

## CHAPTER III

### RESULTS

In this chapter, the binary systems of pure polymer and surfactant in aqueous solution and the ternary systems (PAM / Triton X-100 / water) will be described.

#### 3.1 Binary System (PAM / Water)

##### 3.1.1 Dynamic Light Scattering

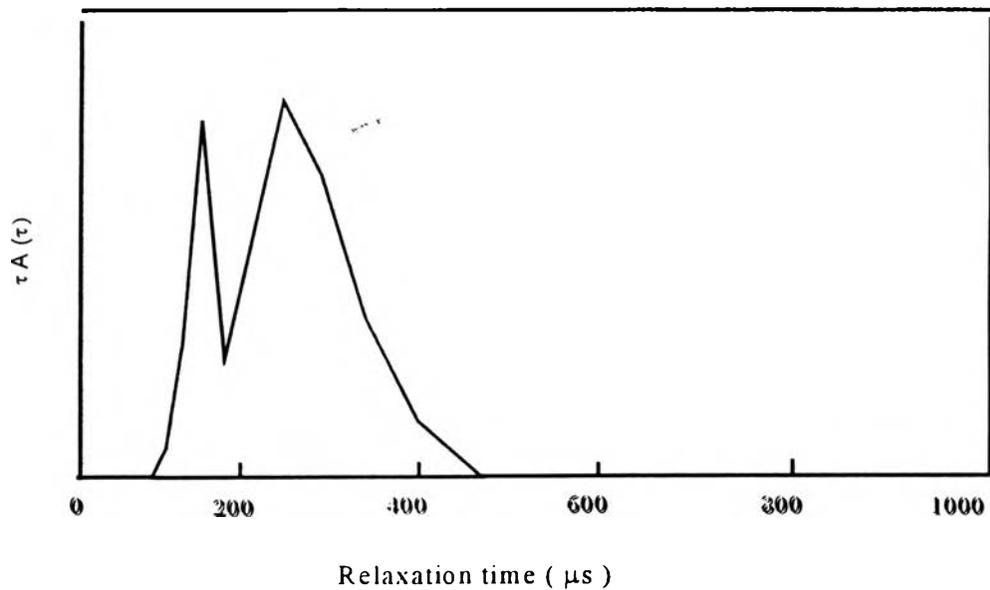


Figure 3.1 Relaxation time distribution for 0.4 g/l solution of PAM.

Figure 3.1 shows the relaxation time distribution for PAM ( $7 \times 10^5 M_w$ ) in water at  $30^\circ\text{C}$  at a concentration of  $0.4 \text{ g/l}$ . This figure indicates a bimodal distribution. The areas of the first peak and the second peak are about 30% and 70% respectively. The fast mode comes from the concentration fluctuation which is presumed to be due to internal relaxation of polymer chains. The slow mode corresponds to the center of mass diffusion. To study the effect of surfactant, the slow mode will only be discussed which contains most of the scattered intensity.

The translational diffusion coefficient vs. concentration plots for two different molecular weights are shown in Figure 3.2. The concentration dependence of diffusion coefficient is given by the following equation:

