CHAPTER II
EXPERIMENTAL SECTION

2.1 Materials

2.1.1 Polymer

Hydroxypropylcellulose (HPC) was used as water-soluble nonionic polymer. It was purchased from Aldrich Chemical Co. The manufacturer claims a weight-average molecular weight (M_w) of 100000.

2.1.2 Surfactants

n-Octyl β-D-thioglucopyranoside (OTG) was used as a nonionic surfactant. It was purchased from Sigma Chemical Co. and used without further purification. The formula weight (FW) of OTG from manufacturer's literature is 308.44 and its melting point is 126-128 °C.

Cetyltrimethylammonium bromide (CTAB) was used as cationic surfactant. It was purchased from Aldrich Chem. Co. and used without further purification. The formula weight (FW) of CTAB from manufacturer's literature is 364.46 and the melting point is greater than 230 °C.

2.1.3 Solvent and Other chemicals

Sterile water was used as a pure solvent. It was purchased from the Government Pharmaceutical Organization. Before use, it was filtered through 0.22 μm Millipore filters three times to remove dust particles.

Sodium azide (NaN_3) was added to the HPC stock solution to retard bacterial growth. It was purchased from Ajax Chemical Company, Inc.

Analytical grade sodium chloride (NaCl), purchased from P&N Company, was used to vary the ionic strength of the sample solutions.

2.2 Instruments

2.2.1 Capillary Viscometric Instrument

2.2.1.1 Cannon-Ubbelohde Viscometer. Viscosity measurements were made by using Cannon-Ubbelohde viscometer. This type of capillary viscometers is used to determine kinetic viscosities of transparent Newtonian liquids. Especially well suited for temperatures above 200 °F, Cannon-Ubbelohde viscometer constants do not vary with temperature and are more durable than standard Ubbelohde viscometers. No kinetic energy corrections are required over a range of 0.5-100,000 cSt. It requires an 11-ml sample volume, with a precision of ± 0.2 %.

In this work, the Cannon-Ubbelohde viscometer is of size 50 which has a viscometer constant of 0.003735 mm^2/s^2, (cSt/s), and the kinematic viscosity range from 0.8 to 4 mm^2/s, (cSt).

2.2.1.2 Viscometer Thermostat and Bath. The digital thermostat model DT-2 with temperature stability ± 0.005 °C from Heto, Denmark was used to control temperature at 30 °C. It also has an effective circulation system. Transparent liquid bath was modified to contain water at a constant temperature.

2.2.1.3 Timing Device. A stop watch was used in the experiment to measure the flowing time of the sample solution with a resolution of ± 0.01 second.

2.2.2 Light Scattering Instrument

Light scattering measurements were performed by using the system 4700 from Malvern Instruments Ltd. The main elements of the system 4700 are shown in Figure 2.1. The system consists of eight separate units:

Computer

PCS 100 spectrometer

Correlator

Temperature controller/power supply, PCS8

Stepper motor controller, PCS7

Pump/filter unit, RR98

Laser power supply

Printer

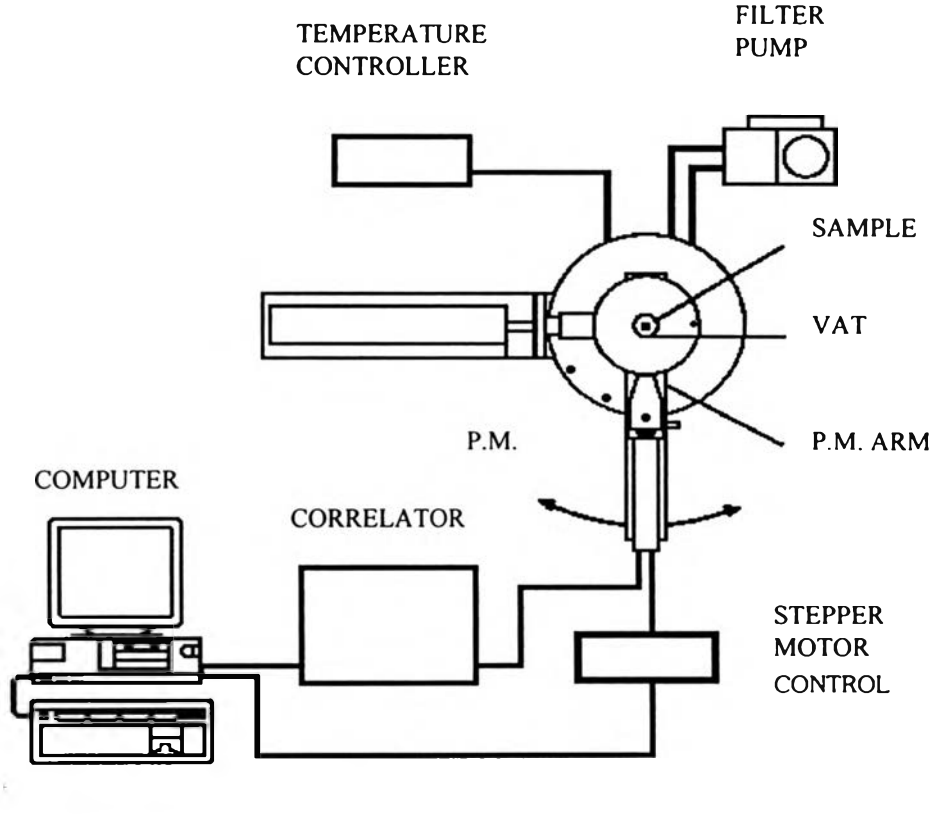

Figure 2.1 Dynamic light scattering instrument (4700 schematic).

