

## CHAPTER II

### EXPERIMENTAL SECTION

#### 2.1 Materials

##### *2.1.1 Polymer*

Hydroxypropyl cellulose (HPC) was purchased from Aldrich Chemical Company, Inc. The manufacturer's literature claims a molecular weight of  $10^6$ .

##### *2.1.2 Cationic Surfactant*

The HPLC grade hexadecyltrimethylammonium bromide (HTAB) was used as a cationic surfactant and obtained from Aldrich Chemical Company, Inc. It was used without further purification.

##### *2.1.3 Solvent and Other Chemicals*

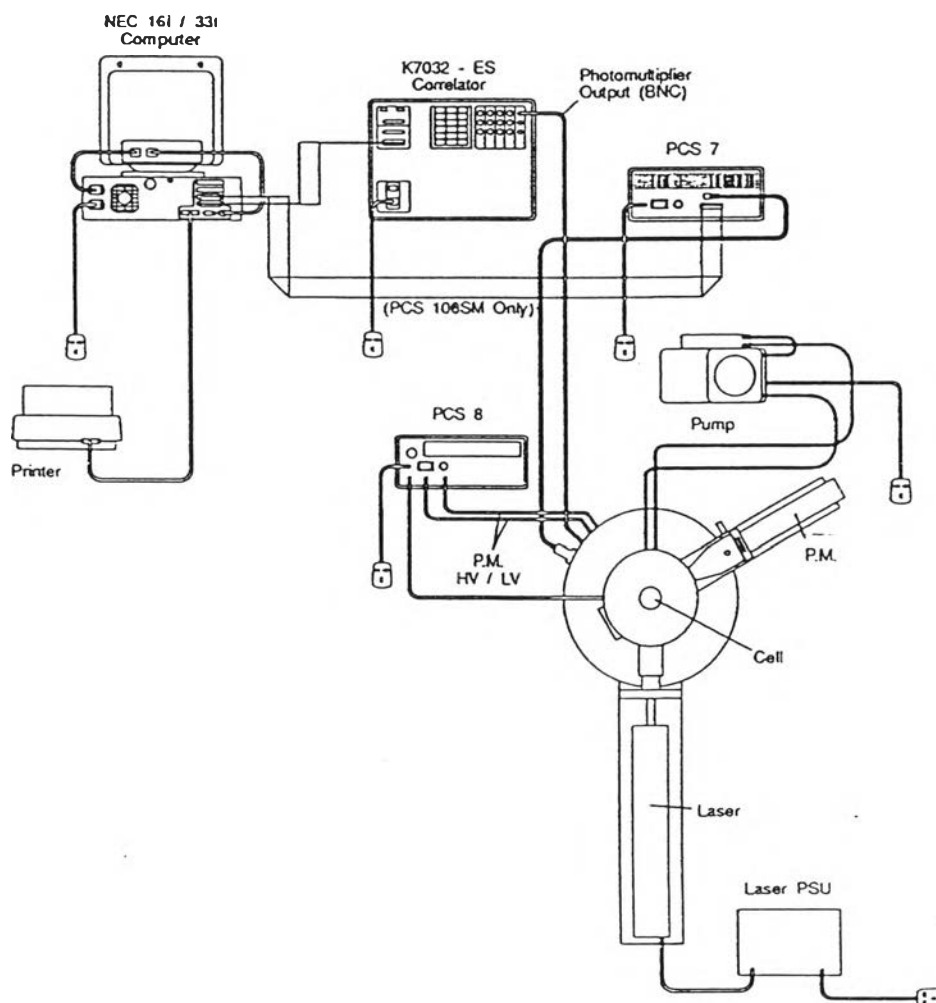
Sterile water was purchased from the Thai Pharmaceutical Organization and used as the pure solvent. Before using, it was filtered through Millipore membrane filter with the pore size of  $0.22\ \mu\text{m}$ .