$$D_t = D_{t,0} (1 + k_D C), \quad (3.1)$$

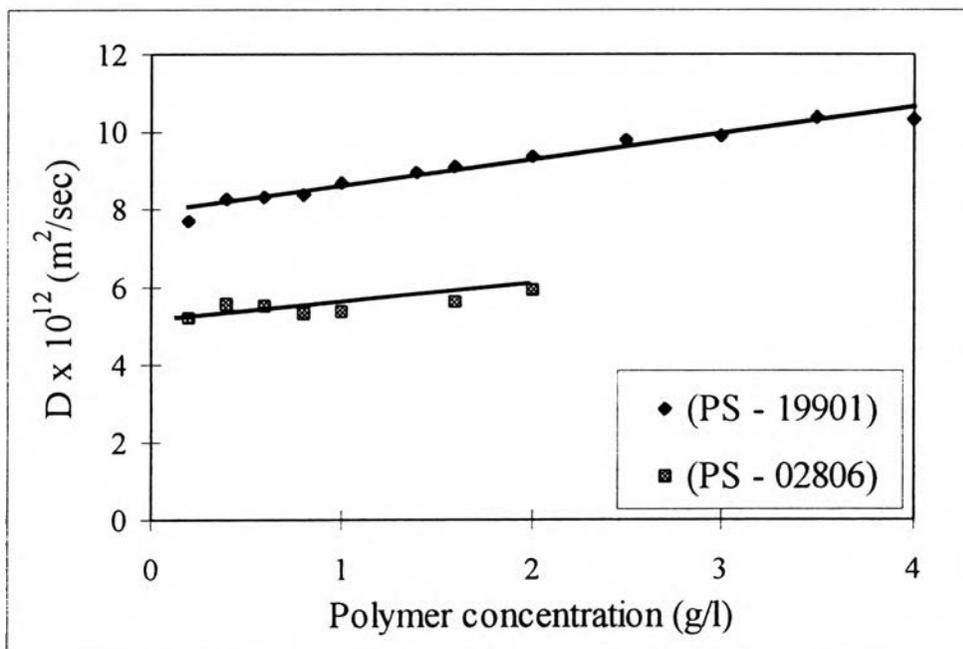


Figure 3.2 Diffusion coefficients of PAM of different  $M_w$  as a function of concentration.

Where,  $k_D = 2A_2M - k_f - V_2$ , (3.2)

$A_2$  is the second virial coefficient,  $M$  is the molecular weight,  $k_f$  is the concentration dependence of the frictional coefficient and  $V_2$  is the partial specific volume. Since water is a good solvent for PAM, the second virial coefficient,  $A_2$ , is large and positive, and therefore  $D_t$  increases with increasing polymer concentration [Wyn Brown, 1993].

From the intercept of these lines, the diffusion coefficients of infinite dilution are obtained. The hydrodynamic radius ( $R_H$ ) for each polymer was calculated by using the Stokes-Einstein equation (Equation 2.10). The results are shown in Table 3.1.

### 3.1.2 Static Light Scattering

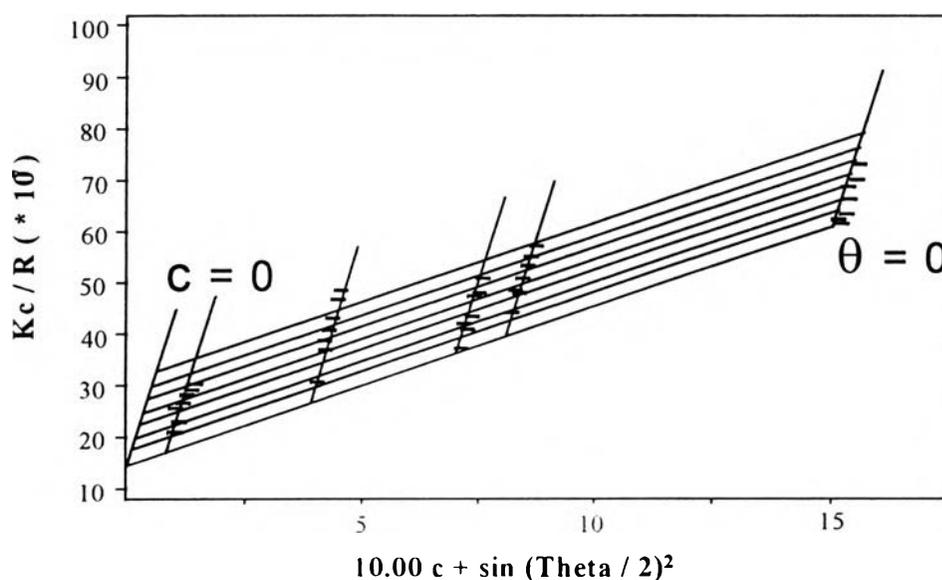


Figure 3.3 Zimm plot for PAM sample (PS - 19901).

