CHAPTER III

RESULTS AND DISCUSSION

Dynamic light scattering has become an extraordinary important tool in the study of polymer solutions. One reason is that, under proper circumstance these data can be interpreted directly in terms of size and configuration of the polymer molecule in a way that sometimes provides an easier route to this information than total intensity elastic scattering.
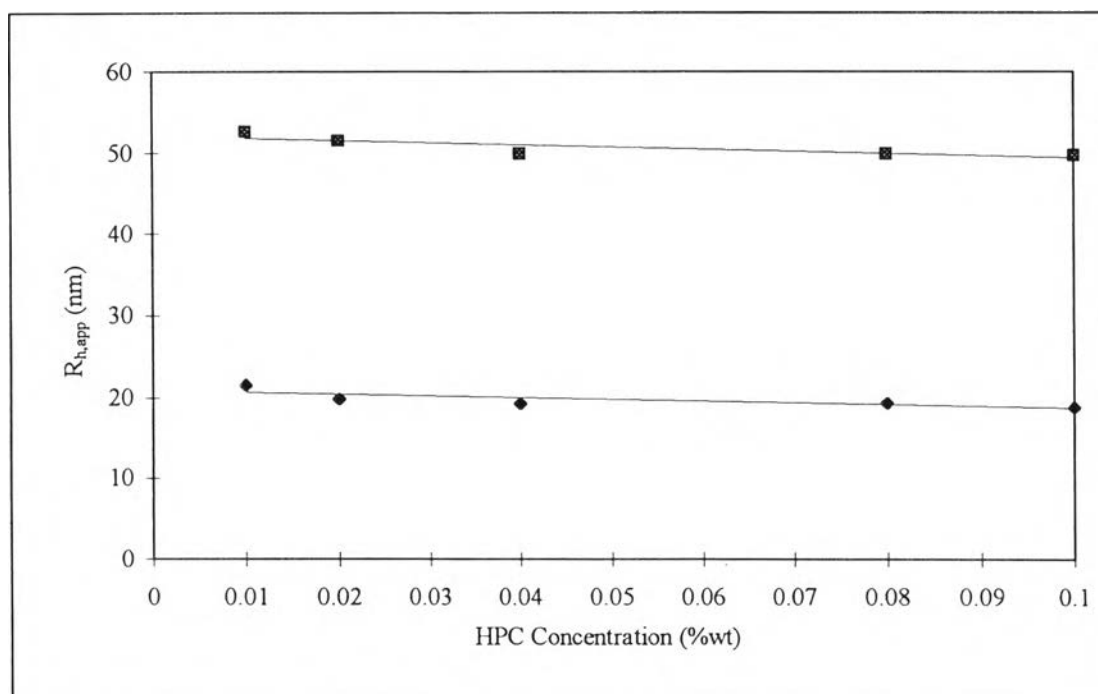

Figure 3.1 Dependence of apparent hydrodynamic radius ($R_{h,app}$) on HPC concentration.

Figure 3.1 shows $R_{h,app}$ of pure HPC. The relaxation time distribution contains two peaks overlaping each other. The areas of the first peak (at about 20 nm) and the second peak (at about 50 nm) are about 30 % and 70 %

respectively. To study the effect of surfactant and salt , we will consider only the second peak which is the main peak.

3.1 Effect of Surfactant Concentration

To study the effect of surfactant concentration, polymer concentration was fixed at 0.02 %wt and the surfactant concentration was varied in both DLS and viscometric measurements. The results, shown in figs.3.2 and 3.3 are demonstrated by dividing HTAB concentration into 5 regions.
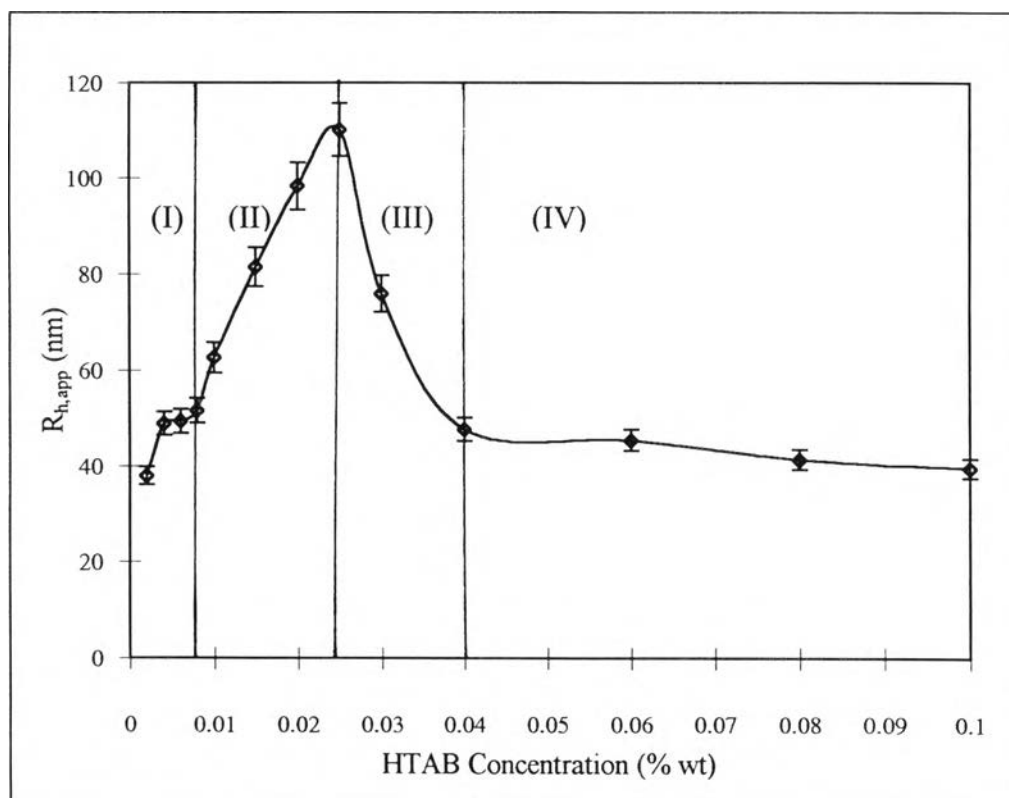

Figure 3.2 Dependence of apparent hydrodynamic radius ($R_{h.app}$) on HTAB concentration at constant 0.02 % wt of HPC.
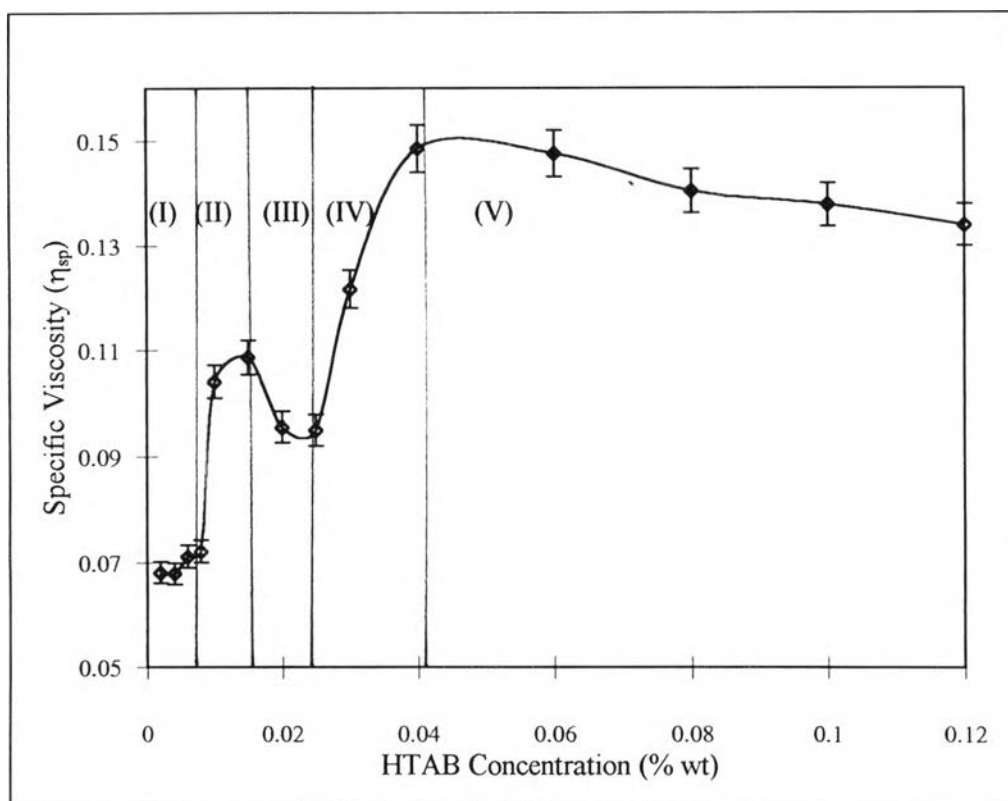
Figure 3.3 Dependence of specific viscosity (η_{sp}) on HTAB concentration, at constant 0.02 % wt of HPC

