mark – Houwink – Sakurada equation with  $K = 1.25 \times 10^{-4} \text{ dL/g}$  and  $a = 0.75$  (Zimm, 1956)

Dynamic and static light scattering measurements, DLS and SLS, (Malvern Instruments Company, model 4700) were made using an argon laser emitting vertically polarized light at wavelength of 514.5 nm. DLS was used to determine the apparent z-average diffusion coefficient,  $\langle D_{\text{app}} \rangle$ , at different scattering angles  $\theta$ , and the center of mass diffusion coefficient,  $D_{\text{cm}}$ , of the polymer chain was then obtained by extrapolation of  $\langle D_{\text{app}} \rangle$  to zero scattering angle based on the following equation:

$$\langle D_{\text{app}} \rangle = D_{\text{cm}} (1 + Cq^2R_g^2 + \dots) \quad [3.1]$$

where  $C$  is a coefficient determined by the slowest internal mode of motion of the particle and by the size, flexibility, and polydispersity of the polymer (Ralton *et al.*, 1947)  $R_g$  is the radius of gyration of the polymer chain. The diffusion coefficient at infinite dilution,  $D_0$ , was obtained by extrapolation of  $D_{\text{cm}}$  to zero polymer concentration,  $c_p$  (g/l), using the following equation.

$$D_{\text{cm}} = D_0 (1 + k_D c_p + \dots) \quad [3.2]$$

where  $k_D$  (l/g) is defined as the concentration dependence of  $D_{\text{cm}}$  ( $\text{m}^2/\text{s}$ ) due to thermodynamic and hydrodynamic interactions. The hydrodynamic radius was calculated from  $D_0$  ( $\text{m}^2/\text{s}$ ) using the well-known Stokes-Einstein equation:

$$R_h = k_B T / 6 \pi \eta_s D_0 \quad [3.3]$$

where  $k_B$  is Boltzmann's constant (N.m/K),  $T$  is the absolute temperature (K) and  $\eta_s$  is the viscosity of solvent (kg/m.s).

Static light scattering data were analyzed and interpreted by the Zimm-Debye equation (Jones, 1967). In the small-angle limit, this can be expressed as:

$$(Kc/\Delta R_{\theta}) = (1/M_w)(1 + (q^2 R_g^2)/3) + 2A_2c \quad [3.4]$$

where  $M_w$  is the weight-average molecular weight,  $A_2$  is the second virial coefficient,  $R_g^2$  is the z-average of the mean square radius of gyration,  $\Delta R_{\theta}$  indicates the excess Rayleigh ratio, calculated from the excess scattering from the solution relative to a standard fluid:

$$\Delta R_{\theta} = ((\Delta I_{\theta(\text{solution})}/I_{\theta(\text{standard})}) \times R_{\theta(\text{standard})} \times (n^2_{(\text{solution})}/n^2_{(\text{standard})})) \quad [3.5]$$

Here  $\Delta I_{\theta(\text{solution})}$  is the excess scattered intensity of the sample solution relative to the solvent;  $n_{(\text{solution})}$  and  $n_{(\text{standard})}$  are the refractive indices of the sample solution and standard fluid.  $K$  is the optical constant:

$$K = 4\pi^2 n^2 (dn/dc)^2 / N_A \lambda^4 \quad [3.6]$$

where  $n$  is the refractive index of the solvent,  $c$  is the polymer concentration ( $\text{g}/\text{cm}^3$ ),  $\lambda$  is the wavelength of incident light (514.5 nm),  $dn/dc$  is the refractive index increment ( $\text{cm}^3/\text{g}$ ),  $N_A$  is the Avogadro's number, and  $q$  is the scattering wave vector ( $\text{cm}^{-2}$ ). In the SLS measurement, toluene (AR grade, Lab-Scan) was used as a standard solution with the Rayleigh ratio of  $3.2 \times 10^{-5} \text{ cm}^{-1}$ .

A conductivity meter (Orion Co., model 160) was used to characterize the electrical conductivity of polymer and surfactant complex solutions in the absence and presence of NaCl.

The equilibrium surface tension of polymer and surfactant complex solutions were measured by a pendant drop tensiometer (Kruss, model DSA10-Mk2). The shape of the sample drop is analyzed automatically and converted to surface tension.

A fluid rheometer (Rheometrics, model ARES V6.5.6) was used to measure turbulent wall shear stresses of PEO and HTAC solutions and their mixtures. The experiment was carried out using two Couette cells: a single Couette cell (SCU), and a double Couette cell (DCU). The single couette cell had a cup diameter of 47.9 mm and a bob diameter of 40.0 mm. For the double couette cell, the diameter of the outer cup and outer bob were identical to those of the single couette cell, whereas the inner cup and inner bob radii were  $R_{IC} = 7.2$  and  $R_{IB} = 18.05$  mm, respectively. The bob length,  $L$ , was 40.0 mm and the gap between the upper bob and the lower cup was set at 0.05 mm. The aspect ratio,  $\alpha$ , and the radius ratio,  $\eta$ , of our couette cell were 3.69 and 0.40, as calculated from  $\alpha = L/(R_{IB} - R_{IC})$  and  $\eta = R_{IC}/R_{IB}$ , respectively. The temperature was controlled by a water bath controller at  $30.0 \pm 1.0$  °C. The torque was measured by a transducer connected to the upper bob.

The inner wall shear stress,  $\tau_w$  ( $N/m^2$ ), of the samples was computed as the difference between the total torque measured by the DCU and the torque measured by the SCU according to the following equation:

$$\tau_w = (M_{DCU} - M_{SCU})K_\tau \quad [3.7]$$

where  $M_{DCU}$  (N.m) is the total DCU torque and  $M_{SCU}$  is the SCU torque, and  $K_\tau$  ( $m^{-3}$ ) is a stress constant, which can be expressed as

$$K_\tau = 1/2\pi L(R_{IB})^2 \quad [3.8]$$

where  $L$  is the bob length (m) and  $R_{IB}$  is the inner radius of the bob (m).

The inner shear strain rate was calculated from the relation

$$\dot{\gamma} = \theta K_\gamma \quad [3.9]$$

where  $\dot{\gamma}$  is shear rate ( $s^{-1}$ ),  $\theta$  is the angular velocity ( $s^{-1}$ ) and  $K_\gamma$  is a strain constant which can be expressed as

$$K_\gamma = \frac{2}{1 - \left(\frac{R_{IC}}{R_{IB}}\right)^2} \quad [3.10]$$

The Reynolds number (Re) and friction factor (f) were calculated for the inner chamber of the double Couette cell using the following equations

$$f = \frac{2\tau_w}{\rho(\theta R_{IC})^2} \quad [3.11]$$

$$Re = \frac{\theta R_{IC}(R_{IB} - R_{IC})}{\nu} \quad [3.12]$$

where  $\nu$  is the kinematic viscosity of sample solutions ( $m^2/s$ ) and  $\rho$  is density of solvent ( $kg/m^3$ ).