The determination of the absolute molecular weights was the most difficult part of this work. Zimm plot analysis was applied to determine the weight - average molecular weights and radius of gyration ( $R_g$ ) of the polymers. Figure 3.3 and 3.4 show Zimm plots for PAM samples (PS - 19001 and PS - 02806) in water at 30°C.

The molecular weights were obtained from the inverse of the intercept at  $C = 0$  and  $\theta = 0$  in the Zimm plots. The slopes of the zero-concentration line as a function of angle are a measure of  $R_g$ . This method is applicable over a range of  $R_g$  between 25 nm and 250 nm [Walter Hoppe, 1983]. The calculated values of molecular weight and radius of gyration are listed in Table 3.1 for different molecular weights of PAM.

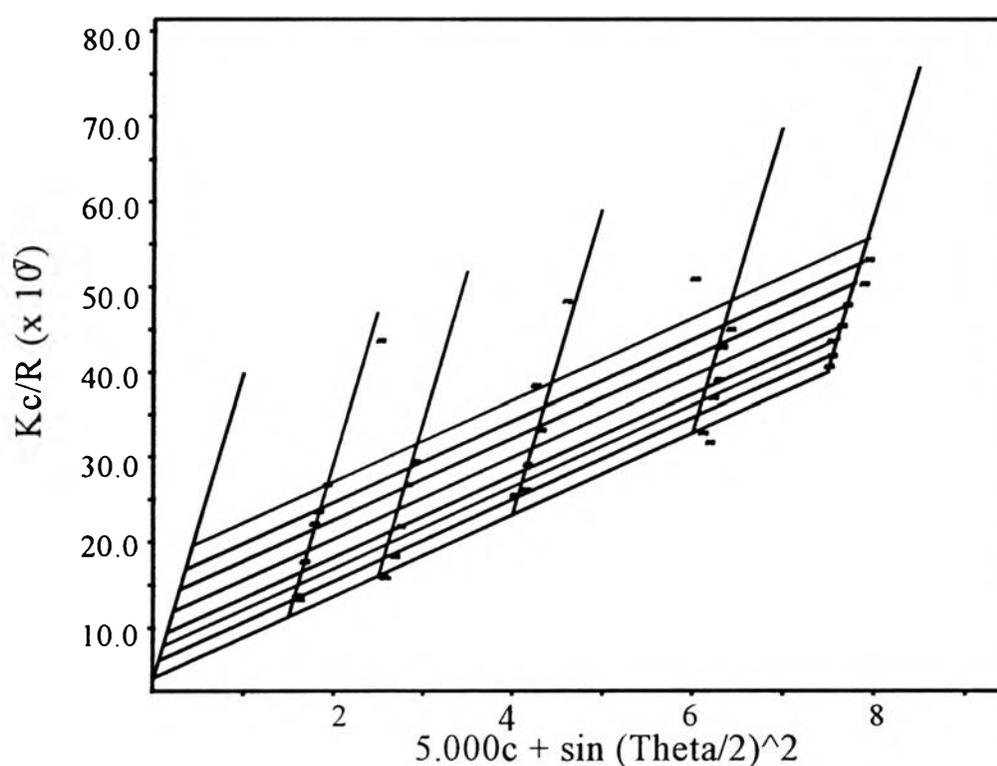


Figure 3.4 Zimm plot for PAM sample (PS - 02806).

Difficulties occurred in the measurement of Zimm analysis for very high molecular weight of polymer (PS - 02806). It was found that the data are quite scattered in the graph. These scattered data raised as a result of very high molecular weight and high polydispersity of PAM sample.

### 3.1.3 Viscosity

Figure 3.5 shows the reduced specific viscosity for PAM of two different molecular weights versus PAM concentration. The plots yield the intrinsic viscosity from the intercept and the Huggins - constant from the slope of the best line through the experimental points according to equation 2.16.