__Region I__ : In solutions of HPC containing sufficiently low concentrations of HTAB such that the cac is not exceeded, both $R_{h,app}$ and specific viscosity are constant. $R_{h,app}$ is equal to the hydrodynamic size of pure HPC which is about 50 nm. This indicates that no identifiable interaction between HPC and HTAB occurred. The HPC is still a neutral polymer. Most of the surfactant molecules apparently exist freely in the form of monomers.

__Region II__ : When the HTAB concentration exceeds the cac, complex formation occurs, as indicated by the increases in both $R_{h,app}$ and specific viscosity. These manifest the polyelectrolyte effects which occur with the HPC on formation with small HTAB micelles. Due to the same charge from cationic micelle-type structure coated onto the HPC chains, repulsive

interactions take place. Consequently, the HPC chains expand. While a substantial amount of HTAB is bound in the form of micelles to the HPC chain, a proportion of HTAB is still present in the free form. Brackman and Engbert (1991) have reported the structure of micelles in the presence and absence of PVME. They found that in the absence of PVME, the cationic surfactant, HTASal are in the form of rodlike micelles, while HTASal micelles bound onto PVME are smaller and almost spherical.

Above cac, the hydrodynamic size and the specific viscosity increase sharply. These indicate strongly cooperative binding between cationic micelles and HPC, when the HTAB concentration increases until it reaches the saturation point of binding.

The marked increase in the hydrodynamic size and the specific viscosity for a dilute solution, corresponding to a more extended conformation of the HPC chains, occurs as a result of the binding of mutually repelling charged micelles. The saturation of binding indicates the most extended conformation of the HPC chains, however the shape of the complex cannot be definitely determined by the present measurements alone. Further binding is inhibited by electrostatic repulsion between micelles; so no more binding of HTAB on HPC chains occured when increasing the HTAB concentration.

The maximum degree of binding measured by viscometric measurement is achieved at 0.015 % wt of HTAB, while the DLS shows a maximum $R_{h,app}$ at 0.025% wt of HTAB. However, HTAB concentration used for saturation of binding from DLS and viscometric data are lower than the regular cmc (0.03% wt) in the absence of polymer. $R_{h,app}$ at the saturation of binding is approximate two times larger than the size of native HPC. Of course, when the sites for binding on HPC chains are saturated, it is expected that the

monomer concentration of HTAB will once more build to the point beyond which regular micelles form in the bulk solution.

Region III. The decrease in $R_{h,app}$ and specific viscosity when HTAB concentration is above that of the saturation of binding is owing to the effect of counterions (Br⁻) that can reduce the repulsive interactions between micelles bound to the HPC chains. The similar situation was evident in the work of Schwuger and Bartik (1980). They reported viscosity results for egg albumin and sodiumdodecyl sulfate (SDS) systems. These authors attributed the initial increase in viscosity to the charging up of the protein molecules by binding of surfactants and the decrease above the maximum to the effect of counterions on the polymer coils.

Region IV. $R_{h,app}$ is slightly smaller than the size of the pure HPC chain which is about 50 nm, while the specific viscosity steeply goes up. The subsequent sharply increase in viscosity at high surfactant concentration has been suggested to be due to the crosslinking of several aggregates by free surfactant micelles in the solution [Schwuger and Bartnik, 1980]. However, Greener et al.(1987) argue that the initial binding leading to an increase in viscosity is itself due to the formation of a micelle-type structure which crosslinks the polymer molecules. These suggestions are similar to the interpretation of recently reported data for polyacrylic acid-tetradecyltrimethyl ammonium bromide systems in which the initial binding involves micelles type aggregates [Kiefer, 1991].

In the recent work of Goddard et al. (1991) and Leung and Goddard (1991), they described the very interesting novel gels in quite dilute cationic cellulose derivative polymer-surfactant systems. In their recent work they have shown that by using a higher molecular weight polymer, even more dramatic

increases in viscosity are encountered in the presence of SDS, resulting in a formation of transparent and strong gels. With reference once more to uncharged polymer, Carlsson et al. (1990), polymer/charged surfactant combinations, demonstrated that the formation of high viscosity systems, including gels, occurred under particular conditions of temperature and added concentration of surfactants (usually HTAB) in the single phase zone. Most of their work involved the polymeric ether ethylhydroxylethylcellulose. Once the gel is formed it is very resistant to salt and mechanical rupture. Furthermore, the system has a long term stability.

Region V. This region is only present in the viscometric measurement. At high surfactant content, the number of polymer groups per micelle decreases. Consequently, the viscosity enhancement is lost, which can be translated into a decrease in the specific viscosity.
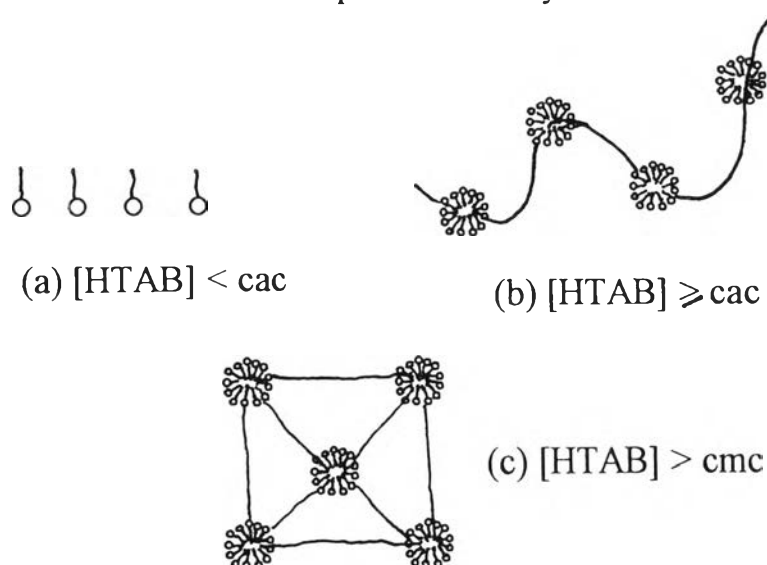
(a) [HTAB] < cac

(b) [HTAB] ⩾ cac

(c) [HTAB] > cmc

Figure 3.4 Schematic representation of the model proposed for the reaction between HPC and HTAB, (a) At low concentrations, [HTAB] <cac, there is no adsorption of HTAB to the HPC chain., (b) HTAB starts to adsorb as clusters to the HPC chain at [HTAB] > cac, the complex chain grows in size as concentration is increased., (c) At higher HTAB concentrations, beyond [HTAB] at saturation of binding, micelles crosslink the polymer chains

Notes   (1). The saturation of binding measured by viscosity takes place at 0.015% wt of HTAB, while DLS shows at 0.025% wt of HTAB. The reason may be explained by two coefficients k_D and k_h. The hydrodynamic virial coefficient, k_D, is defined as the concentration coefficient in $D = D_0$ $(1 + k_D C + ...)$: D_0 is the value of D at infinite dilution

$$k_D = 2A_2 M - k_f - 2\upsilon_2 \tag{3.1}$$

where k_f describes the concentration dependence of the friction coefficient, f : $f = f_0 (1 + k_f C + ...)$, and υ_2 is the partial specific volume. k_D is thus the sum of a static factor proportional to the second virial coefficient, A_2, and the concentration dependence of the friction coefficient .

$$\eta_{sp} = [\eta] C + k_h [\eta]^2 C^2 + ... \tag{3.2}$$

where the coefficient k_h is known as the Huggins constant which depends systematically on solvent quality.

