

CHAPTER II

EXPERIMENTAL

2.1 Materials

2.1.1 Polymer

Two different molecular weights of polyacrylamide (PAM) were purchased from Polysciences Inc. (Catalog no. 19901 and no. 02806). The reported molecular weights for these polymers are 7×10^5 and 5×10^6 .

2.1.2 Nonionic Surfactant

The commercial grade Triton X - 100 [TX - 100] ($M_w = 628 \text{ g mol}^{-1}$) was used as a nonionic surfactant and obtained from Union Carbide Thailand Ltd.. It was used without further purification.

2.1.3 Solvent and Other Chemicals

Sterile water was purchased from Thai Pharmaceutical Organization and used as a pure solvent. It was purified using a Millipore membrane filter with a pore size of $0.2 \mu\text{m}$.

Sodium azide (NaN_3) was purchased from the Clyde Industries Ltd. to prevent the growth of microorganisms in polyacrylamide solution [Munk et al.,1980].

Analytical grade toluene, purchased from J.T. Baker Inc., was used as a standard to measure the molecular weight.

2.2 Apparatus

2.2.1 Light Scattering Instrument

The laser light scattering instrument (model series 4700) is from Malvern Instruments Ltd.. A schematic diagram of the instrument is shown in Figure 2.1. The system consists of the following associated units:

- (i) Gavnometer
- (ii) Ar - ion laser source ($\lambda = 514.5 \text{ nm}$)
- (iii) Photomultiplier
- (iv) Correlator
- (v) Filter pump used to eliminate the dust particles in water connected with the light scattering unit.

2.2.2 Capillary Viscometer

(A) Ubbelohde Viscometer

The Cannon - Ubbelohde viscometers, no: 1067; capillary size 50 and no: 209; size 150, were used to measure the viscosity of the sample solutions at 30°C. Both were supplied from Curtis Matheson Scientific Inc..

The sizes were chosen to cover the suitable efflux time of each solutions. Their specifications are shown below:

1 - Size 50, no. 1067, $K = 0.004183 \text{ Cst / sec}$

Viscosity range : 0.8 to 3.2 Cst

2 - Size 150, no. 209, $K = 0.033490 \text{ Cst / sec}$

Viscosity range : 7 to 28 Cst

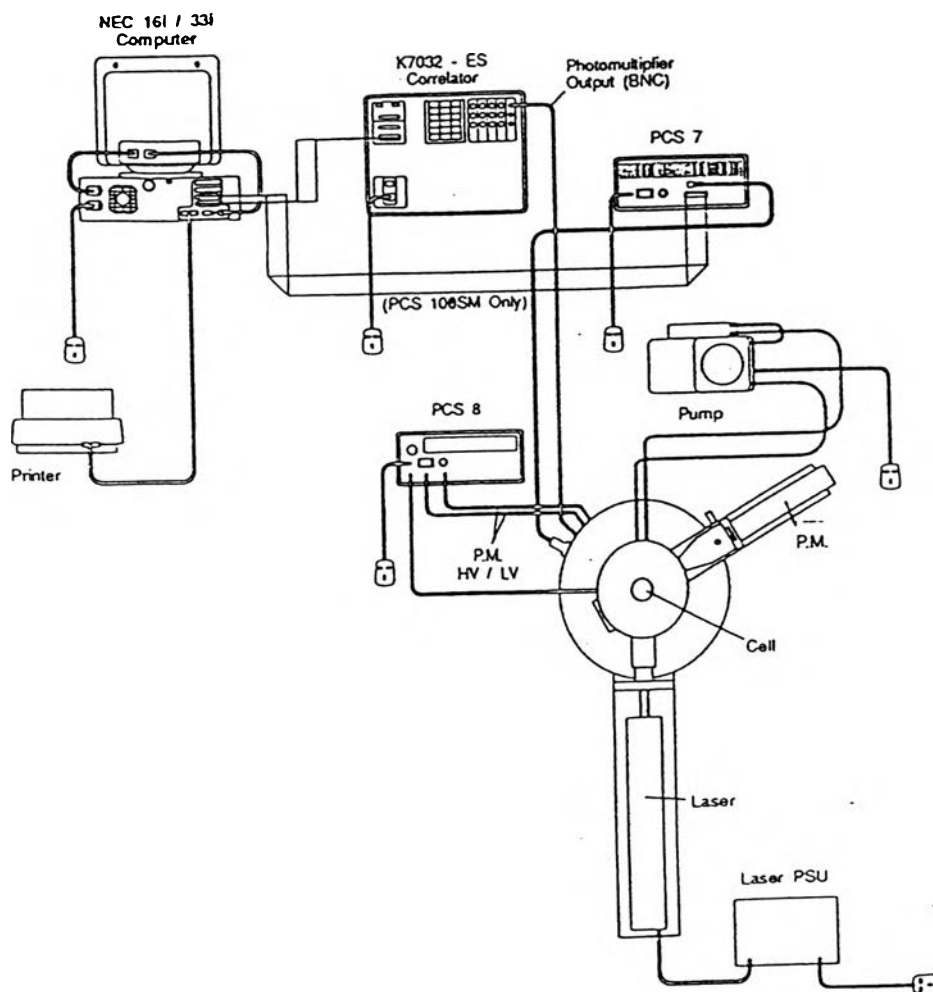


Figure 2.1 A schematic diagram of the light scattering instrument.