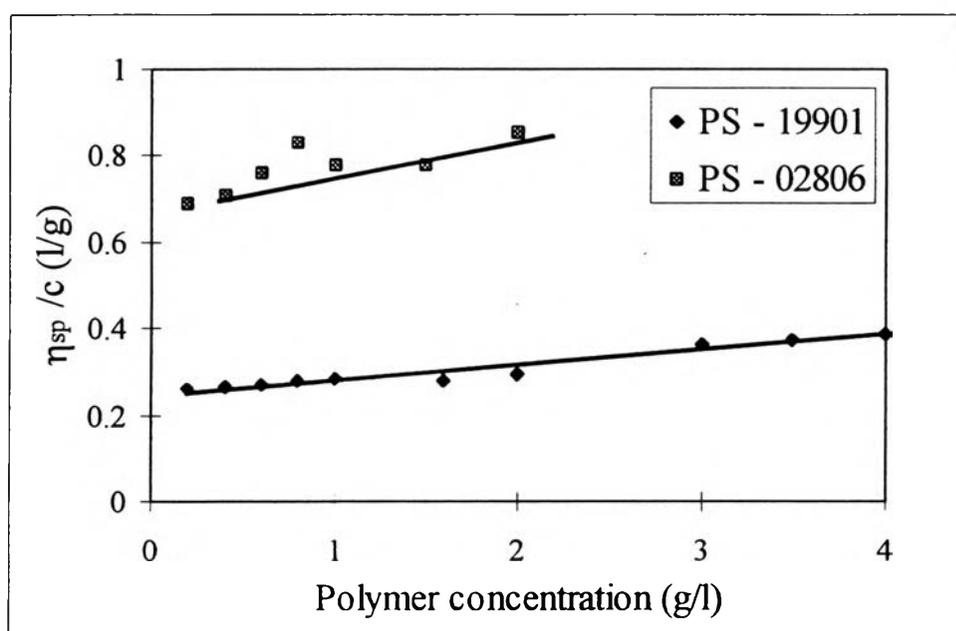


Figure 3.5 Reduced specific viscosity versus concentration for PAM in water

Table 3.1 summarizes the experimental results of molecular weight,  $M_w$ ,  $R_g$ , diffusion coefficient,  $R_H$  and intrinsic viscosity. The values of  $R_g$  and  $R_H$  correlate with the molecular weight. The ratio of  $R_g$  and  $R_H$  has a value of  $\sim 1.9$ . It is close to theoretical value 2, which was calculated from a theory of a polydisperse coil in a good solvent [Ying, Wu and Chu, 1996]. Our results are slightly larger than the values reported by Patterson et al. [1985] for polyacrylamide in 0.1 M NaCl. But the intrinsic viscosity data are well in agreement with the values deduced from the study of Klein [1980].

Table 3.1 Static and dynamic properties of PAM in aqueous solutions

Sample	$M_w$ ( $\text{g mol}^{-1}$ )	$D_0 \times 10^{12}$ ( $\text{m}^2/\text{sec}$ )	$R_H$ (nm)	$R_g$ (nm)	$[\eta]$ (ml/g)
PS - 19901	699,000	7.84	35.37	65.69	$260.30 \pm 15$
PS - 02806	2,560,000	5.22	53.12	101.23	$700.97 \pm 50$

Table 3.2 shows the experimental results of molecular weight based on Zimm analysis and viscosity measurement and also shows the manufacturers' given value. For the PS - 19901 sample, molecular weight is two times lower than the manufacturers' value. The difference may be explained by two factors. One reason is due to the mechanical stirring. The solution should be stirred very gently for a high molecular weight polymer. Otherwise, the chains would be broken and the solution viscosity will be decreased. Another reason is the aging or degradation of PAM solution [Munk, 1980]. The aging of polyacrylamide, arises due to the growth of microorganisms, manifests itself by the generally poor reproducibility of experimental data and by a decrease of the solution viscosity over longer periods of time.

