CHAPTER III
EXPERIMENTAL

3.1   Materials

Hydroxypropylcellulose (HPC) was purchased from Aldrich Chemical Co. The weight average molecular weight (M_w) of HPC from manufacturer's literature is 100 000. It was used as a water-soluble nonionic polymer.

Cocamidopropyl dimethyl glycine (CADG) was supported by Rhone-Poulenc Co. It was used as an amphoteric surfactant. The molecular weight of CADG is about 342 g/mol.

Sodium Hydroxide (NaOH), obtained from P & N Company, was used to vary pH of the sample solutions. Hydrochloric acid (HCl), obtained from J.T. Baker Inc., was used to vary pH sample solutions.

3.2   Instruments

3.2.1 Tensiometer

A digital tensiometer, model K10ST from KRUSS, was used to measure the surface tension in order to obtain critical micelle concentration.

3.2.2 Capillary Viscometer

3.2.2.1 Ubbelohde Viscometer

A Cannon-Ubbelohde viscometer was used to measure the viscosity of the sample solutions at 30^0C. It was used to determine the kinematic viscosity of Newtonion liquids. The size was chosen to cover the suitable flow time of each solution. In this work, the

Cannon-Ubbelohde viscometer is of size 50 which has a viscometer constant of 0.00407 cSt/sec, and the kinematic viscosity range from 0.8 to 4.0 cSt.

3.2.2.2 Thermostatic Water Bath

The digital thermostat, model DT-2 from Heto, Denmark, was used to control the temperature. The water bath was custom built to have a transparent window. It was covered with aluminium foil to maintain a constant temperature. The temperature was controlled with a resolution $\pm 1^0C$ by using a water circulator.

3.2.2.3 Timing Device

A stop watch from Casio was used to measure the flow time of the sample solutions with a resolution of ± 0.01 second.

3.2.3 Light Scaterring Measurement

Light scaterring measurements were performed by using the model series 4700 from Malvern Instrument Ltd.. The base system consists of seven units: i.e.computer, spectrometer, correlator, temperature controller, stepper motor controller, pump and laser power supply.

3.2.4 Centrifuge Machine

A high speed refrigerated centrifuge model PM180R from ALC International Co, Ltd. was used to precipitate dust particles. The sample solutions were centrifuged with a speed of 1.05×10^4 of g, g is equal to 9.81 m/s^2 for 1 hour.

3.2.5 pH Meter

A pH meter model, 920A from Orion, was used to monitor pH for all sample solutions.

3.3   Sample Preparations

3.3.1   Preparation of Hydroxypropylcellulose Stock Solution

Hydroxypropylcellulose (HPC) was dried with a vacuum oven at 80^0C with a pressure of 2000 mbar for 2 hours. The 5 grams of dried HPC was dissolved in 500 ml of distilled water at room temperature. The solution was slowly stirred by using a magnetic stirrer over 5 days to obtain a 10 g/L of homogeneous solution. Finally, the solution was filtered through a 0.45 μm Millipore filter membrane to remove dust particles.

3.3.2   Preparation of Cocamidopropyl Dimethyl Glycine Solution

The stock solution of cocamidopropyl dimetyl glycine (CADG) was prepared by dissolving 8.15 ml of CADG in 500 ml of distilled water. The solution was stirred slowly at room temperature for at least 1 day to get a 50 mM or 17 g/L of homogeneous solution.

3.3.3   Preparation of Water-Surfactant Solution

HPC-CADG solution was prepared by mixing the components in specific amounts. Either HCl or NaOH solution was added to the sample solution to adjust its pH. The sample solution was stirred slowly at room temperature for at least 1 day before experiments were performed.

For light scattering measurement, all sample solutions were centrifuged at 30^0C with a speed of 10 000 rpm for at least 60 minutes. The solutions were filtered directly into a light scattering cell by using a 0.22 μm Millipore filter membrane. For the viscosity measurement, The samples were filtered through a 0.22 μm Millipore filter membrane into the Ubbelohde viscometer.

3.4   Methodology

3.4.1 Surface Tension Measurement

3.4.1.1 Principle of surface tension

Surface tension, or surface free energy per unit area, is the minimum amount of work required to bring sufficient molecules to the surface from the interior to expand it by unit area. The surface tension of a solution of surfactant decreases steadily as the bulk concentration of surfactant is increased until the concentration reached the value known as the critical micelle concentration (cmc), above which the surface tension remains virtually unchanged (Rosen, 1989).