The maximum of the binding determined from DLS and specific viscosity data occurs at different HTAB concentration because the effect of k_D (thermodynamic term) is not equal to k_h (hydrodynamic term).

(2). Region IV. the system behaves as in the semidilute regime. DLS should give information of the two modes of motion. In the present experiment, fast mode of motion was detected. The fast mode of motion provides the diffusion of only segments resulting from concentration fluctuation, so $R_{h,app}$ is small. However, viscosity should correspond with the slow mode diffusion instead of the fast mode diffusion, because viscosity is the macroscopic property while the fast mode diffusion of chains corresponds to a molecular property.
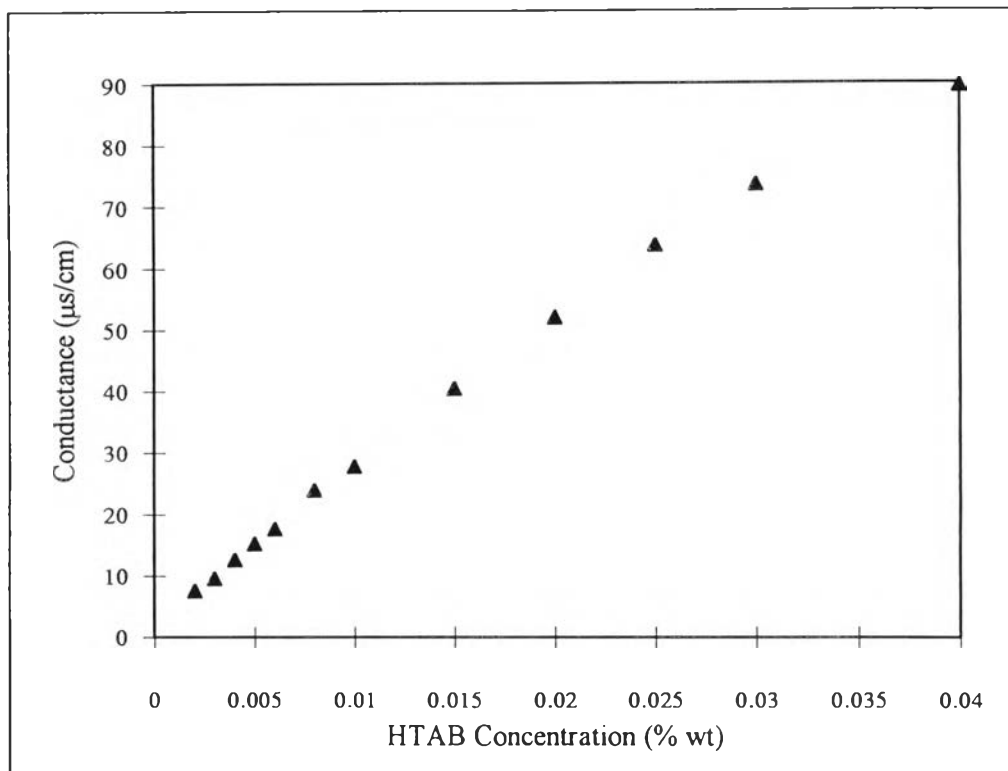
Figure 3.5 Determination of critical aggregation concentration (cac) for the HPC/HTAB system at constant 0.02 % wt HPC by measuring conductance.

Figure 3.5 shows a method to determine cac of 0.02 % wt of HPC and various HTAB concentration systems. A measurement of conductance is a convenient method that can be used to find cac. From plotting the conductance, as expressed in $\mu s/cm$, as a function of surfactant concentration, the point at which the slope slightly changes is cac. From this experiment, cac is about 0.01% wt of HTAB. This cac value is agreement with those from the DLS and viscometric data. Because at this HTAB concentration both $R_{h,app}$ and the specific viscosity begin to increase.

3.2 Effect of Salt

Figure 3.6 depicts the influence of low molar salt on $R_{h,app}$ where the data are displayed as a function of HTAB concentration at a constant 0.02 % wt of HPC. The overall form of the curves shown in this figure is dependent on the screening effect of free ions on the interactions between the fixed charges on the bound micelles. In the stable phase, $R_{h,app}$ of mixed solution in the presence of added salt shows smaller $R_{h,app}$ than that in the absence of salt solution. In the absence of salt, the repulsive interactions show the prominent influence.
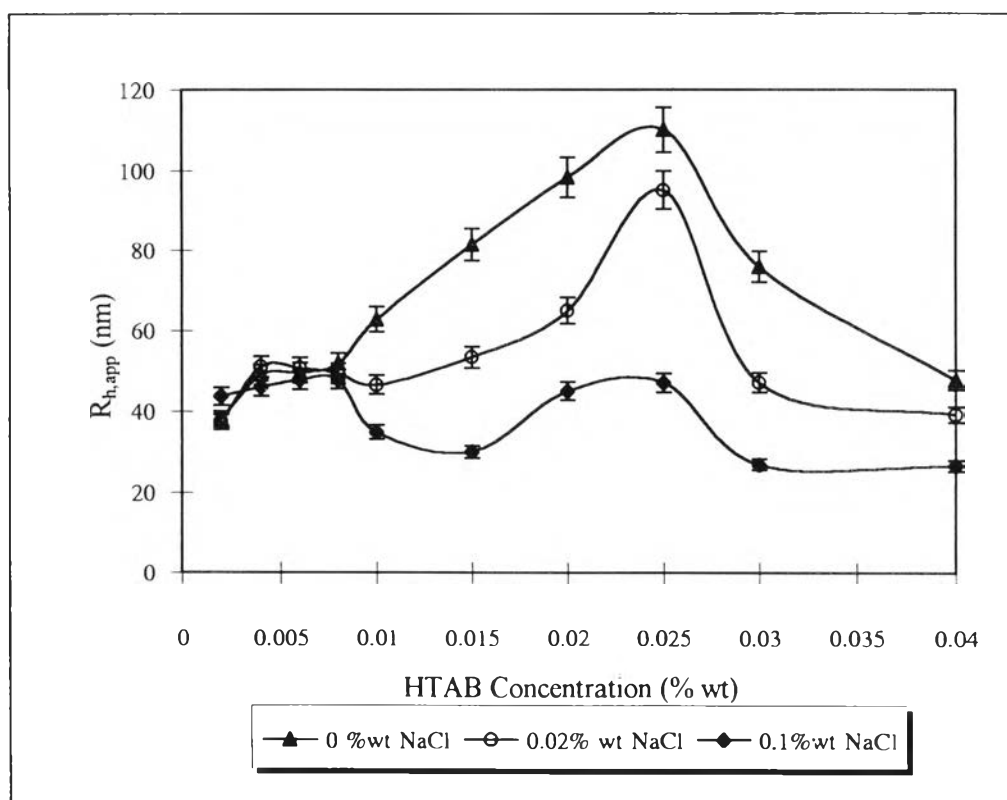

Figure 3.6 Apparent hydrodynamic radius ($R_{h,app}$) as a function of HTAB concentration at different ionic strength and constant 0.02 % wt of HPC.