(B) Thermostatic Water Bath

The digital thermostat model DT - 2 from Heto, Denmark was used to control the temperature at 30°C ($\pm 0.02^{\circ}\text{C}$). Homemade liquid bath was used to contain water. It was modified to have only one side of transparent window. The other sides of bath were made from stainless steel and covered by glassfiber and aluminum foil to maintain the constant temperature.

(C) Timing Device

A stop watch was used to provide the flow time of the sample solutions with an accuracy of ± 0.01 second.

2.2.3 Sintered Glass and Syringe Filter

The 47 mm - diameter of sintered glass filter was used to eliminate dust in stock solutions. Before the sample solutions were poured into the light scattering cell and the capillary viscometer, the solutions were finally cleaned by using a 13 mm - diameter Millipore syringe filter.

2.2.4 Centrifugation

High speed refrigerated centrifuge was used to purify the sample solutions. The ALC model PM 180 R from ALC International Co., Ltd. was utilized in this experiment. The centrifuge has a maximum speed of 12,000.

2.2.5 Tensiometer

Tensiometer with Pt - ring: RI 10 probe was used to measure the surface tension of pure surfactant and polymer - surfactant complex solution.

2.2.6 Refractometer

The refractive index increments (dn/dc) of pure polymer and polymer - surfactant complex solutions were measured using Optilab DSP Interferometric Refractometer at a temperature of 30° C.

2.3 Methodology

2.3.1 Sample Preparation

(A) Preparation of PAM Stock Solution

A weighed amount of PAM was placed in a volumetric flask. The polymers were allowed to dissolve in sterile water containing 0.002 M

NaN_3 for periods of from 10 days to 3 weeks depending on the molecular weight and concentration, without violent agitation. The solutions were then filtered through Whatman paper filter no. 5 to eliminate large dust particles. The PAM stock solutions were stored at room temperature. The PAM concentrations are expressed in gram per litre.

(B) Preparation of Triton X - 100 Stock Solution

The stock solution of Triton X - 100 (TX - 100) was prepared by dissolving TX - 100 in filtered sterile water to a concentration of 50 mM. The solution was shaken mechanically for about 3 hr. The stock solution was stored at room temperature. The concentrations were calculated as moles per 1000 millilitre of solvent (molar scale).

(C) Preparation of PAM - TX - 100 Solutions

A certain amount of PAM and TX - 100 stock solutions were diluted with filtered sterile water. Polymer - surfactant complex solutions were prepared by adding prefiltered diluted PAM solutions to diluted TX-100 solutions. The solutions were then stirred slowly at room temperature at least 2 days and allowed to stay overnight to get an equilibrium condition.

Before each measurement, the sample solutions were centrifuged at a speed of 8,000 rpm for 1 hr and then filtered through Millipore filters (pore sizes 0.22, 0.45, 0.8 μm depending on the concentration and molecular weight).

2.3.2 Static Light Scattering Measurement

The scattering of light by polymer solutions may be expressed in terms of the Debye equation,

$$\frac{Kc}{R_\theta} = \frac{1}{P(\theta)} \left[\frac{1}{M_w} + 2A_2c + \dots \right] \quad (2.1)$$

K is given by the equation;

$$K = \frac{4\pi^2 n^2 (dn/dc)^2}{N_A \lambda^4}, \quad (2.2 a)$$

where n is the refractive index of the solvent, c is the concentration and dn/dc is the concentration dependence of the refractive index of polymer solution. The Rayleigh ratio is

$$R_\theta = R_\theta (\text{solution}) - R_\theta (\text{solvent}) \quad (2.2 b)$$

where R_θ is the Rayleigh ratio, the ratio of the scattered light intensity per unit volume of the scattering solution, per unit solid angle of the detector, to the incident light intensity (I_0) [Campbell and White, 1989].

For small molecules a plot of Kc/R_θ versus c is linear with intercept equal to $1/M_w$. However, as the molecular size increases destructive interference effects are taken into account by inclusion of the function $P(\theta)$.

