

CHAPTER II

EXPERIMENTAL SECTION

2.1 Materials

2.1.1 Polymer

Hydroxypropyl cellulose (HPC) was purchased from Aldrich Chemical Company, Inc.. The reported molecular weights are 370,000.

2.1.2 Cationic Surfactant

Hexadecyltrimethylammonium bromide (HTAB) was used as a cationic surfactant and obtained from Sigma-Aldrich Company, Inc.. It was used without further purification.

2.1.3 Solvent and Other Chemicals

Sterile water was purchased from Thai Pharmaceutical Organization as a pure solvent. It was purified by using a Millipore membrane filter with a pore size 0.2 μm three times.

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

2.2 Instruments

2.2.1 Capillary Viscometer

(A) Ubbelohde Viscometer

Cannon-Ubbelohde viscometers were used to measure the viscosity of the sample solutions at 30°C. They were supplied from Curtis Matheson Scientific Inc.. The size was chosen to cover the suitable efflux time of each solution. The specifications are shown below:

a) Size 25, no. 115, K (by manufacturer) = 0.00203 cSt/sec

Viscosity range 0.3 to 1.6 cSt;

b) Size 50, no. 777, K (by manufacturer) = 0.00407 cSt/sec

Viscosity range : 0.8 to 4.0 cSt.

(B) Thermostatic Water Bath

The digital thermostat model DT-2 from Heto, Denmark was used to control the temperature. Homemade liquid bath was used to contain water. It was modified to have a transparent window. The other sides of bath were made from stainless steel and covered by glassfiber and aluminum foil to maintain a constant temperature. Temperature can be controlled with a resolution of $\pm 1^\circ\text{C}$ in the present circulation system.

(C) Timing Device

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

2.2.2 Light Scattering Instrument

The light scattering instrument, model series 4700, is from Malvern Instruments Ltd.. A schematic diagram of the instrument is shown in Figure 2.1. The full system includes the following associated units: a

gavimeter, an argon-ion laser source with the wavelength of 514.5 nm, a 128-channel correlator, a photomultiplier unit and a filtering system.