Monochromatic light emitted by the laser is focused onto the sample cell, which is held in a glass vat filled with liquid. The "waist of focus" (i.e. the point where the beam is narrowest) coincides with the axis of rotation of the PCS100 spectrometer. The beam enters and leaves the vat through flat optical quality windows. Keeping these windows clean and free from scratches is vital if the PCS100 is to produce good results. An attenuator is mounted on the exit window to reduce back reflection of the laser. The liquid filling the vat has a refractive index close to that of quartz, to reduce flare at the interfaces with the vat and sample cell. The liquid in the vat also couples the sample thermally to the temperature sensor and heating/cooling elements that keep the vat contents to within 0.1°C of the temperature set on the temperature controller. The liquid is either an organic liquid, usually toluene, in our water. Water was filtered in situ using the RR98 filter/pump unit to remove dust. The sample is held in a small cell, usually made of quartz. Light scattered by the sample was collected by an optical system, so called "Pusey optics", after its inventor, and sensed by a photomultiplier (P.M.), which is sensitive enough to count individual photons. There is an aperture selector between the optics and the photomultiplier to control the amount of scattered light detected. Before reaching the photomultiplier, the light passes through a narrow band filter so that only light at the wavelength of the laser is detected. The photomultiplier is mounted on an arm which can be controlled by the stepper motor controller, which is connected in turn to the computer. Using this system any scattering angle between 10 ° and 150 ° can be set from the computer software. The scattering angle is defined as the angle between the beam after it has passed through the sample and light which is detected. If the PCS75 cover is removed the upper angle attainable is reduced to 145 °. The digital signal coming from the P.M. is processed by the correlator and then passed to the computer for final analysis

and display. Electrical lines that are used to connect different parts of the system 4700 are shown in Figure 2.2.

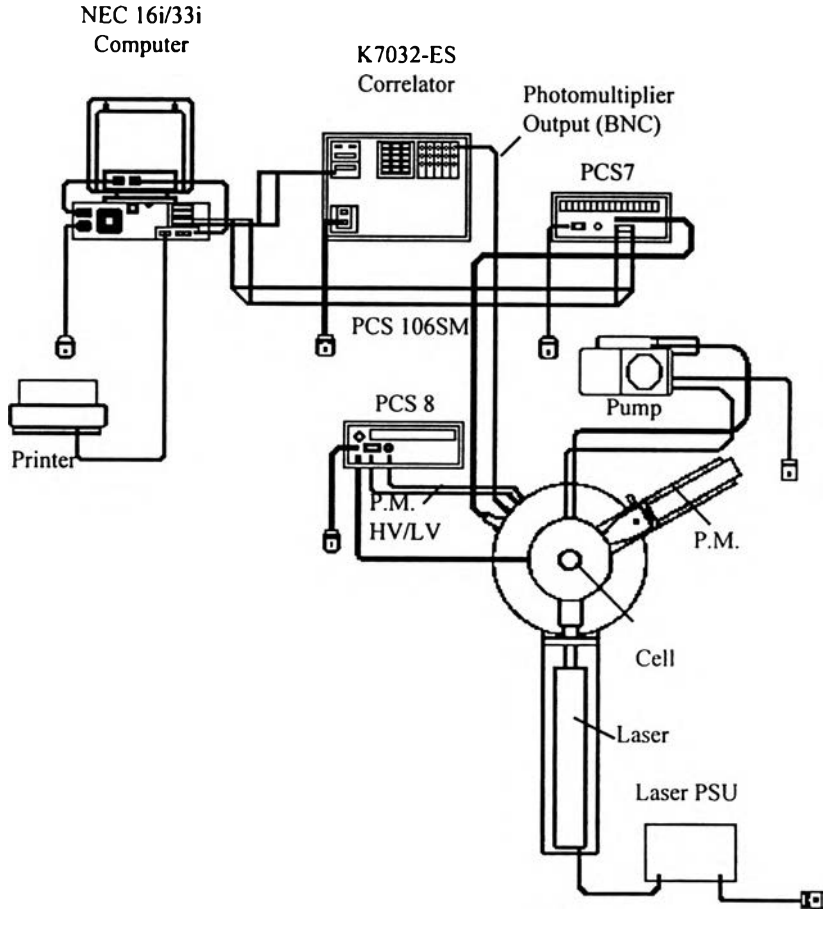

Figure 2.2 Interconnection diagram.

2.2.3 Optilab DSP Interferometric Refractometer

The dn/dc measurements were performed by the optilab DSP interferometric refractometer from Wyatt Technology Corporation. It measures the difference in refractive index between the current liquid sample stream and liquid previously stored as a reference. Since the reflective index of liquids depends critically on temperature, the instrument has a temperature control system for both the sample cell and the optic. The sample temperature control system can be set anywhere between 25.0 °C and 80.0 °C.

2.2.4 Tensiometer

Surface tensions were measured by using a KRUSS tensiometer K10T. It was used to determine the critical micelle concentration (CMC) of surfactants and the critical aggregation concentration (CAC) of the polymer-surfactant system.

2.2.5 Conductivity Meter

Conductivity meter model 160 from Orion Co. was also used to determine the critical micelle concentration (CMC) of cationic surfactant and the critical aggregation concentration (CAC) of the polymer-cationic surfactant system.

2.2.6 Centrifuge Machine

The high speed refrigerated centrifuge model PM 180R from ALC International Co., Ltd. was used to precipitate dust particles out of the sample solution. The rotating head can be changed to obtain different speed and capacity. In this work, we used the rotating head no. A-H-12 with the maximum speed of 12,000 rpm (or 14,326 xg) and the maximum capacity of 38 ml × 8 bottles.

2.3 Methodology

2.3.1 Sample Preparation

2.3.1.1 Preparation of polymer solution. The stock solution of HPC was prepared by dissolving the polymer in sterile water containing 0.02 % sodium azide to prevent bacteria growth. The solution was slowly stirred at room temperature by using magnetic stirrer with a speed of 10 rpm over a

period of 3 to 5 days to get complete solution. Finally, the stock solution was filtered through 0.45 μm Millipore filter to remove dust particles.

2.3.1.2 Preparation of surfactant solution. The stock solution of OTG and CTAB were prepared by dissolving the surfactant in sterile water. The stock solution was then stirred with a speed of 10 rpm at room temperature for at least 24 hours to get homogeneous solution.

2.3.1.3 Preparation of polymer-surfactant solution. All Polymer-surfactant solutions in this study were prepared by mixing the components in specified amounts. The samples were stirred slowly with a speed of 10 rpm at room temperature for at least 24 hours before experiments were performed, and then allowed to settle overnight to make sure that the system was in an equilibrium condition.

Immediately prior to light scattering and viscosity measurements, all the sample solutions were centrifuged at 30 °C with the high speed of 10000 rpm for 60 minutes. Further, the centrifuged solution was filtered slowly and directly into the light scattering cells through 0.22 μm Millipore filters.

2.3.2 Viscosity Measurement

2.3.2.1 Principle.

Nomenclature

The nomenclature used in dilute solution viscometry are summarized in Table 2.1. The terms described as common names have the authority of long usage, and are still found in day-to-day use in most cases. The second set was recommended for use by the International Union of Pure and Applied Chemistry (IUPAC) as more logical. They have been adopted in some texts and to a certain extent in the literature, but are still found in the minority

of cases. Table 2.1 also provides the defining equations for the qualities discussed in this section.