Table 3.2 Comparison of molecular weight by different methods

Sample	Manufacturers' given value	$M_w$ by Zimm analysis	$M_w$ by viscosity
PS - 19901	700,000	699,000	705,000
PS - 02806	5,000,000	2,560,000	2,620,000

### 3.2 Binary System (Triton X-100 / Water)

The physical properties of Triton X-100 micelles have been studied extensively by several authors by using physical techniques including quasi-elastic light scattering [Phillips, 1995] and viscometry [Kushner, 1954]. They inferred a dependence of micellar shape and size distributions on temperature and surfactant concentration. At higher concentrations, they observed clearly an evidence for changes in micelle size with increasing temperature. They described a decrease of the second virial coefficient,  $A_2$ , with increasing temperature, indicating that intermicellar interactions become less repulsive at higher temperature. At 45°C,  $A_2$  goes to zero, corresponding to a cancellation between the excluded volume potential and an attractive pair potential between micelles. Above 45°C, the attractive pair potential dominates and  $A_2$  becomes negative. They proposed that the increase in the attractive pair potential promotes rapid micellar growth or aggregation of surfactant micelles.

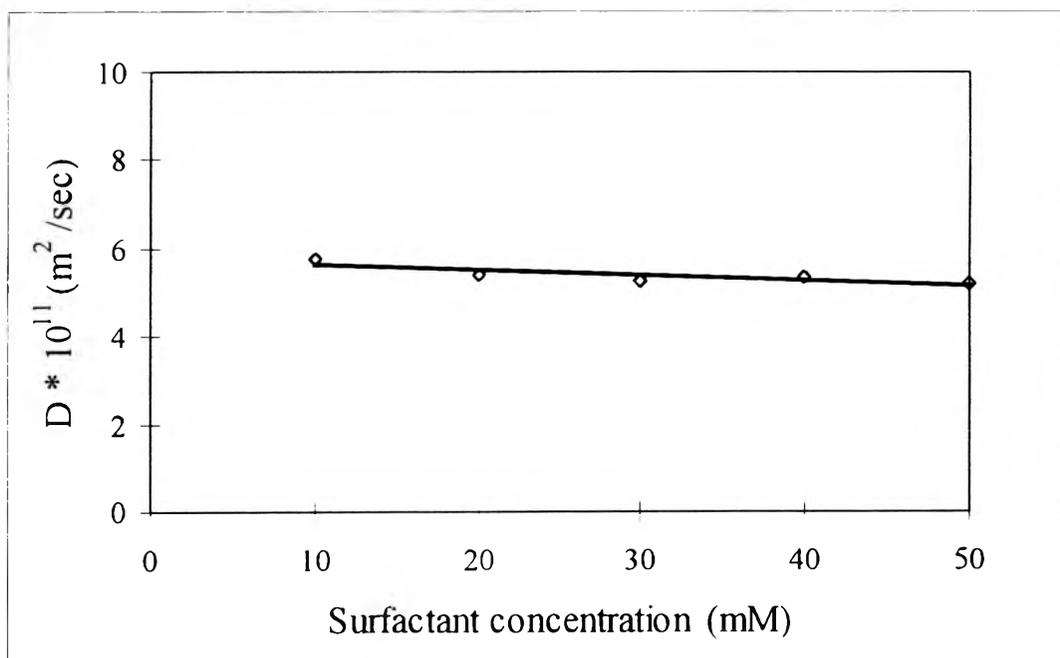


Figure 3.6  $D_{app}$  of TX - 100 micelles in water as a function of concentration.

Figure 3.6 shows the diffusion coefficient of TritonX-100 micelles as a function of concentration. This figure indicates the diffusion coefficient for  $10 \leq C \leq 50$  mM, 10 mM being the lowest surfactant concentration at which high quality spectra of the micelle solution could be obtained. Very weak relaxation time was observed below 10 mM of surfactant. This weak relaxation is due to the presence of individual monomers of surfactants and a small number of premicellar precursor structures.