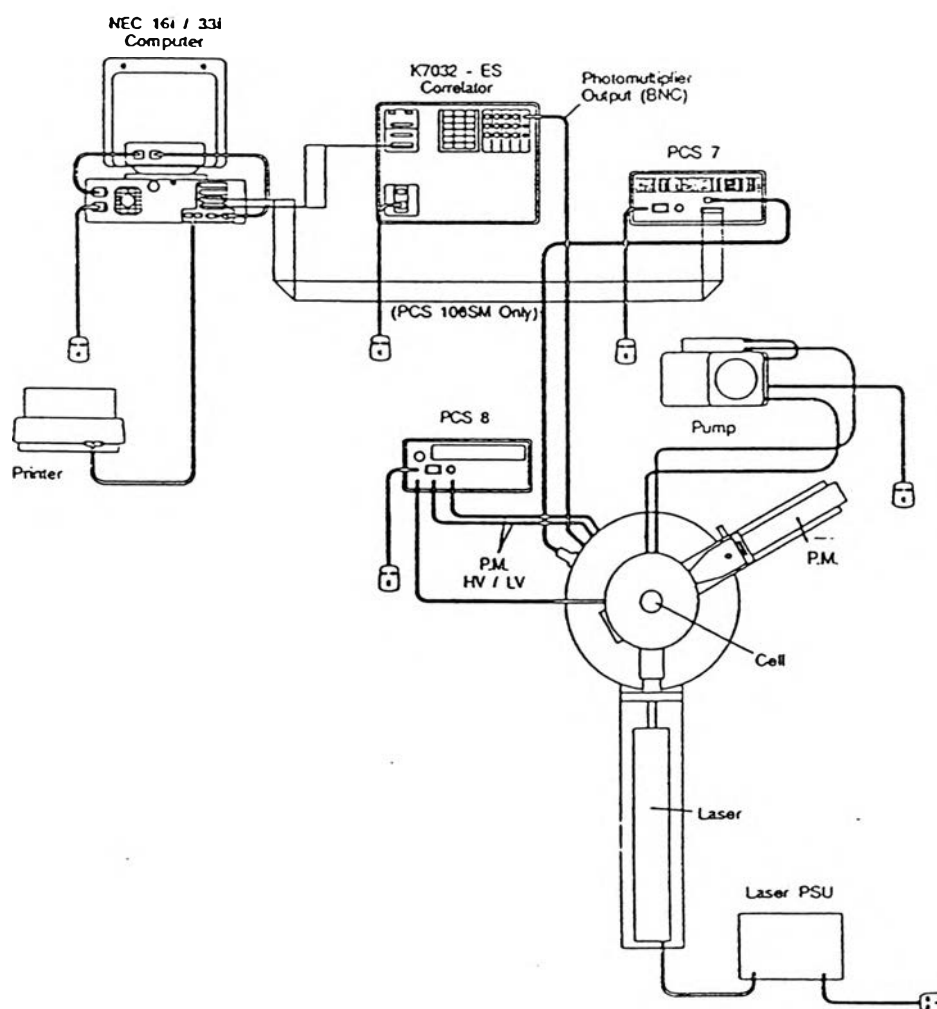


Figure 2.1 The dynamic light scattering instrument (Malvern, model 4700).

2.2.3 Refractometer

The refractive index increment (dn/dc) of pure polymer and polymer-surfactant complex solutions were measured using Dawn Optilap DSP interferometric refractometer.

2.2.4 Rheometer

The fluid rheometer, model ARES, is from Rheometric Scientific Inc.. The base system (Figure 2.2) consists of the test station, a power chassis, and a host computer.

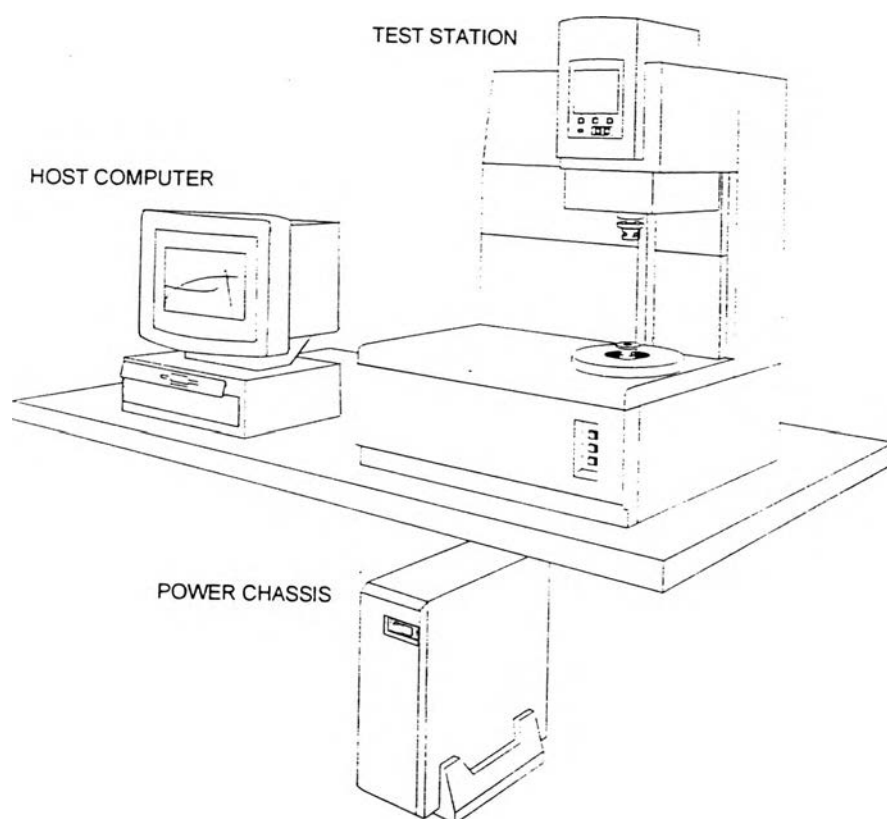


Figure 2.2 The fluid rheometer (Rheometric Scientific Inc., model ARES)

2.2.5 Tensiometer

The digital tensiometer K10ST from KRUSS was used to measure the surface tension of pure surfactant and polymer-surfactant complex solutions.

2.2.6 Conductometer

Conductometer, model 160 from Orion Co., was used to measure the conductance of pure surfactant and polymer-surfactant complex solutions.

2.2.7 Filtering Accessories

The sintered-glass filter from Millipore with 47 mm. Diameter was used to eliminate dusts in solvent. For sample solutions, an Acrodisc syringe filter from Gelman Sciences with 25 mm diameter was used.