Table 2.1 Nomenclature of solution viscosity

Common name	Name proposed by IUPAC	Symbol and Defining Equation
Relative viscosity	Viscosity ratio	$\eta_r = \eta/\eta_o \approx t/t_o$
Specific viscosity	-	$\eta_{sp} = \eta_r - 1 = (\eta-\eta_o)/\eta_o \approx (t-t_o)/t_o$
Reduced viscosity	Viscosity number	$\eta_{red} = \eta_{sp}/c$
Inherent viscosity	logarithmic viscosity number	$\eta_{inh} = \ln(\eta_r)/c$
Intrinsic viscosity	Limiting viscosity number	$[\eta] = \lim_{c\to 0}(\eta_{sp}/c) = \lim_{c\to 0}(\ln \eta_r/c)$

(i) the **viscosity ratio** (the **relative viscosity**) (η_r), which is given by the ratio of the outflow time for the solution (t) to the outflow time for the pure solvent (t_o),

$$\eta_r = t/t_o \qquad (2.1)$$

(dimensionless)

(ii) the **specific viscosity** (η_{sp}), which is the relative increment in viscosity of the solution over the viscosity of the solvent,

$$\eta_{sp} = (\eta-\eta_o)/\eta_o = \eta_r - 1 \qquad (2.2)$$

(dimensionless)

(iii) the **viscosity number** (the **reduced viscosity**) (η_{red}) is the specific viscosity taken per unit concentration (c),

$$\eta_{red} = \eta_{sp}/c = (\eta_r - 1)/c \qquad (2.3)$$

(in decilitres per gram (CGS) or cubic metres per kilogram (SI)), where c is the concentration of polymer (in grams per decilitre (CS) or kilograms per cubic metre (SI))

(iv) the **logarithmic viscosity number** (the **inherent viscosity**) (η_{inh}) is defined as

$$\eta_{inh} = \ln \eta_r/c \qquad (2.4)$$

(in decilitres per gram (CGS) or cubic metres per kilogram (SI))

(v) the **limiting viscosity number** (the **inherent viscosity**) ($[\eta]$) is the viscosity number (the reduce specific viscosity) or the logarithmic viscosity number (the inherent viscosity) extrapolated to $c = o$,

$$[\eta] = \lim_{c \to o} (\eta_{sp}/c) = \lim_{c \to o} (\ln \eta_r/c) \qquad (2.5)$$

An extrapolation to infinite dilution requires measurements of the viscosity at several concentrations. The sample concentration should not be too large because additional effects may then arise from intermolecular forces and entanglements between chains (for very large molecular weights).

There are several empirical equations for calculation of the limiting viscosity number (intrinsic viscosity):

(I) the **Huggins equation**,

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \qquad (2.6)$$

(ii) the **Kraemer equation**,

$$(\ln \eta_r)/c = [\eta] + k''[\eta]^2 c \qquad (2.7)$$

where k' and k'' are known as the Huggins and Kraemer constants, respectively. They are constants for a given polymer at a given temperature in a given solvent. k' and k'' are related by the equation

$$k'-k'' \approx \frac{1}{2} \qquad (2.8)$$

The value of k' is usually in the range: $0.3<k'<0.4$ and increases as solvent power decreases. For a given polymer-solvent system, k' is not usually sensitive to molecular weight. The constants k' and k'' can be determined from conventional measurements in a series of concentrations for a given polymer in a given solvent at a given temperature.

Both equations yield linear plots with the intercept equal to $[\eta]$ at $c = 0$ (Figure 2.3).

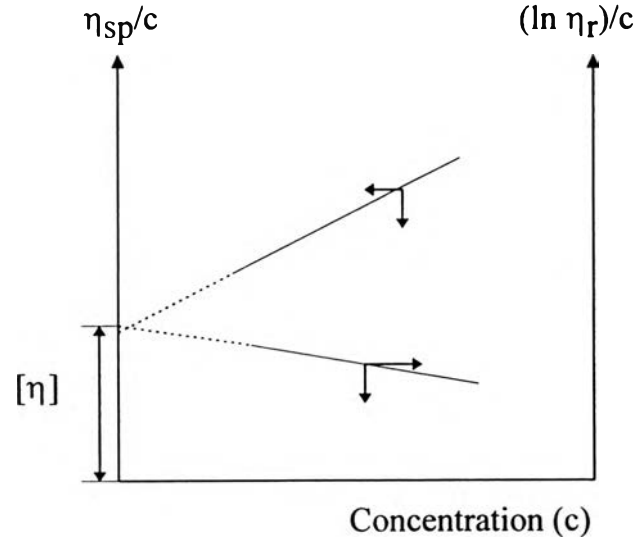

Figure 2.3 Plot of η_{sp}/c or $\ln \eta_r/c$ versus concentration.

Viscometer

Dilute-solution viscosity is usually measured in capillary viscometer which has two general classes, namely U-tube viscometers and suspended-level viscometers (Figure 2.4). A common feature of these viscometers is the measuring bulb, with upper and lower etched marks, is attached directly above the capillary tube. The solution is either drawn or forced into the measuring bulb from a reservoir bulb attached to the bottom of the capillary tube, and the time required for it to flow back between the two etched marks is recorded.

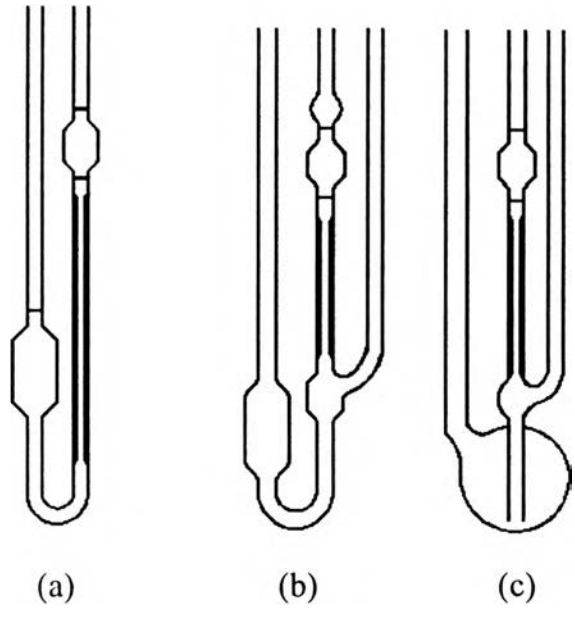

Figure 2.4 Schematic illustrations of (a) an Ostwald U-tube viscometer; (b) an Ubbelohde suspended-level viscometer; (c) a modified Ubbelohde viscometer with a large reservoir bulb for dilution.