In the presence of salt system, $R_{h,app}$ is initially constant as a function of HTAB concentration for any salt concentration because HPC is still a nonionic polymer. Hence, no influence of the salt on the chain conformation is present in this region. At higher HTAB concentration, $R_{h,app}$ becomes smaller at even small amount of salt added (0.02% wt). Owing to the effect of Cl^- counterions adsorbed on the headgroup of bound micelles along the HPC chains, the counterions shield the repulsive interactions along the rigid chain. As a result, the chain contracts and becomes more compact.

At higher concentration of HTAB (above 0.01 and 0.015 %wt of HTAB in the presence of 0.02 and 0.1 % wt of NaCl, respectively), $R_{h,app}$ increases sharply, as shown in this figure, as the repulsive interaction contributes to the interaction potential. This is because the fixed charges of NH_4^+ become increasingly important. At even higher HTAB concentration, there is a decrease owing to the screening effect of free Cl^- counterions from the excess HTAB; this screening effect progressively increases with HTAB concentration after the HPC chains are saturated.

The ability of salt to decrease the size and loosen the rigid structure of HPC after binding with HTAB is remarkably shown with the highest salt concentration (0.1 % wt). The native structure of HPC is a stiff, rodlike molecule resulting from the intramolecular bonds impart a significant stiffness or rigidity to the cellulose molecule [Mandel, 1985]. Thus the HPC chain with bound micelles should not collapse to a point where $R_{h,app}$ becomes smaller than the value for native HPC ($R_{h,app}$ = 50 nm). This seems possible that the binding of HTAB micelles may increae the flexibility of the HPC conformation.

From the plot, the addition of salt does not change the locations of the maximum in $R_{h,app}$. This is in agreement with the work of Murata and Arai (1973). They studied the effect of salt on the transition concentrations of 0.1 % wt of PVP and SDS systems.

Figure 3.7. shows the specific viscosity of the same system measured by DLS. The viscosity data correlates with that of DLS. These results clearly imply a change in polymer conformation. In the salt free system, at the present study range of HTAB 0.02-0.04 % wt, the specific viscosity data can be divided into four regions as mentioned in fig 3.3. In the 0.02 % wt of NaCl system, illustrative diagrams are given in fig 3.7 which follows these steps:

(1) A constancy in specific viscosity at the first addition of HTAB concentration without an identifiable interaction below the critical concentration of the surfactant.

(2) A decrease in specific viscosity, this result implies the effect of salt on polymer conformation and indicates the formation of polyelectrolyte complex. The electrostatic interactions between the bound micelles are shielded by Cl$^-$ ions.

(3) An increase in the specific viscosity manifests the expansion of the HPC chains when the amount of NH^{4+} is significant.

(4) A decrease in the specific viscosity represents the screening effect of Cl$^-$ counterions from free micelles in the solution.

(5) An increase in the specific viscosity is due to micelle-type structure crosslinking with the HPC chains.

At higher salt concentration (0.1% wt NaCl), the system remains in dilute regime throughout the range of HTAB concentration studied. This results from the fact that the effect of Cl$^-$ counterions on reducing the repulsive

interactions between the bound micelles. This makes each chain far away from each other, hence no intermolecular interactions take place.

From the plots of the specific viscosity, the polyelectrolyte nature of the complex is further confirmed in this work by the progressive reduction in the specific viscosity observed upon adding salt. The comparatively low charge density of the polyelectrolyte complex is effectively reduced by the presence of salt.
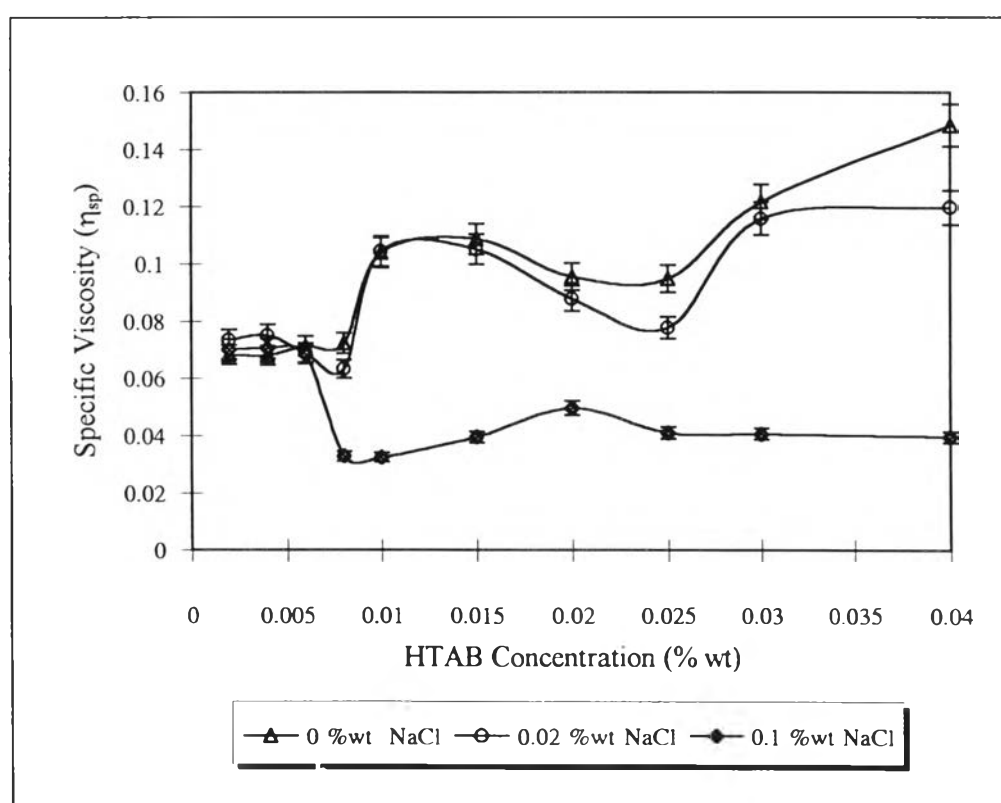

Figure 3.7 Specific viscosity as a function of HTAB concentration at different ionic strength and constant 0.02 % wt of HPC.

The data suggest a maximum at higher HTAB concentration in 0.1 % wt of NaCl than that in the absence and in the 0.02 % wt of NaCl systems. This observation contrasts with the results from DLS. However, from the work of Cabane and Duplessix (1982), the saturation level increases with