3.4.1.2 Experimental conditions

The surface tension measurements were performed by using a Du Nouy ring tensiometer. Before use, The ring was burned with fire for 10 seconds in order to eliminate impurities. In this work, temperature was kept at 30^0C by a thermostat. The solution was placed in the water bath at 30^0C for 20 minutes to obtain a thermal equilibrium. Then, it was poured into the chamber glass prior to the measurement.

3.4.2   Viscosity Measurement

3.4.2.1 Principle of viscosity

The viscosity of a dilute polymer solution is related to the dimension of the polymer molecules in solution. Therefore, the measurements of dilute polymer solution can be used to provide the information about molecular size and polymer-solvent interaction.

The essential quantity for polymer characterization is the Intrinsic viscosity, $[\eta]$, which is a measure of the hydrodynamic volume per mass unit of the polymer. The intrinsic viscosity is related to the specific

viscosity, η_{sp}, and the relative viscosity, η_r, by the Huggins equation and the Kraemer equation.

$$\eta_s / c_p \quad = [\eta] + k_H[\eta]^2 c_p \qquad (3.1)$$

$$(\ln \eta_r)/ c_p = [\eta] + k_K[\eta]^2 c_p \qquad (3.2)$$

where k_H is a dimensionless constant, called the Huggins constant which is independent of molar mass. The values are from 0.3 to 0.5 for good polymer-solvent pairs and poor polymer-solvent pairs, respectively (Sun, 1994). k_K is the Kraemer constant and c_p is polymer concentration. The intrinsic viscosity, $[\eta]$, is obtained from the average of y-intercept between η_{sp}/c and $(\ln \eta_r)/c$. The viscosity of the dilute solutions can be written as

$$\eta_r = \eta/ \eta_0 = \rho t / \rho_0 t_0 \qquad (3.3)$$

where ρ and ρ_0 are the densities of solution and solvent, respectively, and t and t_0 are the flow times of a polymer solution of concentration c_p and of the pure solvent, respectively. For dilute solution, we can assume that $\rho = \rho_0$ then

$$\eta_r = t / t_0 \qquad (3.4)$$

$$\eta_{sp} = \eta_r - 1 = (t-t_0)/ t_0 \qquad (3.5)$$

Substituting equation (3.4) and (3.5) into the equation (3.1) and (3.2), respectively, we can plot graphs between η_s/c and $(\ln \eta_r)/c$ versus polymer concentration. The intrinsic viscosity is determined from the intercepts of both graphs.

3.4.2.2 Experimental conditions

The viscosity measurements were carried out by using a Cannon-Ubbelohde capillary viscometer. The size of viscometer was chosen to measure the viscosity as 50. All sample solutions were filtered through 0.22 μm millipore filter membrane into the viscometer. Further, the viscometer was placed in the water bath at 30^0C for 20 minutes in order to obtain the thermal equilibrium of the solution. Finally, the measurements of the flow time was measured by using a stopwatch.

3.4.3 Dynamic Light Scattering Measurement

3.4.3.1 Principle of dynamic light scattering

Both conventional light scattering and dynamic light scattering can be used to determine the molecular weight, size and shape of macromolecules. More importantly, dynamic light scattering is a powerful tool that can measure the diffusion coefficient in a more elegant manner than many other classical tools.

Dynamic light scattering is characterized by three aspects: (1) the high intensity of the laser source makes possible to measure weakly scattered light and to observe very small frequency shifts. These frequency shifts information relating to the movement of the solute molecules. (2) Time t becomes an important variable in the measurement. The quantity we are interested in is $S(q,\tau)$, a function of both the angle (included in q) and time τ. The correlation function as an experimental device and a technique in the mathematical analysis of the phenomena is extensively employed (Sun, 1994).

The magnitude and frequency of the intensity fluctuations are at a maximum when light scattered by a single volume element is observed. The total intensity of scattered light entering the detector during each of a sequence of time intervals is recorded and analysed by a digital correlator

interfaced to a computer. The time interval between successive photon countings is known as the sample time Δt, and the seperation in time between two particular photon countings is known as their correlation time τ. It is essential to choose Δt so that it is much smaller than the time scale of the intensity fluctuations. Thus if τ is only a few multiples of, the corresponding photon counts will be closely related, and are said to be correlated. However, if τ is many multiples of Δt, the corresponding counts will not be correlated. The autocorrelation function, $G^{(1)}(\tau)$, of the intensity, i_θ, is defined by (Sun, 1994).