2.2.8 Centrifuge

High speed refrigerated centrifuge, model PM180R from ALC International Co. Ltd., was used to purify the sample solutions. The maximum speed of this centrifuge is 12,000 rpm.

2.3 Methodology

2.3.1 Sample Preparation

(A) Preparation of HPC Stock Solution

A weighed amount of HPC was mixed with filtered sterile water. This solution was then slowly stirred for 3 to 5 days depending on the molecular weight and concentration. The stock solution of HPC was stored at 8°C in a refrigerator.

(B) Preparation of HTAB Stock Solution

The stock solution of HTAB was prepared by dissolving HTAB in filtered water. The solution was then slowly stirred for at least 1 day.

(C) Preparation of HPC-HTAB Solution

A certain amount of HPC and HTAB stock solutions were diluted in a filtered sterile water. The solutions were then stirred slowly at room temperature for at least 2 days and allowed to stay overnight to get an equilibrium condition [Rujithumkul, 1996].

2.3.2 Viscosity Measurement

The viscosity of a dilute polymer solution is considerably higher than the pure solvent or similar to dilute solutions of small molecules, because of the large differences in size between polymer and solvent molecules. The magnitude of the viscosity increase is related to the dimension of the polymer molecules in solution. Therefore, measurements of dilute polymer solution can be used to provide information about (a) molecular size (b) degree of polymerization from molar mass (c) effects upon chain dimensions of polymer structure and (d) polymer-surfactant interactions.

(A) Intrinsic Viscosity

The quantity of greatest importance for the purposes of polymer characterization is the intrinsic viscosity, $[\eta]$, since it relates to the intrinsic ability of a polymer to increase the viscosity of a particular solvent at a given temperature.

The specific viscosity, η_{sp} , and the relative viscosity, η_r , are related to $[\eta]$ by the Huggins equation and Kraemer equation,

$$\eta_{sp}/C_p = [\eta] + k_H[\eta]^2C_p \quad (2.1)$$

$$\ln \eta_r/C_p = [\eta] + k_K[\eta]^2C_p, \quad (2.2)$$

where k_{H1} is Huggins constant which is independent of molar mass. The range of k_{H1} value is from 0.3 for good polymer-solvent pairs to 0.5 for poor polymer-solvent pairs. k_K is Kraemer constant and C_p is polymer concentration.

The Huggins equation and Kraemer equations provide the most common procedure for evaluation of $[\eta]$ from experimental data. [Young, 1991]

(B) Interpretation of Intrinsic Viscosity Data

The intrinsic viscosity of a polymer is related to its viscosity-average molar mass, M_v , by the Mark-Houwink equation

$$[\eta] = KM_v^a, \quad (2.3)$$

where K and a are characteristic constants for a given polymer/solvent/temperature system. For Gaussian coils, a varies from 0.5 in a theta solvent to a limiting values of 0.8 in a good solvent. The value of K tends to decrease as a increases. For flexible chains, K is in the range 10^{-3} to $10^{-1} \text{ cm}^3\text{g}^{-1}$.

For spherical particles in infinitely dilution, the true hydrodynamic radius, R_h , and hydrodynamic volume, V_h , can be calculated from $[\eta]$ by using the expression

$$[\eta] = 2.5N_A V_h/M = 10N_A \pi R_h^3/3M. \quad (2.4)$$

where N_A is Avogadro's number and M is molecular weight of polymer.

(C) Measurement of Solution Viscosity

The Ubbelohde viscometer is a type of capillary viscometer used for dilute polymer solutions. Before use, it is essential to ensure that the

viscometer is thoroughly clean and both of solvent and solutions are free from dusts by filtration.

Under conditions of steady laminar Newtonian flow, the volume V of liquid which flows in time t through a capillary of length L and radius r is related to both the pressure P across the capillary and the viscosity η of the liquid by Poiseuille's equation

$$\eta = \frac{\pi r^4 P t}{8 L V} \quad (2.5)$$

During the measurement of flow time, P continuously decreases and is normally given by

$$P = \rho g h, \quad (2.6)$$

where h is the average pressure head, ρ is the density of the liquid and g is the acceleration due to the gravity. Thus Poiseuille's equation can be rearranged to have the form

$$\eta = K \rho t, \quad (2.7)$$

where K is a constant for a given viscometer.