The function $P(\theta)$ is directly related to the radius of gyration (R_g) according to this equation,

$$\frac{1}{P(\theta)} = 1 + \left(\frac{16\pi^2}{3\lambda^2} \right) R_g^2 \sin^2(\theta/2) \quad (2.3)$$

and therefore,

$$\frac{Kc}{R_\theta} = \left\{ 1 + \frac{16\pi^2 R_g^2}{3\lambda^2} \sin^2 \frac{\theta}{2} \right\} \cdot \left\{ \frac{1}{M_w} + 2A_2c \right\} \quad (2.4)$$

The weight average molecular weights of PAM and radius of gyration were determined by static light scattering measurements by using the above equation. The measurements were made at a temperature of 30°C, using toluene as a reference standard solution. The light source was Ar-ion laser operating at 514.5 nm. The light scattering intensities were investigated over the angular range $30^\circ < \theta < 90^\circ$ and were analyzed by Zimm plots to determine the molecular weight and R_g .

2.3.3 Dynamic Light Scattering Measurement

Dynamic light scattering (DLS) or photon correlation spectroscopy (PCS) measurements were made at 90° scattering angle with a Malvern 4700 spectrometer, using Ar-ion laser as a light source. The photomultiplier aperture was set between 100 and 200 μm .

(A) Data Analysis

In dilute solutions, the normalized intensity - intensity correlation function, $g^2(t)$, is an exponential decaying function, from which the mutual diffusion coefficient may be derived through the Siegert relation with the electric field correlation function, $g^1(t)$;

$$g^2(t) = B (1 + \beta |g^1(t)|^2) \quad (2.5)$$

where β is a nonideality factor accounting for deviation from ideal correlation and B is a baseline. The Z - average translational diffusion coefficients were determined by using the method of cumulant analysis which characterizes the distribution of relaxation rate.

For a system exhibiting a distribution of relaxation rate, the intensity - intensity autocorrelation function:

$$g^1(t) = \int_0^{\infty} G(\Gamma) \exp(-\Gamma t) d\Gamma, \quad (2.6)$$

where $\Gamma = \int_0^{\infty} G(\Gamma) \Gamma d\Gamma$ is the mean relaxation rate. Expansion of the correlation function leads to a polynomial expansion:

$$\ln g^1(t) = \Gamma \tau + \frac{1}{2!} \frac{\mu_2}{\Gamma^2} (\Gamma \tau)^2 - \frac{1}{3!} \frac{\mu_3}{\Gamma^3} (\Gamma \tau)^3 + \dots, \quad (2.7)$$

The above equation is called the cumulant fit. The first moment, Γ , can be related to the Z - average translational diffusion coefficient, $\langle D_t \rangle_Z$:

$$\Gamma = 1/\tau = \langle D_t \rangle_Z q^2 \quad (2.8)$$

where $q = (4\pi n/\lambda) \sin \theta/2$, q is the magnitude of the scattering vector, λ is the wavelength of the incident light in a vacuum, n is the refractive index of the media and θ is the scattering angle. The mutual diffusion coefficient determined at a finite concentration is characterized by the concentration, k_D ;

$$D = D_0 (1 + k_D c_p + \dots), \quad (2.9)$$

where D_0 is the mutual diffusion coefficient at infinite dilution and D is the value at concentration c .

The second moment, μ_2 , related to the variance by $\sigma = \mu_2 / \Gamma^2$, represents the deviation of the relaxation rates with respect to the width of the distribution [Wyn Brown, 1993]. The translational diffusion coefficient, $\langle D_t \rangle_Z$, can be calculated from the parameter of q and τ_q which indicates the size and

the structure of particles in solution. The hydrodynamic radius, R_H , can be calculated by using the Stokes - Einstein equation,

$$R_H = \frac{k_B T}{6\pi\eta_s D_0} \quad (2.10)$$

where k_B is Boltzmann's constant, T is the absolute temperature, η_s is the viscosity of the solvent and D_0 is the diffusion coefficient of the infinite dilution.

In the dilute solution, the translational diffusion coefficient, D , refers to the centre of mass diffusion in the limit of $qR_g \ll 1$, and the case of $qR_g \gg 1$, D is the diffusion coefficient resulting from the internal motions of the polymer chain. In semidilute solutions ($C > C^*$, where C^* is the overlap concentration), the correlation length, ξ , of entangled coils is obtained instead of hydrodynamic radius, R_H . In this regime, two modes of motion exist. One is the fast diffusion mode (D_f) which corresponds to the concentration fluctuation and the other is the slow diffusion mode (D_s) which is attributed to the relaxation of the multichains in solution.

2.3.4 Viscosity Measurement

Viscosity measurement is a straightforward tool to study the hydrodynamic volume of polymers in the solution. The viscosity of a polymer solution would be dependent both on concentration and on the average molecular size of the sample and hence the molecular weight.