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

## 2.2 Apparatus

### 2.2.1 *Light Scattering Instrument*

The light scattering apparatus (model series 4700) is from Malvern Instruments Ltd.. A full system includes several associated units: a gavinometer, a correlator, an argon-ion laser source ( $\lambda = 514.5 \text{ nm}$ ), a photomultiplier unit and a filtering system used to eliminate the dust particles in water connected with the light scattering unit.



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

### ***2.2.2 Capillary Viscometric Instrument***

(a) **The Ubbelohde Viscometer** (number 115 of size 25) was used to measure the viscosity of the sample solutions. It was supplied from Curtis Matheson Scientific Inc..

#### **(b) Viscometer Thermostat and Bath.**

The digital thermostat model DT-2 with temperature stability  $\pm 0.005$  °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.

#### **(c) Timing Device**

A stop watch was used in the experiment to provide the time of flowing of the sample solutions with a resolution of  $\pm 0.01$  second.

### ***2.2.3 Sintered Glass and Syringe Filter***

Millipore sinterglass filter with 47 nm diameter was used to eliminate extraneous matters from the solvent. The sample solutions were filtered by using Acrodisc syringe filter from Gelman Sciences prior to DLS and viscometric measurements.

#### *2.2.4 Conductivity Meter*

Conductivity meter model 160 from Orion Co. was used to determine cac value in salt free system.

#### *2.2.5 Tensiometer*

Tensiometer with Pt-Ir-Ring: RI 10 probe was used to measure surface tension in determining cac on the presence of salt system.

### **2.3 Methodology**

#### *2.3.1 Sample Preparations*

##### **(a) Preparation of HPC Stock Solution**

A weighed amount of HPC was mixed with approximately 1/4 of the total amount of sterile water. This solution was slowly stirred for about 30 min. The rest of the water was then added and the mixture was stirred in an icebath for about 24 hrs. in order to get a homogeneous solution. The solution was then filtered through Whatman paper filter no. 5 to eliminate large residues. The stock solution of HPC was stored at 8° C

##### **(b) Preparation of HTAB Stock Solution**

The stock solution of HTAB was prepared by dissolving HTAB in filtered water. The solution was then stirred for at least 30 hrs.

### (c) Preparation of HPC-HTAB Solution

The required amounts of the HPC stock solution was added into approximately diluted HTAB stock solutions by weighting with a 4 - digital weight balance. The sample were stirred slowly at room temperature at least 24 hrs, and then allowed to settle overnight to make sure that the system was in an equilibrium condition.

Prior to each DLS and viscometric measurement, the sample solutions were purified freshly by filtering through a 0.22  $\mu\text{m}$  Millipore membrane (GV type).

### 2.3.2 Dynamic Light Scattering Measurement

#### (a) Principle

DLS measurements were made at scattering angle  $90^\circ$ . A 200  $\mu\text{m}$  pinhole aperture was used for photomultiplier tube. We obtain the homodyne intensity-intensity correlation function  $G^2(q,t)$ , where  $q$  is the amplitude of the scattering vector given by  $q = (4\pi n/\lambda) \sin(\theta/2)$ , where  $n$  is the refractive index of the medium,  $\lambda$  is the wave length of the excitation light in a vacuum, and  $\theta$  is the scattering angle. For a Gaussian distribution of intensity profile of the scattered light,  $G^2(\tau)$  is related to the electric field correlation function  $g^1(\tau)$  through the Siegert relation :

$$G^2(\tau) = A ( 1+ B (g^1(\tau))^2 ), \quad (2.1)$$

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

$$g^1(t) = \int_0^{\alpha} G(\Gamma) \exp(-\tau\Gamma) d\Gamma \quad (2.2)$$

where  $D_{\text{app}}$  is the apparent translational diffusion coefficient at the wave vector  $q$ .  $g^1(\tau)$  can be expanded in a Taylor series and a polynomial expansion of the  $\ln g^1(\tau)$  leads to

$$\ln g^1(\tau) = -\Gamma\tau + \frac{1}{2!} \frac{\mu_2}{\Gamma^2} (\Gamma\tau)^2 - \frac{1}{3!} \frac{\mu_3}{\Gamma^3} (\Gamma\tau)^3 + \dots \quad (2.3)$$

$$\text{with } G = \int_0^{\alpha} G(\Gamma) \Gamma d\Gamma \quad ; \quad \mu_2 = \int_0^{\alpha} (\Gamma - \Gamma)^2 G(\Gamma) d\Gamma$$