The U-tube viscometers, the pressure head giving rise to flow depends on the volume of solution contained on the viscometer, and so it is essential that this volume is exactly the same for each measurement. This

normally is achieved after temperature equilibration by carefully adjusting the liquid level to an etched mark just above the reservoir bulb.

Most suspended-level viscometers are based upon the design due to Ubbelohde, the important feature of which is the additional tube attached just below the capillary tube, with atmospheric pressure acting both above and below the flowing volume of liquid. Thus the pressure head depends only upon the volume of the solution contained in and above the capillary, and there is particularly useful because it enables solutions to be diluted on the viscometer by adding more solvent. When U-tube viscometers are used, they must be emptied cleaned, dried and refilled with the new solution each time the concentration is changed.

Measurement of solution viscosity

In capillary instrument, the basis for viscosity determination is *Puiseuille's equation* for a laminar Newtonian flow:

$$V/t = \pi r^4 P/8\eta l. \qquad (2.9)$$

Where V is the volume of liquid which flows in time t through a capillary of length l and radius r. P is the pressure difference across the capillary and η *is the viscosity* of the liquid.

The total velocity profile corresponding to this equation is parabolic, with maximum velocity along the axis of the capillary tube and zero velocity at the wall. During the measurement of flow time, P continuously decreased normally is given by

$$P = \langle h \rangle \rho g, \qquad (2.10)$$

where $<h>$ is the average pressure head, ρ is the density of the liquid and g is the acceleration due to gravity. Thus Poiseuille's Equation (2.9) can be rearranged to give

$$\eta = \pi r^4 <h> \rho g t / 8Vl \qquad (2.11)$$

which has the form

$$\eta = A\rho t, \qquad (2.12)$$

where A is a constant for a given viscometer. Poiseuille's equation does not take into account the energy dissipated in imparting kinetic energy to the liquid, but is satisfactory for most viscometers provided that the flow times exceed about 180s.

Absolute measurements of viscosity are not required in dilute viscometry since it is only necessary to determine the viscosity of a polymer solution relative to that of the pure solvent. Application of equation (2.12) leads to the following relation for the relative viscosity.

$$\eta_r = \eta/\eta_o = \rho t/\rho_o t_o \qquad (2.13)$$

where ρ and ρ_o are the densities, and t and t_o are the flow times of a polymer solution of concentration c and of the pure solvent respectively. Since dilute solutions are used, it is common practice to assume that $\rho = \rho_o$ so the relative viscosity is simply given by the ratio of the flow time t/t_o. The other quantities required are then calculated from η_r and c. In a more accurate analysis work kinetic energy and density corrections are applied, and when necessary the values $[\eta]$ obtained are extrapolated to zero shear rate (Young and Lovell, 1991).

2.3.2.2 Data Analysis. Viscosity measurement is a dependable and straightforward tool to study the hydrodynamic volume of polymers in solution, the essential quantity to follow being the reduced viscosity η_{sp}/c.

Extrapolating η_{sp}/c to zero concentration gives the intrinsic viscosity $[\eta]$, which is a measure of the hydrodynamic volume per mass unit of the polymer (at infinite dilution).

The above theory is well-known and straightforward for most normal polymer solutions composed of single solvents. However in the present case there is always an equilibrium between the free surfactant and the polymer-surfactant complex. Changing the total concentration of either the polymer or the surfactant will change the solution properties of the polymer, and this will be immediately reflected in viscosity changes. Since the concentration of the complex is unknown, the specific viscosity is used here than the more usual reduced viscosity (η_{sp}/c).

The viscosity measurements have been performed in sets of constant polymer concentration allowing the overall surfactant concentration to vary. Various such sets have been measured with different polymer concentrations.

2.3.2.3 Experimental Condition. The viscosity measurements were carried out in Cannon-Ubbelohde capillary viscometer. Before use, it is essential to ensure that the viscometer is thoroughly clean and that the solvent and solutions are freed from dust by filtration, otherwise incorrect and erratic flow time can be anticipated. The solutions were filtered through the Millipore membrane 0.22 μm pore size before transferring into the viscometer. Then the viscometer is placed in a thermostatted water bath at 30 °C for 30 minutes. After allowing sufficient time for temperature equilibration of the solution, several measurements of the flow time are made and should be reproducible to ±0.2 % when measured visually using stopwatch.

2.3.3 Static Light Scattering Measurement

2.3.3.1 Principle. In static light scattering experiments the time-averaged (or "total") intensity of the scattered light is measured, and for solutions is related to the time-averaged mean-square excess polarizability which in turn is related to the time-averaged mean-square concentration fluctuation. Static light scattering is a standard technique to extract information about the size and structure as well as equilibrium polymer-polymer coil interactions of flexible, linear polymer chains in dilute solution.

The working equation for the determination of the weight-average molecular weight by light scattering, due to Debye, is

$$Kc/\Delta R_\theta = 1/P(\theta)\,[1/Mw + 2A_2c + 3A_3c^2 + \ldots] \quad (2.14)$$

where ΔR_θ is commonly know as the excess Rayleigh ratio and for static light scattering depends upon the time-averaged mean-square excess polarizability of a volume element arising from the local solute concentration. The *optical constant*, K, is given by

$$K = 2\pi^2\eta_o^2(dn/dc)^2/N_A\lambda^4 \quad (2.15)$$

where n is refractive index of solvent, dn/dc is the specific reflective index increment, N_A is Avogadro's number, and λ is the wavelength of incident light.

The quantity $P(\theta)$ is a particle scattering factor which describes the angular dependence of the scattered light and relates to particle size for a given model such as a sphere, random coil, or other type. For a small molecule $P(\theta) = 1$ for all values of θ, whereas for long molecule $P(\theta)$ can be very much smaller than unity but increases as θ decreases and at $\theta = 0$ becomes

equal to unity. For $\theta \rightarrow 0$, the general shape-independent expression for $P(\theta)$ is given by

$$1/P(\theta) = 1 + (16\pi^2/3\lambda^2)R_{g,z}^2\sin^2(\theta/2) \quad (2.16)$$

where $R_{g,z}$ is the z-average mean-square radius of gyration for random coil polymer.