$$G^{(1)}(\tau) = \lim_{\tau \to 0} \left(1/T \int_0^T i_\theta(t)\, i_\theta(t + \tau)\, dt \right) \qquad (3.6)$$

where i_θ is the total intensity of scattered radiation

T is the total measurement time and its normalized value, $g^{(1)}(\tau)$, by

$$g^{(1)}(\tau) = G^{(1)}(\tau) / G^{(1)}(0) \qquad (3.7)$$

where $G^{(1)}(0)$ is the time- averaged value of the square of the intensity. The decay of $g^{(1)}(\tau)$ with increasing τ carries information relating to the rate of movement of the solute molecules. For a monodisperse solute undergoing Brownian motion

$$g^{(1)}(\tau) = \exp(-\Gamma\tau) \qquad (3.8)$$

where Γ is the characteristic decay rate; $\Gamma = q^2 D_0$, q is the scattering wave vector; $q = (4\pi n / \lambda)\sin(\theta/2)$, n is the refractive index and D_0 is the translational diffusion coefficient.

However, for a polydisperse system, such as in the present study, the first-order electric field time correlation function $g^{(I)}(\tau)$ is related to the characteristic line width (Γ) distribution function $G(\Gamma)$ through a Laplace transform relation:

$$g^{(I)}(\tau) = \int_0^\infty G(\Gamma)\, e^{-\Gamma \tau}\, d\Gamma \qquad (3.9)$$

where τ denoted the decay time. $g^{(I)}(\tau)$ is measured and known. $G(\Gamma)$ is the unknown characteristic line width distribution. There are several techniques that can be employed to solve for distribution, some of which accomplish this inversion through minimization of a least-square fit such as the method of cumulant, and a technique similar to that of Provencher's contrained regularization (Campbell, 1991).

Cumulant refers to the full measured correlation function being represented by a theoretically infinite serves each term representing a "statistical moment" of successively higher order. In principle these can be interpreted as giving information about the shape of the distribution of 'decay times' and hence particle sizes.

In this method the normalized first-order electric field correlaton function $g^{(I)}(\tau)$ is expanded in powers of the delay time as

$$\ln g^{(I)}(\tau) \quad = \quad -\Gamma\tau + 1/2!\ (\mu_2/\Gamma^2)(\Gamma\tau)^2 - 1/3!\ (\mu_3/\Gamma^3)(\Gamma\tau)^3 \qquad (3.10)$$

where $\Gamma = \int \Gamma G(\Gamma) d\Gamma$ and $\mu_i = \int (\Gamma - \Gamma)^i G(\Gamma)\, d\Gamma$.

The cumulant expansion is valid for small τ and sufficiently narrow $G(\Gamma)$. One should seldom use parameters beyond μ_3, because over fitting data with many parameters in a power-series expansion will render all the parameters, including Γ and μ_2, less precise. This expansion has the

advantage of getting information on $G(\Gamma)$ in terms of Γ and μ_2 without a prior knowledge of the form of $G(\Gamma)$, and is fairly reliable for a variance $\mu_2/\Gamma^2 \leq 0.3$ (Sun, 1994)

The z-average mutual diffusion coefficient, D_z, obtained from the first cumulant Γ_1 from the relation $D_{app} = \Gamma_1 / q^2$.

$$D_{app}(q) = D_c(1 + Cq^2Rg^2 - ...) \quad \text{for } qR_g < 2 \quad (3.11)$$

and $$D_c = D_0(1 + k_Dc_p) \quad (3.12)$$

where k_D is the diffusion virial coefficient that equal to $2A_2M\text{-}k_p\text{-}V_2$, A_2 is the second virial coefficient, M is molecular weight, k_p is the concentration dependence of the friction coefficient and V_2 is the partial specific volume. C is a coefficient depends on the macromolocular architecture. Actually, the C-parameter is determined by the slowest internal mode of motion in the particle and thus also depends on particle polydispersity (Brown, 1993).

The translation diffusion coefficient, D_0, of a macromolecule is related to the hydrodynamic radius, R_h, by using the Stoke-Einstein equation.

$$D_0 = k_BT / 6\pi\eta_0R_h \quad (3.13)$$

where η_0 is the solvent viscosity, k_B is the Boltzmann constant, and T is the temperature.

The normalized second cumulant, μ_2/Γ^2, or the 'polydisperse factor' is then a measure of the width of the distribution of particle sizes in solution.

3.4.3.2 Experimental conditions

Dynamic light scattering measurements were performed at 50^0 to 130^0 scattering angle using an Ar ion laser as a light

source at $\lambda = 514.5$ nm. All measurements were performed in the homodyne mode and the sampling time was chosen as an automatic sampling time. The sample cell was immersed in a temperature controller. In this work, the temperature was kept at 30^0C and was controlled with a resolution $\pm 1^0$C. The aperture setting of photomultiplier tube was 150 µm or 200 µm.