The zeroth order moment,  $\Gamma$ , is related to the z-average value of  $D_{\text{app}}$  by  $\Gamma = \langle D_{\text{app}} \rangle_z q^2$  and  $\mu_2$  is related to the variance by  $\sigma = \mu_2 / \Gamma^2$ . The equation (2.3) is called the cumulant fit.

In the present work, we analyze the distribution function by the exponential sampling method. In this method (also referred to as Pike-Ostrowsky),  $G^2(\tau)$  is sampled in a series of exponentially spaced sample times. The procedure is automated to determine the best analysis width in an

iterative process. First the cumulant result is checked to see if the polydispersity exceeds a certain threshold (normally 0.05). A set of analyses of reducing width are then tried until the fit error no longer improves.

The diffusion coefficients contain information about the size and the structure of particles in solution. Previous work on polyelectrolytes in dilute solution indicates only one apparent diffusion mode which indicates the motion of an isolated polyelectrolyte chains in the solution with only weak intermolecular interactions such as the hydrodynamic interaction or the electrostatic interactions between adjacent chains. Above the overlap concentration, in the semidilute regime, the motion of each chain is strongly coupled with near neighbor chains. Consequently, two modes of motion exist in this regime. One is a fast mode diffusion coefficient ( $D_{fast}$  or co-operative diffusion coefficient) which corresponds to relaxation of concentration fluctuations due to the coupled diffusion of polyions and counterions.  $D_{fast}$  is mainly dominated by the counterion's influence. So,  $D_{fast}$  reflects the polymer chain motion of strands or the size of screening length, not the overall motion. On the other hand, the other mode called slow mode ( $D_{slow}$ ) is attributed to a relaxation of the center chains in solution, or the polyelectrolyte reptation.

### **(b) Hydrodynamic Radius ( $R_h$ )**

The hydrodynamic radius is effectively the diameter of the volume occupied by the light scattering polymer as it moves about with kinetic energy. It may contain information about both the physical size of the polymer chains and the range of solution interactions which control the particle motion through frictional forces [Barth H.G., 1991].

From the diffusion coefficient  $D$ , calculated from the experimental parameters  $q$  and  $\tau_q$ , the effective hydrodynamic radius,  $R_{h,app}$  can be obtained by using the Stokes-Einstein equation

$$R_{h,app} = k_B T / (6\pi\eta_s D), \quad (2.4)$$

where  $T$  = the absolute temperature

$\eta_s$  = the viscosity of the solvent at temperature  $T$

$k_B$  = Boltzmann constant

### 2.3.3 Viscosity Measurement

The properties of the uncharged polymer, HPC are changed considerably when HTAB is redistributed or bound to it. Charges are added which will render the molecule a polyelectrolytic character. Part of the hydrophobic groups on the macromolecular backbone will be shielded by the added surfactant which will change the polymer-solvent interaction. The hydrodynamic volume is a sensitive parameter by which to monitor these chemical changes.

Viscosity measurement is a dependable and straightforward tool to study the hydrodynamic volume of polymers in the solution. The more usual quantity is the reduced viscosity,  $\eta_{sp}/c$

$$\eta_{sp}/c = (\eta - \eta_s) / \eta_s c \quad (2.5)$$

where  $c$  = the polymer concentration

$\eta_{sp} = (\eta - \eta_s) / \eta_s$ ; the specific viscosity which refers to the enhanced viscosity of solvent by the addition of polymer.



$\eta$  = the solution viscosity

$\eta_s$  = the solvent viscosity

However, it is difficult to achieve the reduced viscosity in ternary system of HPC/HTAB/water because the concentration of the complex is unknown. So, the specific viscosity is used here rather than the reduced viscosity.