Absolute measurements of viscosity are not required in dilute solution viscometry if we want to determine the relative viscosity of a polymer solution and the solvent from Equation (2.7)

$$\eta_r = \frac{\eta}{\eta_0} = \frac{\rho t}{\rho_0 t_0}, \quad (2.8)$$

where ρ and ρ_0 are the densities, and t and t_0 are the flow times of a polymer solution of concentration c and of the pure solvent. Since dilute solutions are used, it is assumed that $\rho = \rho_0$, then

$$\eta_r = t/t_0 \quad (2.9)$$

$$\eta_{sp} = \eta_r - 1 = (t - t_0)/t_0 \quad (2.10)$$

Substituting Equation (2.9) and (2.10) into Equation (2.1) and (2.2) and plot graph η_{sp}/C_p and $\ln \eta_r/C_p$ vs concentration. The intrinsic viscosity is obtained from average y-intercept of both values.

Reduced viscosity, η_R , describes the change in the specific viscosity per unit concentration of polymer, C_p ,

$$\eta_R = \eta_{sp}/C_p \quad (2.11)$$

However in ternary system, the concentration of the complex is unknown so the specific viscosity is used instead of the reduced viscosity to monitor the behavior of the complex.

(D) Conditions

In this work, temperature was always fixed at 30°C and controlled by a thermostat. Before each measurement, the sample solution was filtered through Millipore filters (pore sizes 0.45 μm) because dust particles can affect the flow time. The solution was kept in the water bath for 15 to 20 minutes to achieve a thermal equilibrium.

2.3.3 Dynamic Light Scattering

Dynamic light scattering involves analysis of the time dependence of the light scattering by a polymer solution. For a Gaussian distribution of intensity profile of the scattered light, $g^{(2)}(\tau)$ is related to the electric field correlation function, $g^{(1)}(\tau)$ by

$$g^{(2)}(\tau) = A[1+B(g^{(1)}(\tau))^2], \quad (2.22)$$

where A is experimental baseline, B is a constant which depends on the number of coherence areas that generates the signal ($0 < B < 1$). It is a function of the detecting optics and the sample time. $g^{(1)}(\tau)$ is the normalized electric field autocorrelation function. By Siegert relation, $g^{(2)}(\tau) = e^{-\tau t}$. $g^{(1)}(\tau)$ is related to the normalized distribution function, $G(\Gamma)$, by

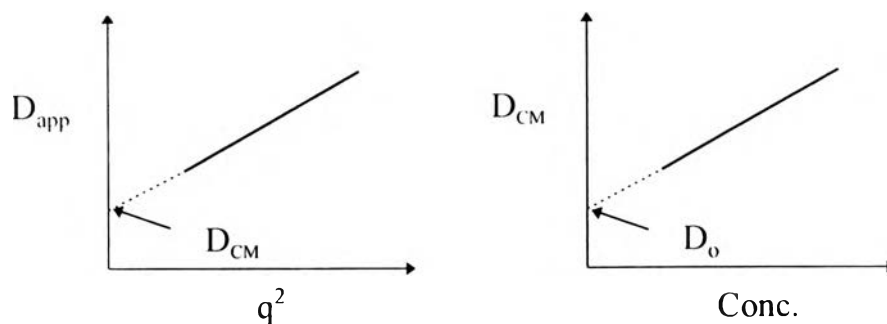
$$g^{(1)}(\tau) = \int G(\Gamma) \exp(-\tau\Gamma) d\Gamma, \quad (2.23)$$

where Γ is characteristic decay rate which is related to the translational diffusion coefficient, D of the solute by

$$\Gamma = q^2 D_{app}. \quad (2.24)$$

Thus by fitting the experimental $g^{(1)}(\tau)$ data to an exponential curve, it is possible to evaluate Γ and hence D_{app} .