Combining equation (2.14) and (2.15) leads to a general expression for static light scattering

$$Kc/\Delta R_\theta = [1/M_W + 2A_2c + 3A_3c^2 + ...][1 + (16\pi^2 n_0^2 \sin(\theta/2)/\lambda^2)R_{g,z}^2] \quad (2.17)$$

which enable M_W, A_2, and $R_{g,z}$ to be determined from measurements of ΔR_θ at different angles for each of several polymer solutions at different concentrations.

2.3.3.2 Data analysis. In order to evaluate the molecular weight of polymer, we must extrapolate value of $Kc/\Delta R_\theta$ not only to vanishing concentration c, but also to vanishing angle θ. It is usual to plot the experimental data in the dimensionless using a way suggested by Zimm, which allows for simultaneous graphical extrapolation of concentration and scattering angle. In the *Zimm plot*, $Kc/\Delta R_\theta$ is plotted against the sum $sin^2(\theta/2) + k'c$. The arbitrary constant k' is selected to make the plot looks nice. A grid like graph is obtained, such as that shown schematically in Figure 2.5, and consists if two sets of lines, and one joining points of constant c and the other joining points with the same value of θ. Both sets are extrapolated to yield lines at $\theta = 0°$ and $c = 0$. The extrapolated line must meet at the axis; their common intercept marks $1/M_W$. The line at $\theta = 0°$ represents the second virile coefficient (A_2);

from its initial slope the second virial coefficient A_2 is easily calculated. The line at $c = 0$ reflects the function $P^{-1}(\theta)$, and its initial slope divided by the intercept yields the z-average radius of gyration of the particular polymer; from this we can guess the shape of the particle.

Here, $M_{w,app}$ and $R_{g,app}$ are defined as the apparent molecular weight and radius of gyration, respectively.

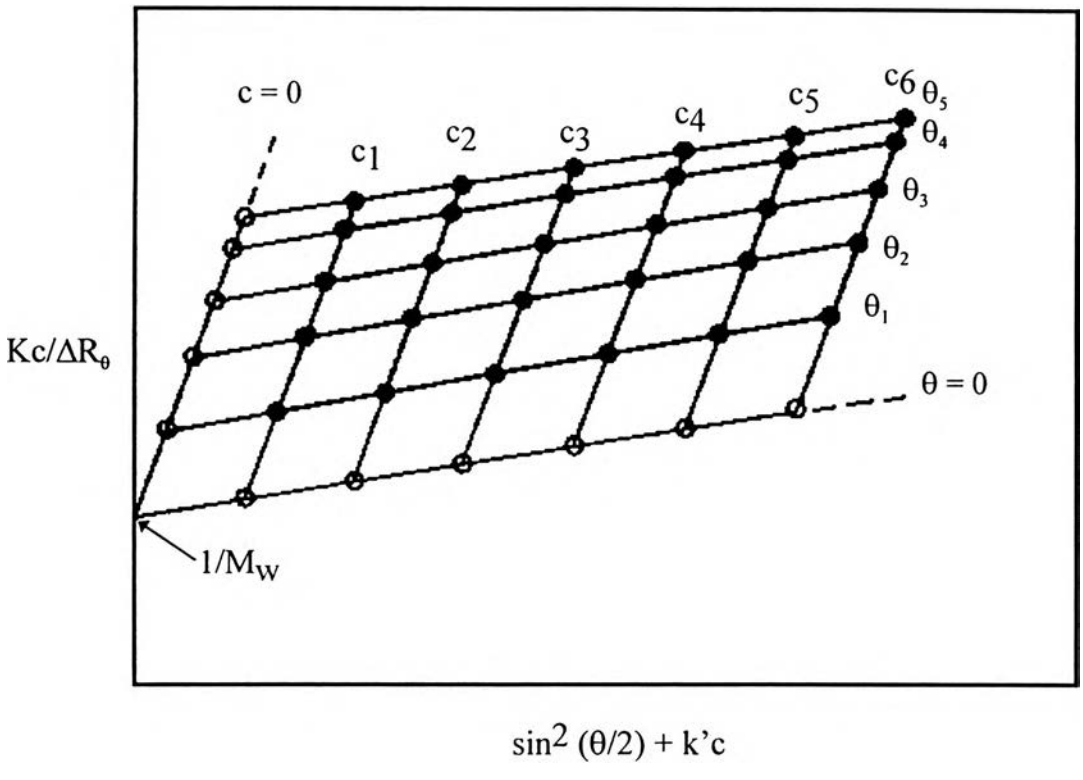

Figure 2.5 Schematic illustration of a Zimm plot for analyzing light scattering data. The solid points represent experimental measurements, the open circle are extrapolated points.

2.3.3.3 Experimental Condition. Intensity light scattering measurements were performed at 30 °C. The optilab constant for vertically polarized light is $K = 4\pi n_O^2(dn/dc)^2 N_A \lambda^4$ where n_O is the solvent refractive indexes and λ = 514.5 nm wavelength from an Argon laser. Intensity of scattered light was measured at scattering angle θ = 30°-140°.

Rayleigh ratio ΔR_θ of the scattered light was calculated on the basis of Rayleigh ratio, ΔR_θ = 18 $\times 10^{-6}$ cm^{-1} of toluene at the wavelength λ = 514.5 nm. Specific refractive index increment *dn/dc* of HPC in water at 30 °C was measured by using an Optilab DSP Interferometric Refractometer. The measurement value of *dn/dc* is 0.164 ml/g.

2.3.4 Dynamic Light Scattering Measurement

2.3.4.1 Principle. Dynamic light scattering has become an extraordinarily important tool in the study of polymer solutions over the last decade. The rational for this is at least two fold. One reason is that it provides data on the molecular mobility and diffusion coefficients of macromolecules which are of increasing conceptual and practical importance. The second is that, under proper circumstances, these data can be interpreted in terms of the size and coil configuration of the polymer molecule, in a way that sometimes provides an easier route to this information than static light scattering.

Dynamic light scattering experiment measures the real-time fluctuation in the intensity of the scattered light which means this measurement monitors the real-time random motion (i.e. Brownian) of the solute molecules. This motion gives rise to a *Doppler effect* and so the scattered light possesses a range of frequencies shifted very slightly from the frequency of the incident light (the scattering is said to be *quasi-elastic*). These frequency shifts yield information relating to the movement (i.e. the dynamics) of the solute molecules, and can be measured using specialized interferometers

and spectrum analyzers provided that the incident light has a very narrow frequency band width (i.e. much smaller than the magnitude of the frequency shifts). Thus the availability of laser light sources has greatly facilitated measurement.