(A) Definition of Terms

The kinematic viscosity, ν , is obtained from the measured efflux time, t , multiplied by the calibration constant, K :

$$\upsilon = K t. \quad (2.11)$$

The dynamic viscosity, η , is calculated from the kinematic viscosity and the density of the solution:

$$\eta = \upsilon \rho, \quad (2.12)$$

where η is dynamic viscosity (centipoise or mPa. sec), ρ is the density of the solution (g/ml), and υ is the kinematic viscosity (centistoke or mm^2 / sec).

The viscosity of the polymer solution is η and the solvent viscosity is η_s , usually expressed in centipoise or centistokes. The relative viscosity is the ratio of the two and the quantity is larger than unity.

$$\eta_{\text{rel}} = \eta / \eta_s. \quad (2.13)$$

The specific viscosity, η_{sp} , is the relative increment in viscosity of the solution over that of the solvent:

$$\eta_{\text{sp}} = (\eta - \eta_s) / \eta_s = \eta_{\text{rel}} - 1. \quad (2.14)$$

Reduced viscosity, η_R , describes the change in the specific viscosity per unit polymer concentration, c_p :

$$\eta_R = \eta_{\text{sp}} / c_p. \quad (2.15)$$

The intrinsic viscosity was determined by extrapolation of the reduced specific viscosity to zero concentration by the Huggins equation:

$$\eta_{sp} / c_p = [\eta] + k_H [\eta]^2 C + \text{-----} \quad (2.16)$$

(B) Intrinsic Viscosity Measurement

The molecular weights of the binary system were calculated directly from the intrinsic viscosity measurement by using the Mark - Houwink equation.

$$[\eta] = KM^a, \quad (2.17)$$

where K and a values are constant for a given polymer, solvent, and temperature.

In this work, the values of K and a were obtained from the previous work [Patterson and A.M.Jamieson, 1985] and Encyclopedia of Polymer Science and Engineering [1988]:

$$[\eta] = 1.00 * 10^{-2} M_w^{0.755}. \quad (2.18)$$

However, the reduced viscosity in ternary system of PAM / TX - 100 / water is not well defined because the concentration of the complex is not known. Therefore, the specific viscosity was used for ternary system instead of the reduced viscosity.

2.3.5 Refractive Index Increment

The refractive index increment (dn/dc) of the polymer / solvent system is a necessary prerequisite for the calculation of molecular weight. The measurements were carried out at the wavelength ($\lambda = 488 \text{ nm}$) and the temperature of 30°C . Figure 2.2 shows a linear plot to determine dn/dc for two

different molecular weights of polymer. From the slope, the value of dn/dc was obtained to be 0.175 ml/g.

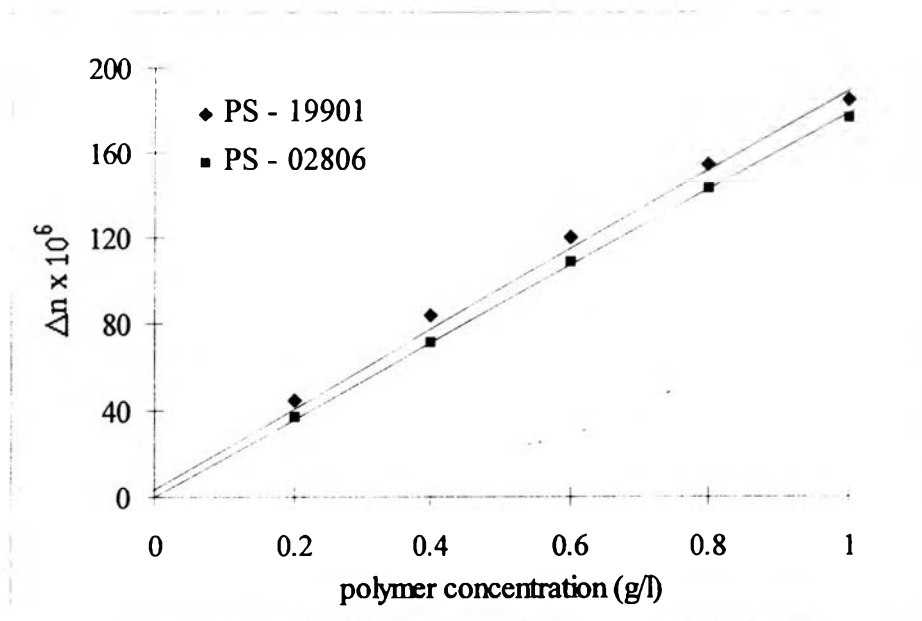


Figure 2.2 Determination of dn/dc for two different molecular weights of PAM.