## 2.4 Experimental Techniques

There are several factors which affect the preparation of the solutions. The major source of uncertainty within a set of DLS and viscometric data result from the practical difficulties in preparing the solutions. The accuracy of the results will be achieved only for very careful experiments. A formidable experimental problem peculiar to these techniques is the difficult removal of small particles of extraneous matter from the solvents and solutions. The aspects of this practical problem are discussed under three main headings ;

### (a) Apparatus cleaning

To avoid the contamination during the solution preparation, glassware should be thoroughly cleaned by cleaning solution. Then the apparatus are soaked and rinsed with filtered water to avoid the cleaning materials themselves becoming contamination. Repeated washing with dust free water is particular important for aqueous solutions.

The cleaning of viscometer and scattering cell is also important. Charged particles of extraneous material adhered on the walls of the viscometer and the scattering cell can be desorbed in contact with aqueous

polyelectrolyte solutions. These can bring about the erratic results. Cleaning methods similar to those used for the general apparatus can be successfully applied. Further rinsing several times with filtered sample solutions is an effective treatment for preparing dust free apparatus.

### **(b) Solvent**

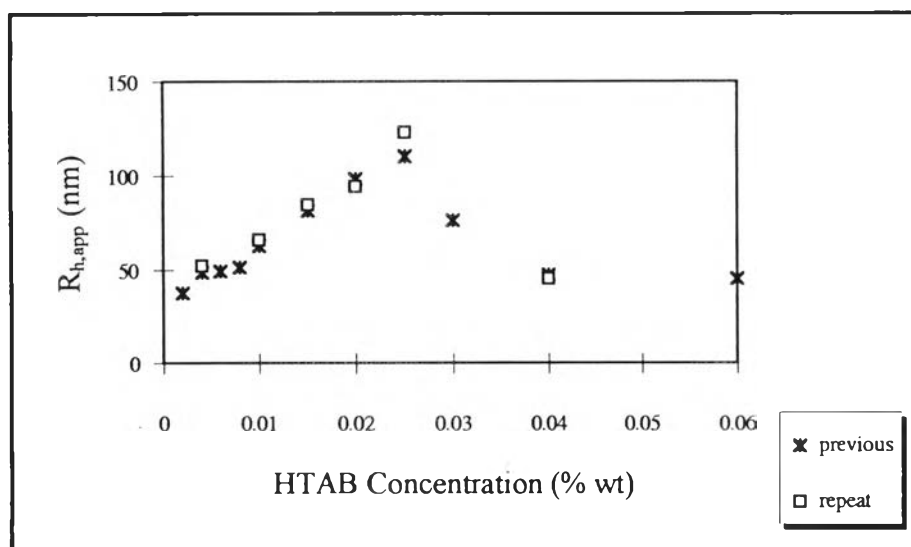
The clarification of the solvent should always receive careful attention. In general, filtration of distilled water through ultrafine membrane (0.22  $\mu\text{m}$ ) and sintered glass filters have all proved to be an effective method .

### **(c) Sample Solutions**

Cellulose polymer and water interactions can lead to solution at lower temperature. Polymer solutions are prone to degradation in the inappropriate conditions. Even when of limited extent this can have a large effect on properties determined from DLS and viscosity. To avoid the degradation from bacteria and the possibility of aggregation, it is necessary to keep the filtered stock HPC solution at low temperature. The sample solution is filtered several times through 0.22  $\mu\text{m}$  Millipore membrane freshly prior to each measurement.

### **Reproducibility**

*Figure 2.2* shows the reproducibility of DLS measurement. The data which were obtained two months later are close to the previous data. This indicates to us that techniques used for preparation and storing sample solutions were appropriate and suitable.



**Figure 2.2** The reproducibility of dynamic light scattering was shown between apparent hydrodynamic radius and HTAB concentration of 0.02 % wt of HPC/HTAB system in aqueous solution.