To avoid the problem from large particles, the measurement is performed by plotting D_{app} vs q^2 and extrapolated to $q^2=0$ to get the center of mass diffusion, D_{CM} ;



At last, D_0 can be determined from the plot between D_{CM} and concentration. The translational diffusion coefficient of a molecule is related to its frictional coefficient, f_0 , by Einstein diffusion equation.

$$D_0 = kT / f_0, \quad (2.25)$$

where k is the Boltzmann constant and T is the temperature. Using this equation from the Stoke's equation, it is possible to evaluate R_h of the polymer molecules

$$f_0 = 6\pi\eta_0 R_h. \quad (2.26)$$

(A) Interpretation of Dynamic Light Scattering Data

In this technique, Cumulant method and Multimodal method can be used. The cumulant method gives information about polydispersity of the polymer system while Multimodal method can analyze into 2 modes: fast mode and slow mode. In dilute solution if $qR_h < 1$, the multimodal method will show only the slow mode due to center of mass diffusion. On the other hand, if $qR_h > 1$, a slow mode due to center of mass diffusion and a fast mode due to segmental diffusion are observed. In semi-dilute solution, the interpretation is

different. For this system, fast mode is correspond to concentration fluctuation and slow mode is related to translational diffusion of complex aggregation.

(B) Conditions

Sample solutions were prepared in the same way as the static light scattering. Dynamic light scattering measurements were made at 30° to 120° scattering angle using an Ar-ion laser as a light source at $\lambda = 514.5$ nm. The sample cell was maintained at 30°C in a water refractive index matching bath and pin hole size was fixed at 150 μm .

2.3.4 Static Light Scattering

The phenomenon of light scattering is encountered widely in everyday life. For example the light scattering by airborne water droplets causes the poor visibility resulting in a fog. Also, light scattering by gas molecules in the atmosphere gives rise to the blue color of the sky and spectacular colors that can sometimes be seen at sunrise and sunset. These are all examples of static light scattering since the time-averaged intensity light is observed.

Scattering of the radiation is a result of the interaction between a electromagnetic radiation and a molecules. The scattered radiation which has the same wavelength as the incident radiation is termed Rayleigh scattering. Additionally a small amount of the scattered radiation which has a higher or lower wavelength than the incident radiation arises from Raman scattering which is the basis of Raman spectroscopy.

The Rayleigh scattered light from dilute polymer solutions can be used to determine

- (a) weight average molar mass
- (b) yield values for the Flory-Huggins interaction parameter
- (c) the radius of gyration of the polymer molecules.

(A) Light Scattering by Small Molecules

The theory of light scattering was first developed by Lord Rayleigh in 1871. He assumed that (a) the molecular dimensions are very smaller than the wavelength of the incident monochromatic light (b) the scattering is perfectly elastic [Campbell and White, 1989].

The Rayleigh equation for ideal elastic scattering of unpolarized incident radiation

$$\frac{i_{\theta}}{i_{0}} = \frac{2\pi^2 (dn/dc)^2 Mc}{\lambda^4 N_A} \quad (2.12)$$

where	dn/dc :	the refractive index increment
	i_0 :	total intensity of scattered radiation
	M :	the molar mass of the gas molecules
	c :	gas concentration (mass per unit volume)
	θ :	the angle between detector and transmitted beam
	λ :	wavelength of the incident light

It is convenient to introduce a quantity called the Rayleigh ratio, R, which is the reduced relative scattering intensity defined by

$$R = \frac{2\pi^2 (dn/dc)^2 Mc}{\lambda^4 N_A} \quad (2.13)$$

(B) Light Scattering by Liquids and Solutions of Small Molecules

The molecules contained in liquid are very much smaller than wavelength and polymer molecules can be considered as point scatters. For dilute polymer solutions, only the scattering due to the polymer molecules is required. Thus the scattering arising from the local solvent density fluctuations

is eliminated by taking the difference, ΔR , between the Rayleigh ratios of the solution and pure solvent

$$\Delta R = R_{\text{solution}} - R_{\text{solvent}} \quad (2.14)$$

where ΔR is commonly known as the excess Rayleigh ratio.

It is usual to define an optical constant, K , as follows

$$K = \frac{2\pi^2 \eta_0^2 (dn/dc)^2}{\lambda^4 N_A} \quad (2.15)$$

The main useful expression is obtained by rearranging Equations (2.14) and (2.15) into the form

$$\frac{Kc}{\Delta R_0} = \frac{1}{M} + 2A_2c + 3A_3c^2 + \dots \quad (2.16)$$

(C) Light Scattering by Large Molecules in Solution

Equation (2.16) is often inappropriate for polymer solute molecules. The theory for ΔR begins to fail when solute molecules have dimensions of the order of $\lambda'/20$ where λ' is the wavelength of the light in the medium (λ/η_0). Most polymer molecules of interest have dimensions which are close to or exceeding $\lambda'/20$. In order to account for such interference effects, a particle scattering factor $P(\theta)$ is introduced and is given by the ratio