increasing ionic strength. Moreover, the location of the maximum in $R_{h,app}$ gives more precisely the point at which the binding reaches saturation than does the specific viscosity data. This is because the maximum specific viscosity is broader on the HTAB concentration scale.
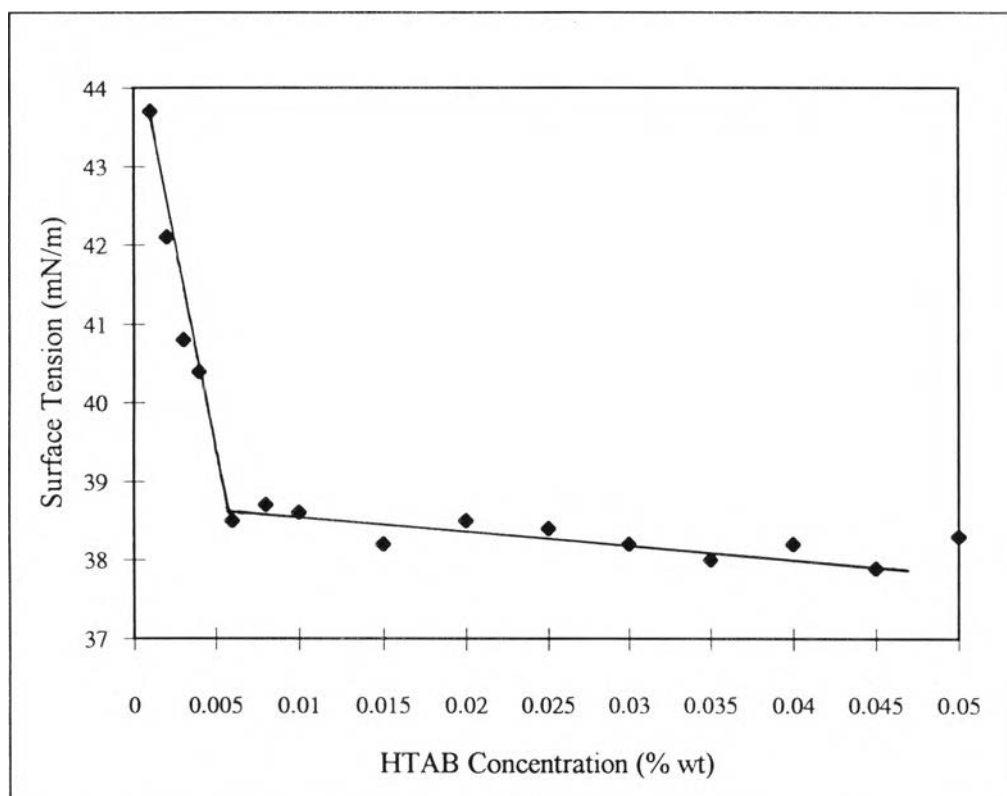

Figure 3.8 Determination of critical aggregation concentration (cac) for the HPC/HTAB in 0.10 % wt of NaCl and at constant 0.02 % wt of HPC system by surface tension measurement.

There are several methods to determine the cac value. In this fig. 3.8, in the present system and when salt is present, it is suitable to use surface tension measurement. Surface tension is the work required to create a unit area of the interface and expressed as mN/m. The point at which slope abruptly changes represents the cac value which is about 0.006 % wt of HTAB. The cac is approximately 0.01 % wt of HTAB in the absence of NaCl and at fixed 0.02 % wt of HPC. So, the addition of inorganic electrolyte depresses the cac value

and promotes the formation of the complexes. This is in good agreement with the work of Murata and Arai (1973). They found a linear relationship in a log-log plot of cac value against Na^+ ions concentration for the PVP/SDS association. Addition of salt reduces the cac value and also increases the binding ratio of surfactant to polymer. A similar effect occurs with polyethylene oxide, PEO and SDS system studied by Cabane and Duplessix (1982). They reported an increase in binding ratio of SDS to ethylene oxide group (EO) when ionic strength is increased.

Figure 3.9 depicts the effect of salt on the conformation of HPC-HTAB complex at the maximum of binding as shown in the DLS data (from fig. 3.2) at fixed 0.02% wt of HPC and 0.025% wt of HTAB. Both of $R_{h,app}$ and the specific viscosity decrease steeply on an initial addition of NaCl to the solution. This is due to the change of the electrical environment in the solution. The Cl^- ions from NaCl suppress the repulsive forces by screening the ionized charges of bound micelles on the polymer chains and lead to the contract conformation of the single chain.

Beyond a critical salt concentration, both of $R_{h,app}$ and the specific viscosity curves become nearly constant and independent of salt concentration. As more salt is added, the chains pack closely and the fluctuation of counterions from the added salt cannot affect the motion of the complexes. The shielding is complete and the polyelectrolytes can no longer shrink or are in the asymptotically collapsed state
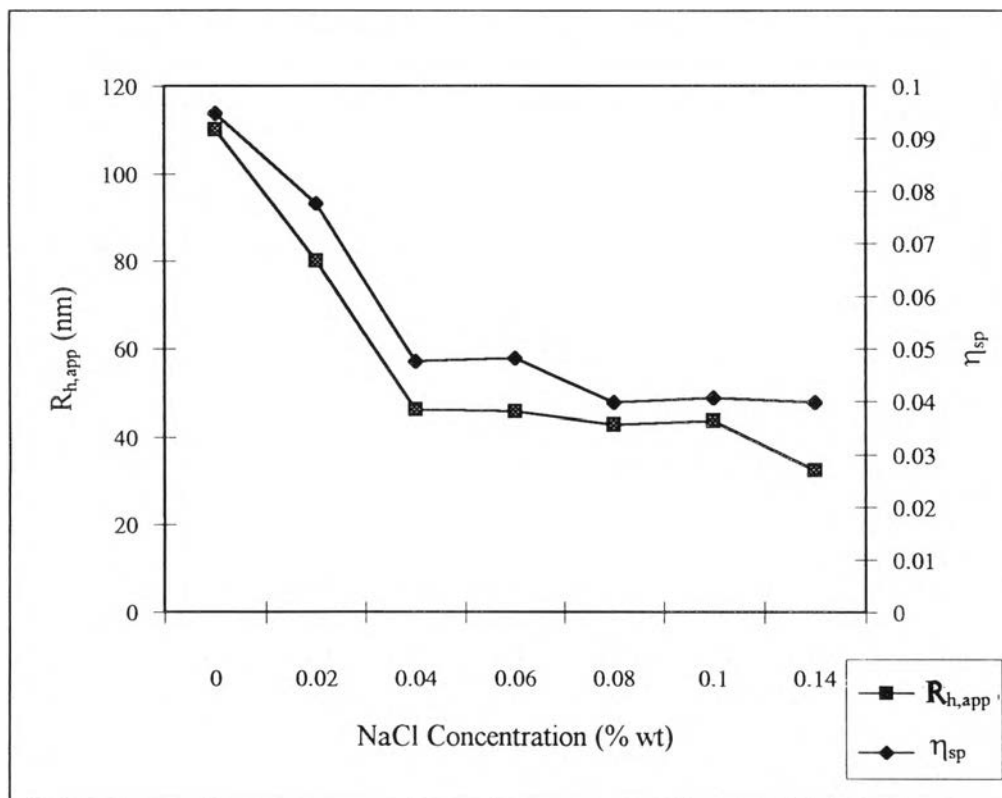
Figure 3.9 Dependence of apparent hydrodynamic radius ($R_{h,app}$) and specific viscosity (η_{sp}) on concentration of NaCl at constant 0.02 % wt of HPC and 0.025 % wt of HTAB.