The magnitude of frequency of the intensity fluctuations is at a maximum when light scattered by a single volume element is observed (i.e. corresponding to a specific point in the solution). They are reduced if the overall intensity of light scattered by several volume elements is measured by the detector. In view of this, highly sensitive photomultiplier or photodiode detectors with very small aperture are used so that the scattered light entering the detector can be considered to have derived from a single point in the solution. The total number of photons of scattered light entering the detector during each sequence of time interval between successive photon counting is known as their separation 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, which for polymers is typically in the range 1 μs to 1 ms. Thus if τ is only a few multiples of Δt, the corresponding photon counts will be closely related, and are said to be correlated. However, if τ is many multiples of Δt (i.e. larger than the time scale of the intensity fluctuations), the corresponding photon counts will not be correlated. The *autocorrelation function*, $G^{(1)}(\tau)$, of the intensity, i_θ, is defined by

$$G^{(1)}(\tau) = \lim_{T\to\infty} [1/T \int_0^T i_\theta(t) i_0(t+\tau) dt] \qquad (2.18)$$

and its normalized value, $g^{(1)}(\tau)$, by

$$g^{(1)}(\tau) = G^{(1)}(\tau)/ G^{(1)}(0) \qquad (2.19)$$

where $G^{(1)}(0)$ is the time-averaged value of the square of the intensity. In the time scale of the experimental measurement, the correlator evaluates $g^{(1)}(\tau)$ for a series of values of τ from the photon countings. Hence this technique of dynamic light scattering is known as *photon counting spectroscopy* which is a powerful technique to probe dynamic, on different length and time scales, in system of various complexities. When the scattered light obeys Guassian statistics, the measured homodyne *intensity autocorrelation function* $G^{(2)}(\tau)$ is related to the theoretically amenable first-order *electric field correlation function* $g^{(1)}(\tau)$ through the Siegert relation

$$G^{(2)}(\tau) = A + [1 + \beta | g^{(1)}(\tau) | 2] \qquad (2.20)$$

where A is the base line and β is an equipment-related constant or so called coherence factor.

The decay of $g^{(1)}(\tau)$ with increasing τ carries information relating to the rate of movement of the solution molecules. For a monodisperse solution undergoing Brownian motion the decay curve is that of a single exponential and

$$g^{(1)}(\tau) = \exp(-\Gamma\tau) \qquad (2.21)$$

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

$$\Gamma = q^2D \qquad (2.22)$$

where $q = (4\pi n/\lambda)\sin(\theta/2)$ is the scattering vector. Thus by fitting the experimental $g^{(1)}(\tau)$ data to an exponential curve, it is possible to evaluate Γ and hence D.

The translational diffusion coefficient D of a macromolecule is related to the hydrodynamic radius R_h by using the *Stokes-Einstein* equation:

$$D = k_B T/6\pi\eta_o R_h \qquad (2.23)$$

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

However, for a polydisperse system, such as in the present study, the first-order electric field time correlation function $g^{(1)}(\tau)$ is related to the characteristic line width (Γ) distribution function $G(\Gamma)$ through a Laplace transform relation:

$$g^{(1)}(\tau) = \int_0^\infty G(\Gamma)\, e^{-\Gamma\tau}\, d\Gamma \qquad (2.24)$$

where τ denoted the decay time. $g^{(1)}(\tau)$ 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 constrained regularization.

2.3.4.2 Data Analysis. In the present work, the full photon counting time autocorrelation function was analyzed by the *cumulant method* or the *monomodal analysis*. This method assumes nothing about the distribution form. Simply a polynomial to the ln of normalized correlation function.

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 correlation function $g^{(1)}(\tau)$ is expanded in powers of the delay time as

$$\ln g^{(1)}(\tau) = -\Gamma\tau + 1/2!\,(\mu_2/\Gamma^2)(\Gamma\tau)^2 - 1/3!\,(\mu_3/\Gamma^3)(\Gamma\tau)^3 \quad (2.25)$$

where $$\Gamma = \int_0^\infty \Gamma G(\Gamma)\, d\Gamma,$$

$$\mu_i = \int_0^\infty (\Gamma - \Gamma)^i\, G(\Gamma)\, d\Gamma$$

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 $\mu_2/\Gamma^2 \leq 0.3$.

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

$$D_{app}(q) = D_c(1+Cq^2R_g^2 - \ldots) \quad \text{for } qR_g < 2 \quad (2.26)$$

and $$D_c = D_O(1+ k_D c) \quad (2.27)$$

where C is a coefficient depends on the macromolecular architecture. Actually, the C-parameter is determined by the slowest internal mode of motion in the particle and thus also depends on particle polydispersity.

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.

2.3.4.3 Experimental Condition. The light source is an Argon ion laser operating at 514.5 nm. The goniometer and photomultiplier assembly were components of a Malvern PCS100 spectrometer. The Malvern 7032 correlator (128 channels) was used to generate the full autocorrelation function of the scattered intensity. All measurements were performed in the homodyne mode and the sampling time was chosen as an automatic sampling time. The aperture setting of photomultiphier tube is 150 μm. The sample cell was a 10 mm round quartz cell; this was immersed in a vat of water, which nearly matches the refractive index of quartz, in order to reduce flare at the interfaces with the vat and sample cell. In this work, the temperature was set at 30 °C and was controlled to within ± 0.1 °C of the temperature set on the temperature controller.

2.3.5 The Refractive Index Measurement

2.3.5.1 Principle. The OPTILAB DSP is a differential refractometer based on a wavefront shearing (rotation) technique. It measures the difference in refractive index between the current liquid sample stream and a liquid previously stored as a reference. The two beams are polarized at right angles to one another and at 45 ° from a single incident plane wave (see Figure 2.6). Any difference in refractive index between the two fluids results in a phase shift of one beam relative to the other. This phase shift is directly proportional to the refractive index difference. This instrument responds to the

phase difference between the two beams by producing a single plane polarized beam of light that has been rotated relative to the pre-split beam (A) through an angle exactly equal to one half of the phase shift introduced by the difference of the two fluid paths. The angle of rotation is readily measured by reference to another plane polarized element.

Now for some detail Figure 2.7 shows a schematic of the first part of the interferometer. A light source is marked and collimated before passing through a polarize oriented at 45 ° to the horizontal (instrument base).