$$P(\theta) = \Delta R_\theta / \Delta R_{\theta=0}, \quad (2.17)$$

where ΔR_0 is the measured value of ΔR at the scattering angle, θ . For small molecules $P(\theta) = 1$ for all values of θ . By combining equation (4.15) and (4.16) a more general expression is obtained

$$\frac{Kc}{\Delta R_0} = \frac{1}{P(\theta)} \left[\frac{1}{M_w} + 2A_2c + 3A_3c^2 + \dots \right]. \quad (2.18)$$

$$\lim_{\theta \rightarrow 0} P(\theta) = 1 - \frac{q^2 R_g^2}{3} \quad \text{where } q \text{ is a magnitude of scattering}$$

wave vector, $q = \frac{4\pi\eta_0}{\lambda} \sin \frac{\theta}{2}$, so

$$\frac{Kc}{\Delta R_0} = \frac{1}{M_w} \left[1 + \frac{q^2 R_g^2}{3} \right] + 2A_2c + \dots \quad (2.19)$$

According to Zimm, the key equations at the limit of zero angle and zero concentration relate the light scattering intensity to the weight average molecular weight, M_w , and the Z-average radius of gyration, R_g , as:

$$\left[\frac{Kc}{\Delta R_\theta} \right]_{\theta \rightarrow 0} = \frac{1}{M_w} + 2A_2c + \dots, \quad (2.20)$$

$$\left[\frac{Kc}{\Delta R_\theta} \right]_{c \rightarrow 0} = \frac{1}{M_w} \left[1 + \frac{q^2 R_g^2}{3} \right]. \quad (2.21)$$

(D) Conditions

The scattered light is very sensitive to dust particles so sample solutions must be filtered through Millipore filters (pore size 0.45 μm) and then centrifuged at a speed of 8,000 rpm for 1 hour. After that clean sample solutions were sucked by a syringe at about 3 ml and injected into sample cells.

They were closed and wrapped by parafilm. Each sample cell was left in light scattering unit for 20 to 25 minutes to achieve thermal equilibrium.

Static light scattering intensity measurements were made by using a 514.5 nm source, at scattering angles from 75° to 120° with pin hole size 500 μm .

2.3.5 Refractive Index Increment

The refractive index increment (dn/dc) of the polymer system is necessary prerequisite for the calculation of molecular weight. The measurement was carried out at the wavelength, λ , = 488 nm and the temperature of 30°C. Figure 2.3 shows a linear plot to determine dn/dc for two measurements. From the slope, the value of dn/dc was obtained to be 0.137 ml/g.

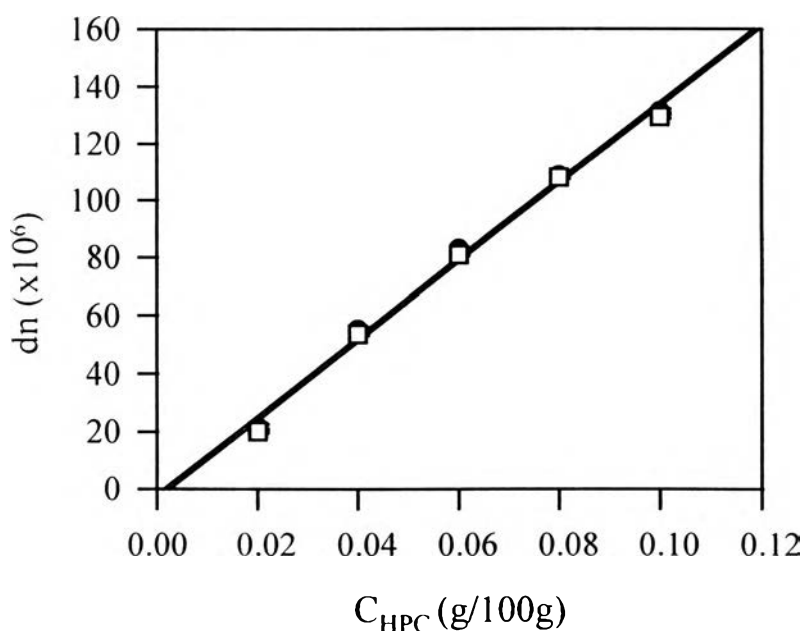


Figure 2.3 Determination of dn/dc for two measurements of HPC solutions.