3.3   Effect of HPC Concentration as a Function of Gram Ratio of HTAB/HPC

Figure 3.10 shows the effect of gram ratio of HTAB/HPC at various constant HPC concentrations. The polymer concentration is varied from 0.005 % wt to 0.04 % wt. This concentration range covers both dilute and semidilute regions. These plots in fig.3.10 can be classified into three cases by using HPC concentrations as shown in fig. 3.10(a) , fig.3.10(b), and fig 3.10(c)
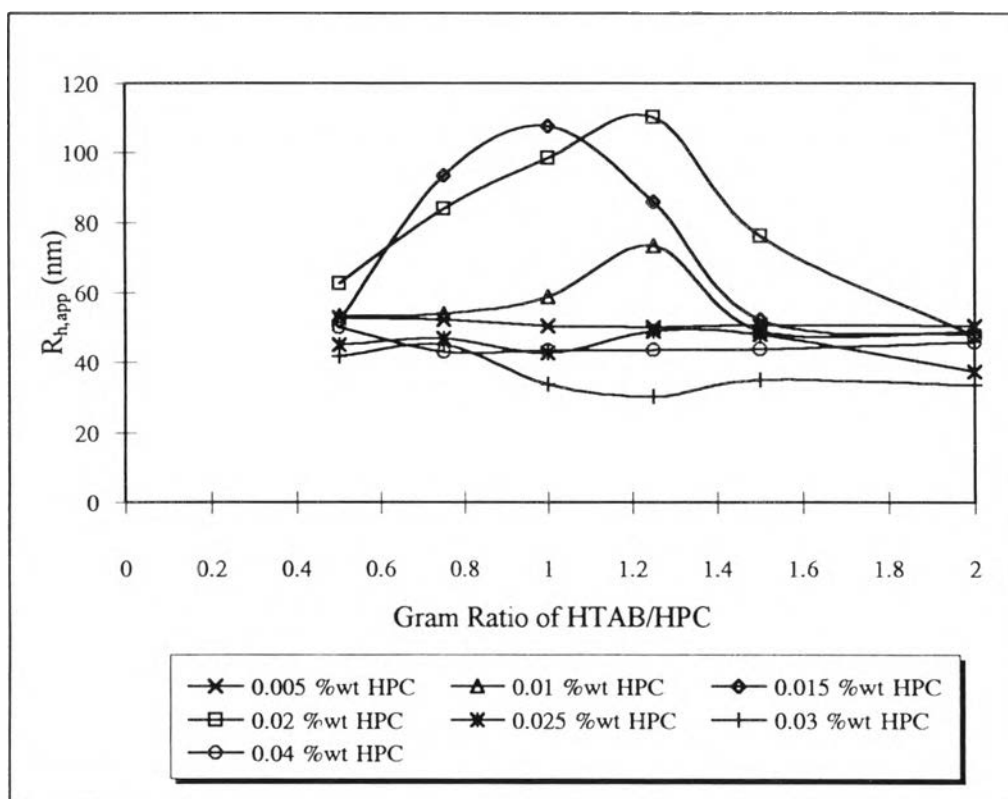
Figure 3.10 Relationship between apparent hydrodynamic radius ($R_{h,app}$) and gram ratio of HTAB/HPC at different HPC concentrations.

Figure 3.10 (a) depicts $R_{h,app}$ of 0.005 % wt of HPC as a function of gram ratio of HTAB/HPC from 0.5 to 2. A constancy in $R_{h,app}$ on the gram ratio scale implies that no complex formation occurs in this range. This presumably results from the fact that the amount of HTAB is not sufficient to reach cac value. So, the surfactants will apparently exist freely in the solution in the form of monomers and $R_{h,app}$ is equal to the size of pure and neutral HPC (50nm).
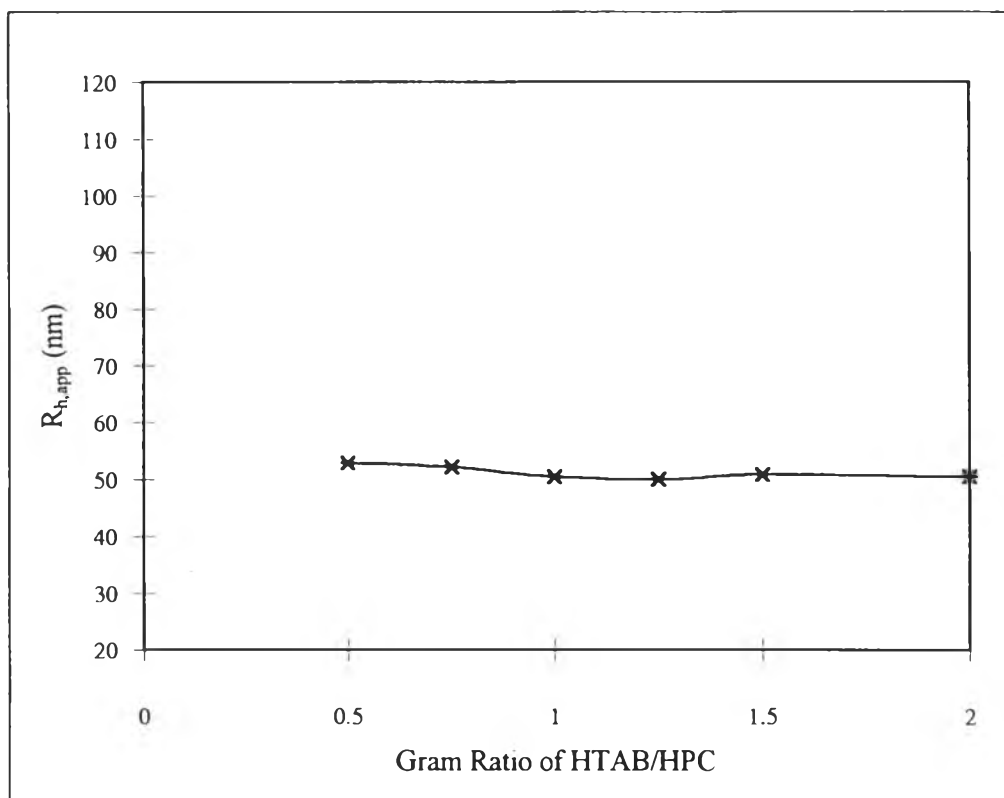
Figure 3.10 (a) Apparent hydrodynamic radius ($R_{h,app}$) as a function of gram ratio of HTAB/HPC at 0.005 % wt of HPC.

The effect of the amount of polymer on the value of cac was studied by Cabane and Duplessix (1982). In their most recent phase diagram, they suggests that the cac value slightly decreases with the polymer concentration. The value of cac in 0.02 % wt of HPC and HTAB system that is determined from fig. 3.2, fig. 3.3, and fig. 3.5 is about 0.01 % wt of HTAB. As shown in fig 3.10(a), at gram ratio of HTAB/HPC = 2 and at 0.01 % wt of HTAB, $R_{h,app}$ is still equal to 50 nm or the native HPC size. This indicates that no interactions between HPC and HTAB occur at 0.01 % wt of HTAB. So, this result is in agreement with that of Cabane and Duplessix (1982).

A further study was carried out by us at higher HTAB concentration than 0.01 % wt of HTAB and $R_{h,app}$ is larger than 50 nm; the result will be compared with the work of Cabane and Duplessix.

Figure 3.10(b) shows $R_{h,app}$ at 0.01, 0.015, 0.02 % wt of HPC at various gram ratios of HTAB/HPC. No complex formation occurs for 0.01% wt and 0.015 % wt of HPC at gram ratio at HTAB/HPC = 0.5 This is because $R_{h,app}$ are still about 50 nm, while $R_{h,app}$ of the fixed 0.02% wt of HPC system is about 62 nm. So, at this ratio there are interactions between HPC and HTAB in the latter system. We can see that the cac value is independent of the gram ratio of the surfactant to the polymer. Jones (1967) have demonstrated that the concentration of surfactant for aggregate formation is mainly a function of surfactant concentration for a particular polymer.

The concentrations of HTAB used to reach the maximum of binding at fixed 0.01, 0.015, and 0.02 % wt HPC are 0.0125 , 0.015 and 0.025 % wt HTAB respectively. These results are consistent with these observed in the system of PVP/SDS studied by Lange (1969), and Arai and co-workers (1973), and the system of PEO/SDS as studied previously by Francois et al. (1985). In each case, it was reported that the concentration of the surfactant at the saturation of binding increases with polymer concentration.