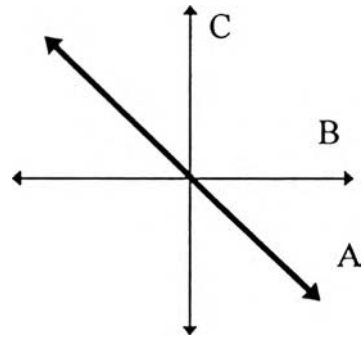

Figure 2.6 Plane polarized beam A is split into two orthogonal plan wave B and C by a Wollaston prism. The direction is into the plane of the figure. Beam A lies at 45° to the optical axes B and C of the prism.

The linearly polarized beam then strikes a Wallaston prism which splits it into two orthogonally polarized beams (horizontal and vertical) of equal intensity. The beams are then focused by the lens and pass, respectively, through a reference cell and a sample cell. The light passing through the reference cell is horizontally polarized. As the beam enters the cells they are in phase with one another.

The refractive index n of a material is defined as the ratio of the speed of light in vacuum (denoted by c) to the speed of light through the material:

$$n = c/v \tag{2.28}$$

For example, the speed of light in water is found to be approximately 75 % that of its speed in air. Thus

$$n_{water} \cong c/(0.75c) \cong 1.33 \tag{2.29}$$

Since the frequency of oscillation of the light waves in independent of the surrounding medium, the physical effect of the medium on a wave of light is to change its wavelength in that medium:

$$\lambda = \lambda_O/n \tag{2.30}$$

where λ_O is the wavelength in vacuum and n is the medium's refractive index. This wavelength change is due to the fact that the product of wavelength times frequency equals the velocity of light in the medium.

The refractive index of a solution changes as the concentration of a substance dissolved in it changes. In principle, by measuring the relative index change of a solution, one may deduce the concentration change of a dissolved solute. To do this, one must know the *refractive index increment dn/dc*.

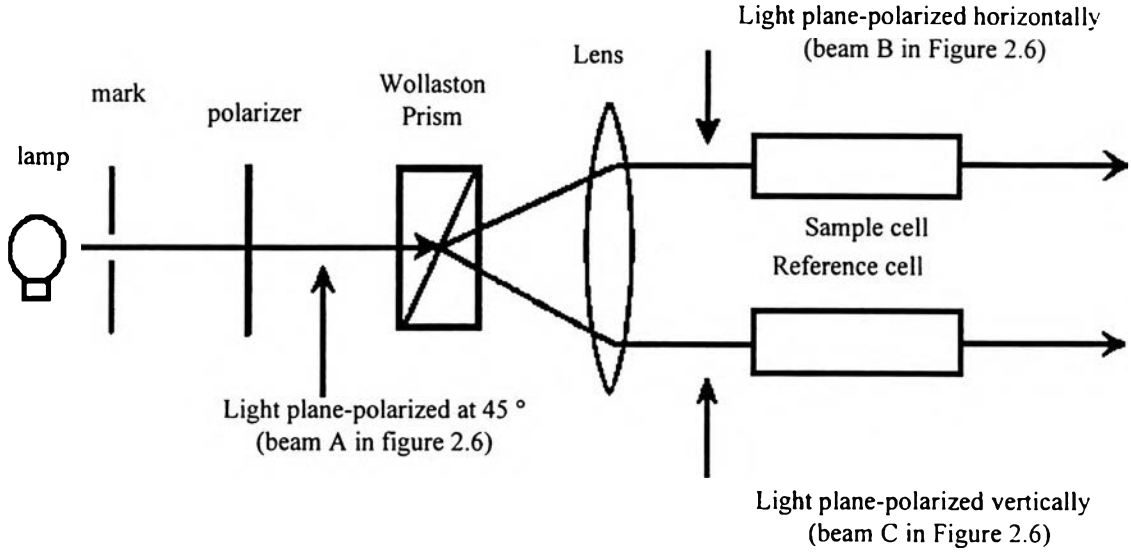

Figure 2.7 Illustration of two orthogonal plane polarized beams produced from a single polarized beam by means of a Wollaston prism.

Consider that each cell of Figure 2.7 has a length L. Let the refractive index of the reference cell fluid be n_r and that of the sample cell be n_s. This means that in the reference cell, there will be L/λ_r wavelength present, where

$$\lambda_r = \lambda_o / n_r \qquad (2.31)$$

In the sample cell, there will be L/λ_s wavelengths. Upon emerging from the two cells, the two waves will again have the same wavelength (the medium external to the cells is air) but will differ in phase by an amount

$$L/\lambda_s - L/\lambda_r = L(1/\lambda_s - 1/\lambda_r) \text{ wavelengths} \qquad (2.32)$$

This phase difference is usually expressed in angular to radian units by noting that each wavelength difference introduces a 360° angular difference between the waves. Since 2π radians equals 360 °, the phase difference between the two waves in radian measure is just

$$\begin{aligned} \phi &= 2\pi L(1/\lambda_S - 1/\lambda_r) \\ &= 2\pi L(n_S/\lambda_O - n_r/\lambda_O) \\ &= 2\pi L(\Delta n/\lambda_O) \end{aligned} \qquad (2.33)$$

where $\Delta n = n_S - n_r$. Thus by measuring ϕ, we have a direct measure of Δn.

Figure 2.8 shows the sample and reference beams being focused onto a second Wollaston prism which recombines the two beams. However, due to the relative phase shift introduced by the different refractive induced, the light is now elliptically polarized. A quarter wave plate is placed after the Wollaston prism with its fast axis at 45 ° with the respect to the horizontal. This converts the elliptically polarized beam into a linearly polarized beam rotated by an angle $\phi/2$ with respect to beam A in Figure 2.6.

Following the quarter wave plate is an analyzer (plane polarizer) placed at an angle of 90°- β with respect to the axis of the incident plane polarizer. The relationship between the beams, angles, and analyzer is shown also in Figure 2.9. The angle β is chosen so that for $\phi = 0$ (no phase difference between the two beams), the unattenuated incident beam would be reduced to 35% of its incident intensity after passing through the analyzer.