2.3.6 Rheology

Rheology is the science dealing with the flow and deformation of material. This subject can be applied (a) to characterize material when deformed e.g. from equilibrium shear compliance, J_e , which gives information about permanent deformation (b) to study flow phenomena on a macroscopic level e.g. melt fracture and die swell (c) to provide a linkage between molecular structure and processing flow (d) to investigate complex structures on a microscopic level. In this thesis, a parallel plate rheometer is used to study the viscoelastic behavior of complexes. This apparatus contains 2 plates, stationary upper plate and oscillating lower plate. Strain is applied as a function of frequency, ω , and time, t , at the bottom plate so torque is applied to keep the stationary plate stay still. Torque can be converted to shear stress and other viscoelastic properties.

In a semidilute solution of polymer-surfactant complex system, surfactants act as a crosslinking agent and make the complex structure a transient network. Viscoelastic properties of this system will change due to its structure, and oscillatory shear moduli are frequently used to monitor continuously the viscoelastic properties of gelation.

(A) Basic Consideration

Several theoretical analyses have been developed for expressions for the frequency dependence of G' , G'' and the complex viscosity, $\eta^*(\omega)$, at the gel point. using the fractal scaling concept to define the gel network structure. The results of these investigations indicate that at the sol-gel transition point:

$$G' = A\omega^n \quad (2.27)$$

$$G'' = B\omega^n \quad (2.28)$$

and
$$\tan\delta = G''/G' = B/A = \tan(n\pi/2) \quad (2.29)$$

where A and B are related to the material strength factor of the gel. S. by

$$S = G'\omega^{-n}\Gamma(1-n)^{-1}\cos(n\pi/2) \quad (2.30)$$

$$S = (A^2+B^2)^{1/2}\Gamma(n)\sin(n\pi/2) \quad (2.31)$$

The exponent n is determined by experiments and can be related to the fractal dimension of the network, the stoichiometry of gel and the strength of the hydrodynamic interaction between the polymer chain segments. [Winter et al., 1988 and 1991, Hsu and Jamieson, 1993]

For the gel point measurement, there are 2 conditions used for investigating gel point:

- 1) $\tan\delta$ is independent of frequency and G' and G'' exhibit a power law dependent of the oscillation frequency.
- 2) gelation may occur before or after the crossover of G' and G'' at a specified frequency.

Two modes of dynamic testing were carried in this work, the strain sweep and the frequency sweep.

(a) Strain Sweep

Usually, the rheological properties of a viscoelastic material are independent of strain up to a critical strain level, γ_c . Beyond this critical strain level, the material's behavior is nonlinear and the moduli decline so measuring the strain amplitude dependence of the storage and loss moduli is usually the first step taken in characterizing viscoelastic behavior i.e. a strain sweep will establish the extent of the material's linearity.

The tests were performed by using the Fluid rheometer with a parallel plate geometry with a diameter of 50 mm. The experiment frequency

was 1 rad/s with a gap range 0.040 ± 0.002 mm. The level of strain was checked in order to ensure that all measurement took about 30 minutes.

(b) Frequency Sweep

After the fluid's linear viscoelastic region has been established by a strain sweep, its structure can be further characterized using a frequency sweep at a strain below the critical strain. This provides more information about rheological properties at different length scales. In a frequency sweep, measurements are made over a range of oscillation frequencies at a constant oscillation amplitude and temperature.

Below the critical strain, the elastic modulus is usually nearly independent of frequency, as would be expected from a structured or solid-like material vs. fluid-like material. The more frequency dependent the elastic modulus, the more fluid-like the material. If measurements are made on the sample at a strain amplitude above the critical strain, the moduli are much lower and show much more frequency-dependent behavior as well as a higher $\tan\delta$, indicating a more fluid-like behavior.

The measurements were also performed by using the Fluid rheometer with a parallel plate geometry and a diameter of 50 mm. The experiments were carried out in the temperature range 40 to 60°C with a gap range 0.040 ± 0.002 mm. A layer of silicone oil was added to the sample to avoid evaporation of solvent. At each temperature the sample was allowed to equilibrate for about 1 hour before measurement were taken. Each measurement (temperature) took about 20 minutes and the whole set of experiment took about 15 hours.