Most studies show an increase in $R_{h,app}$ with polymer concentration. This could be illustrated by the work of Treiner and Nguyen (1990) who investigated the interaction of cationic surfactant Copperdodecylsulfate [Cu $(DS)_2$] with PEO and PVP by using a Cu^{2+}-specific electrode. The surfactant molecules form micelles adsorbed to PEO and the degree of counterion binding decreases with an increasing polymer concentration. So, in dilute solution, the higher polymer concentration corresponds with the lower degree of counterion (Br⁻) binding and the more expansion or larger $R_{h,app}$ The smaller sizes in 0.02 % wt of HPC system than those in 0.015 % wt of HPC system may arising from the screening effect.
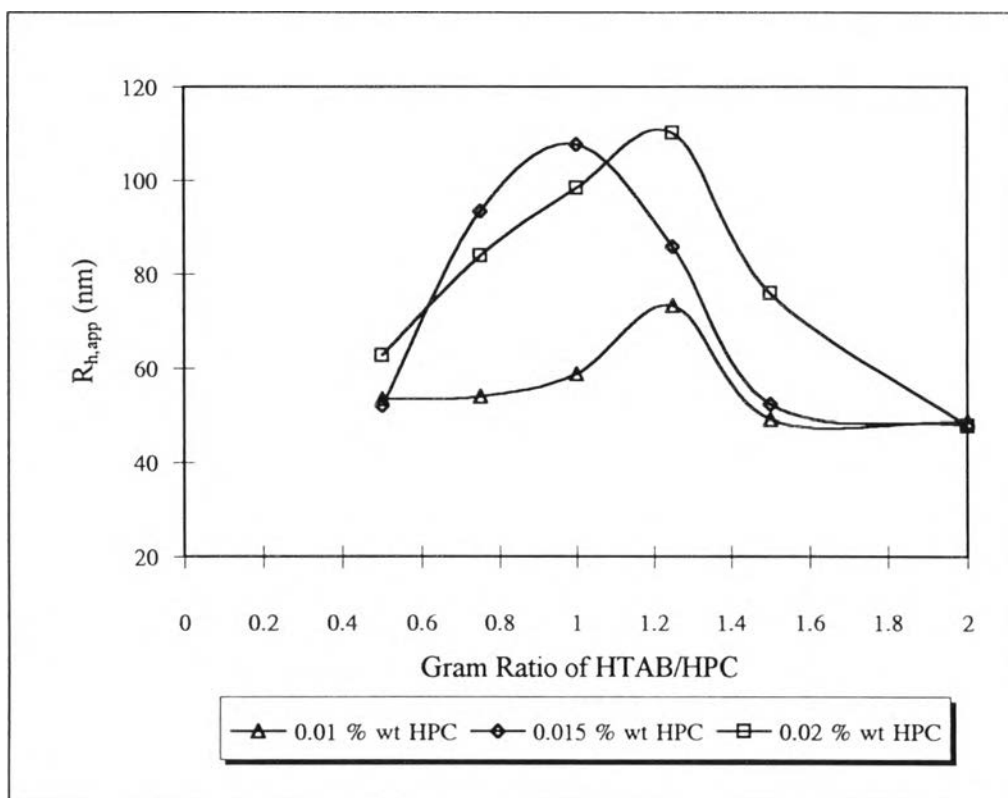
Figure 3.10 (b) Apparent hydrodynamic radius ($R_{h,app}$) as a function of gram ratio of HTAB/HPC at 0.01, 0.015, and 0.02 % wt of HPC.

Figure 3.10(c) shows $R_{h,app}$ at fixed 0.025, 0.03, and 0.04 % wt of HPC as a function of gram ratio of HTAB/HPC. Each data point corresponds to the polyelectrolyte and semidilute system. At low gram ratios of HTAB/HPC, the chains entangle or overlap to form transient network. For higher gram ratios of HTAB/HPC between 1.5-2, there are two possible phenomena. They are either polymer entanglement or crosslinking of micelles with the polymer chains.
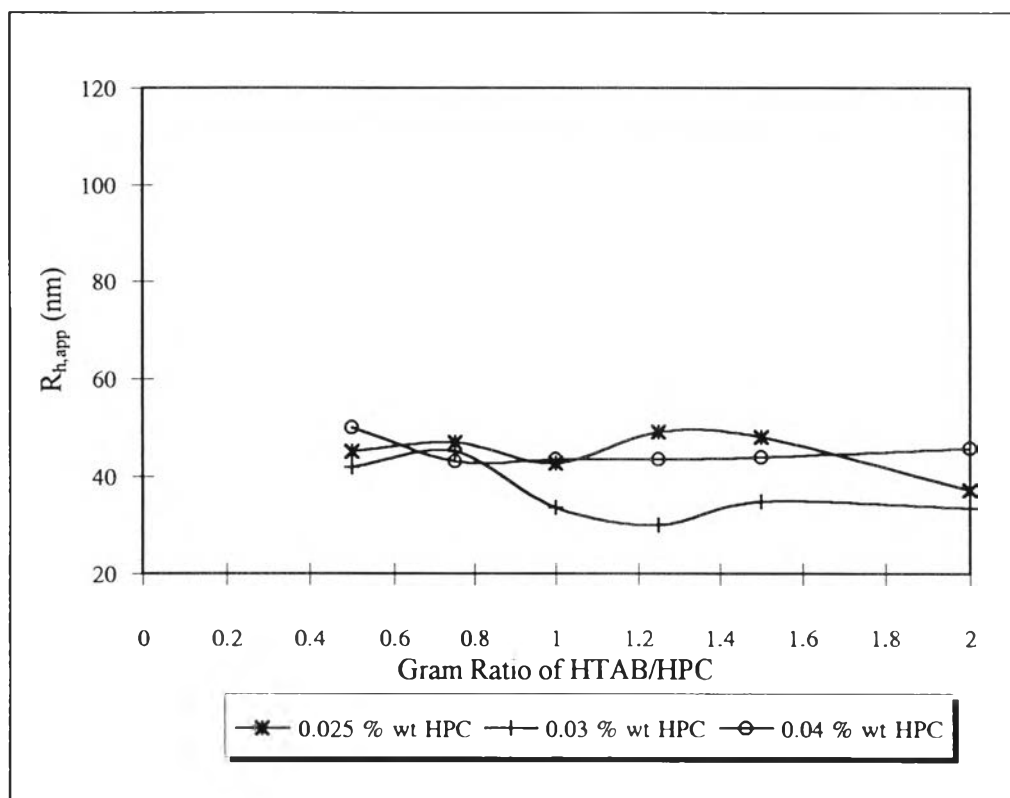
Figure 3.10 (c) Apparent hydrodynamic radius ($R_{h,app}$) as a function of gram ratio of HTAB/HPC at constant 0.025, 0.03, and 0.04 % wt of HPC.

The reasons why this figure shows a semidilute regime are as follows:

(1) The molecular weight of HPC used in this study is quite large, so it is easy to achieve the semidilute system when the polyelectrolytes are present.

(2) Some data show smaller size than the size of the natural HPC, although there is no salt in this system. This situation should not occur because of the rigid structure of the HPC chain. The chain should not collapse where $R_{h,app}$ becomes less than 50 nm.

(3) With an increase in the amount of HTAB, the process does not follow patterns for the complex formation as shown in fig. 3.9(b). Most of the trend is constant, with no influence from increasing the HTAB concentration.

(4) It is likely that fast mode of motion is detected in the present study (for this range).