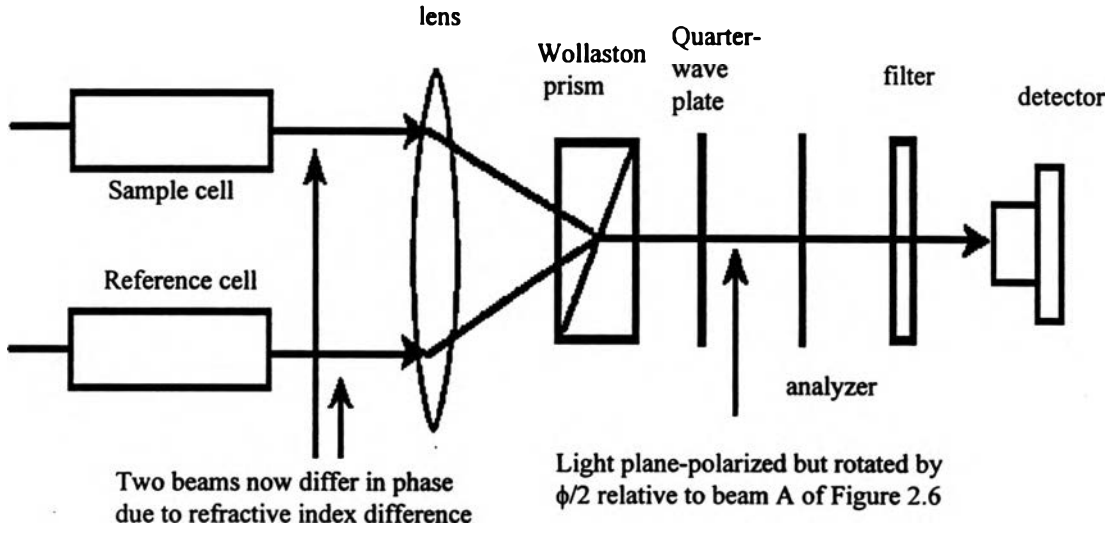

Figure 2.8 Recombination of two beams at the second Wollaston prism resulting in a rotated plane-polarized wave. A quarter wave plate and analyzer detect the rotation of the plane of polarization.

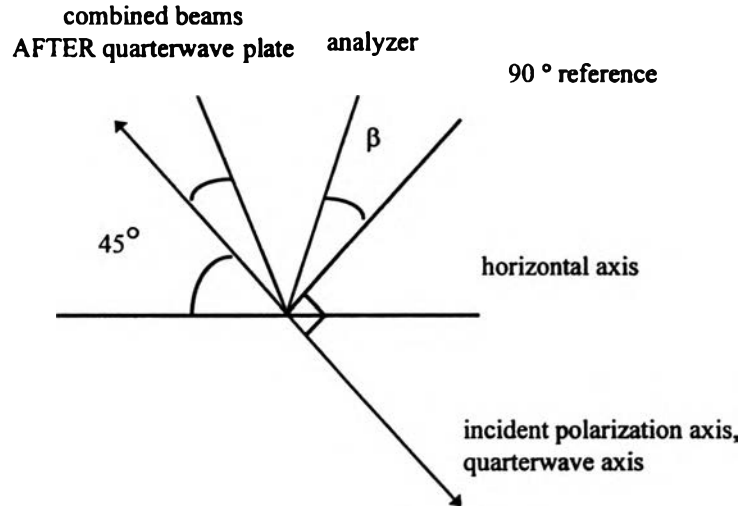

Figure 2.9 Upon recombining, the resultant beam is plane polarized at angle $\phi/2$ with respect to the incident beam.

Suppose the incident intensity of the combined beam is I_O and $\phi = 0$. It turns out that the angle β is given by

$$I/I_O = \cos^2(90° - \beta) = \sin^2\beta = 0.35 \quad (2.34)$$

The angle θ between the combined beam and the analyzer is, for the general case,

$$\theta = 90 - \beta - \phi/2 \quad (2.35)$$

and the result is

$$I/I_O = \sin^2(\beta - \phi/2) \quad (2.36)$$

By measuring the intensity relative to I_O, the phase angle $\phi/2$ and hence Δn maybe deduced by the instrument.

2.3.5.2 Data Analysis and Experimental Condition. The measurements were performed at 30 °C. The range of HPC concentration is from 0.1 g/l to 0.6 g/l. Before making measurements, both sample and reference cells were flushed by distilled water for at least 24 hours to stabilize the instrument with a new solvent. The measurement started with the lowest concentration and used the flow rate 1.0 ml/min. The dn/dc of HPC can be obtained from the slope of the plot between dn versus HPC concentration as shown in Figure 2.10. The dn/dc of HPC is equal to 0.164 ml/g.

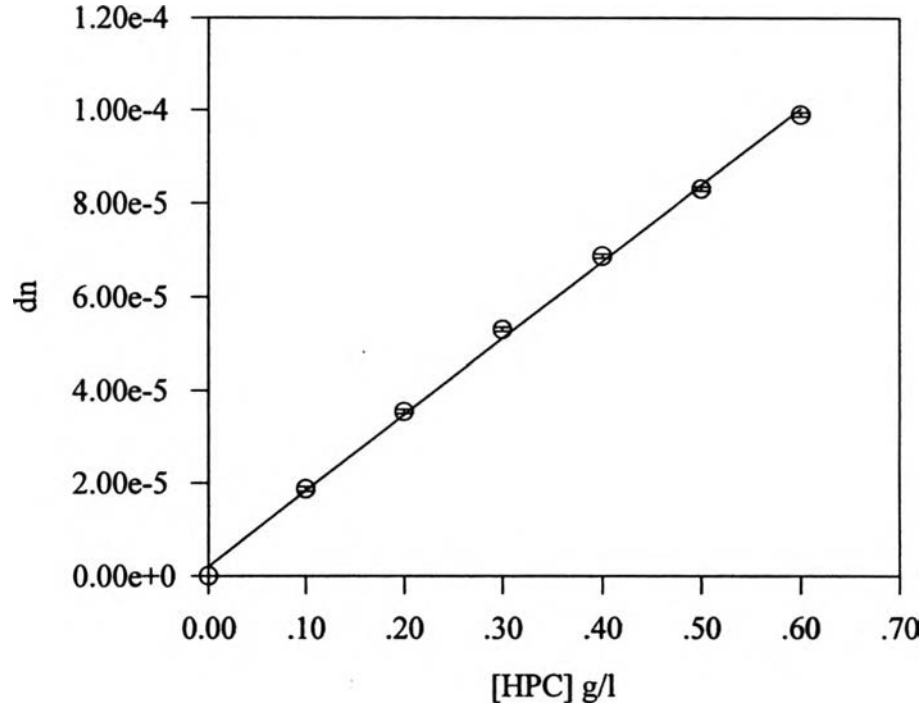

Figure 2.10 Plot of dn as a function of HPC concentration at 30 °C.