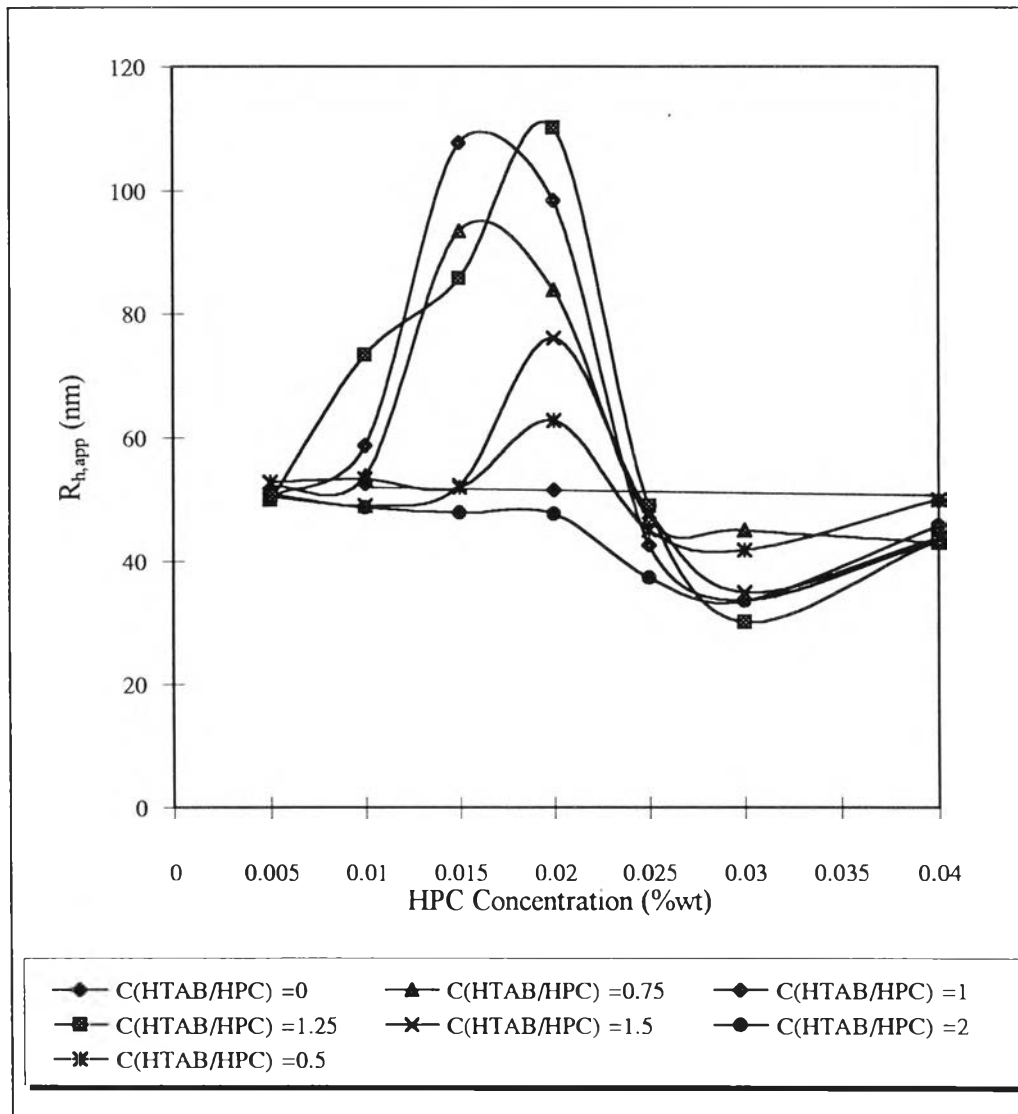## 3.4 Effect of Gram Ratio of HTAB/HPC as a Function of HPC Concentration

Figure 3.11 Relationship between apparent hydrodynamic radius ($R_{h,app}$) and HPC concentration at different gram ratio of HTAB/HPC.

Figure 3.11 shows $R_{h,app}$ data for HPC concentrations varied from 0.005 to 0.04 % wt at different gram ratios of HTAB/HPC. These plots are similar to those in fig.3.9 but emphasize the effect of C_{HTAB} / C_{HPC} on $R_{h,app}$. In

the absence of HTAB system, $R_{h,app}$ is weakly independent of HPC concentration. $R_{h,app}$ data for C_{HTAB} /C_{HPC} = 0.5 to 1.25 clearly demonstrate the polyelectrolytic character of the HPC-HTAB complex, with a strong change in the coil size and conformation as the C_{HTAB} /C_{HPC} ratio is increased. In the dilute solution, $R_{h,app}$ increases with increasing polymer concentrations because of increasing interactions among the polyions, which are very extended. At higher HPC concentration, electrostatic screening sets in among the polyions, reducing the Debye lenght and the size. Beyond the ratio C_{HTAB} / C_{HPC} = 1.25, $R_{h,app}$ data are smaller because of crosslinking of HTAB clusters with HPC chains as previously mentioned. The same events occur above 0.025 % wt of HPC.
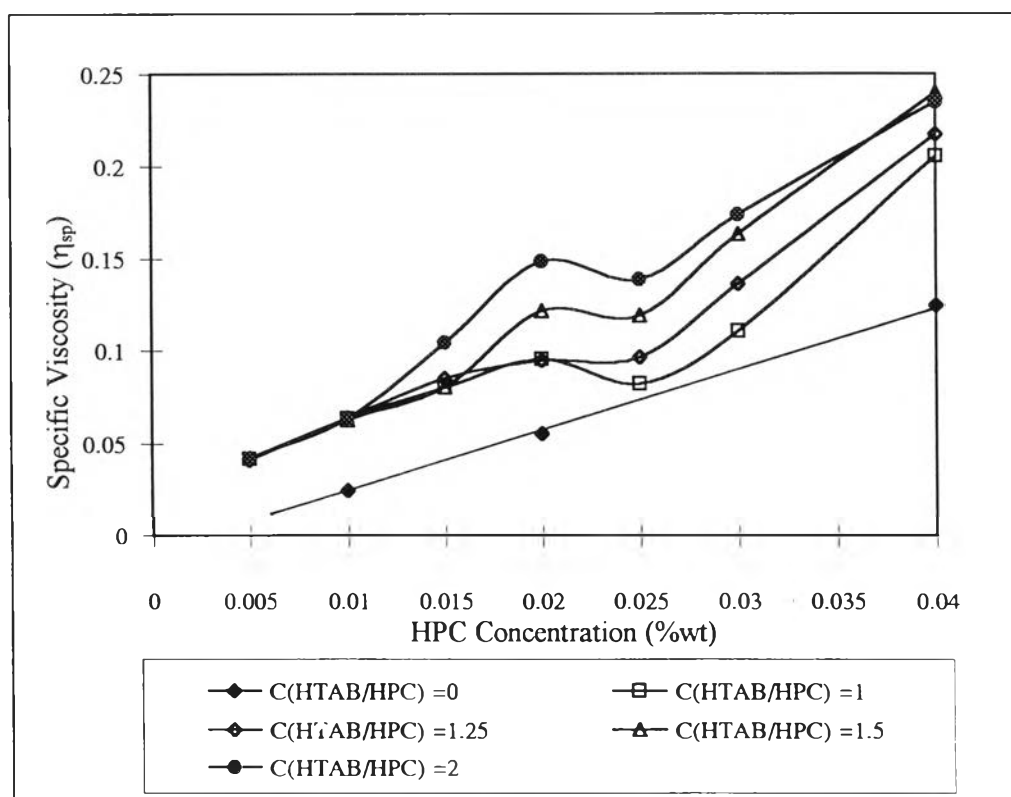

Figure 3.12 Relationship between specific viscosity (η_{sp}) and HPC concentration at different gram ratio of HTAB/HPC.

Figure 3.12 shows the specific viscosity versus HPC concentration at different ratios of C_{HTAB}/C_{HPC}. These resulting plots are in agreement with those of fig. 3.11. The higher specific viscosity of the complex at the ratio C_{HTAB}/C_{HPC} above 1.25 or above HPC concentration of 0.025 % wt comes from the significance of the second term of (3.2) eq. on the right hand side.This manifests the transient network region. The result that $R_{h,app}$ is smaller in these regions possibly arise from the detection of the fast mode of motion in the semidilute regime. In the semidilute regime, DLS cannot distinguish an isolated complex structure.