The diffusion coefficient of infinite dilution was used to calculate the effective hydrodynamic radius according to equation 2.10 and the value of  $R_H$  of 4.84 nm at 30°C was obtained. This value is in good agreement with the value reported by Phillis [1995].

### 3.3 Ternary System (PAM / Triton X-100 / Water)

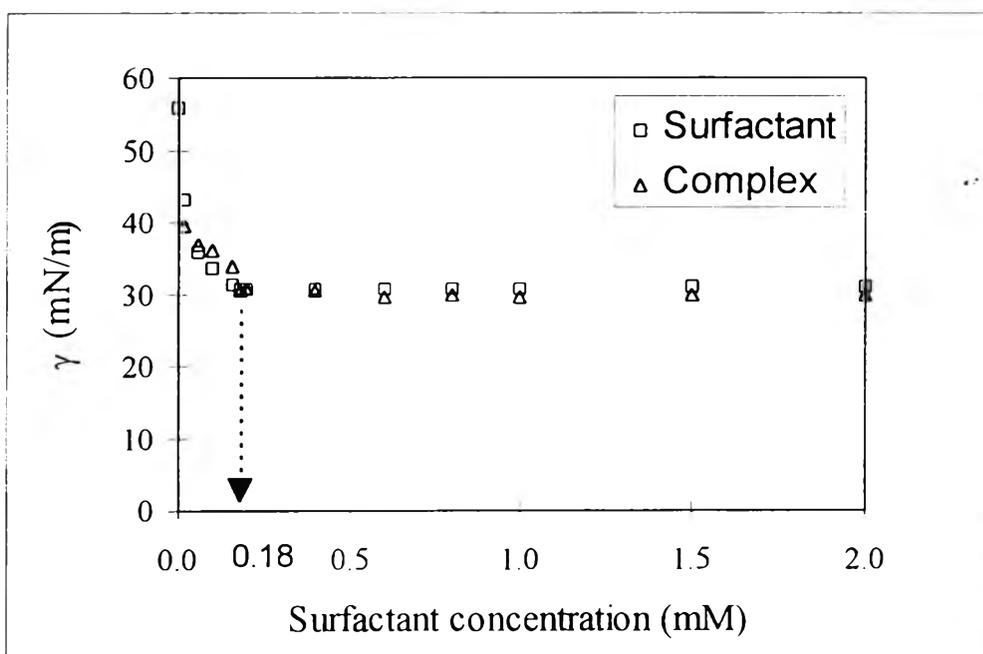


Figure 3.7 Surface tension versus concentration for pure surfactant and polymer-surfactant system.

Figure 3.7 shows a method to determine cmc of pure surfactant and polymer-surfactant systems. There are several methods to determine the cmc value. In the present system, 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 cmc value which is about 0.18 mM for Triton X-100. The surface tension of a surfactant solution decreases monotonically until the cmc is reached and then stays constant above the cmc. The cmc value does not change in the presence of polymer. This is in contrast to the lower cac value when ionic surfactants interact with neutral polymers. Nevertheless, it does not imply the absence of interaction. It probably means that the interactions do not involve the same type of specificity in the binding of surfactant molecules to the polymer chains. This is well in agreement with the work of Brown and Hansson [1996]. They reported that nonionic surfactants have the same value for the cmc in the presence of the polymer as in water, which does not unequivocally exclude the presence of interaction.

In this part of work, the effects of surfactant concentration, polymer concentration and the molecular weights of polymer will be discussed.

### 3.3.1 Effect of Surfactant Concentration

To study the effect of surfactant concentration, polymer concentration was fixed at 0.4 and 1.0 g/l and the surfactant concentration was varied in both dynamic light scattering and viscometric measurements.

Figure 3.8 shows the relaxation time distributions for a solution containing 0.4 g/l of PAM with successive increases in Triton X-100 concentration at 30 °C. The lowest curve represents the pure polymer without surfactant. The bimodal distributions were also observed below a certain minimum concentration of surfactant for a given concentration of PAM.

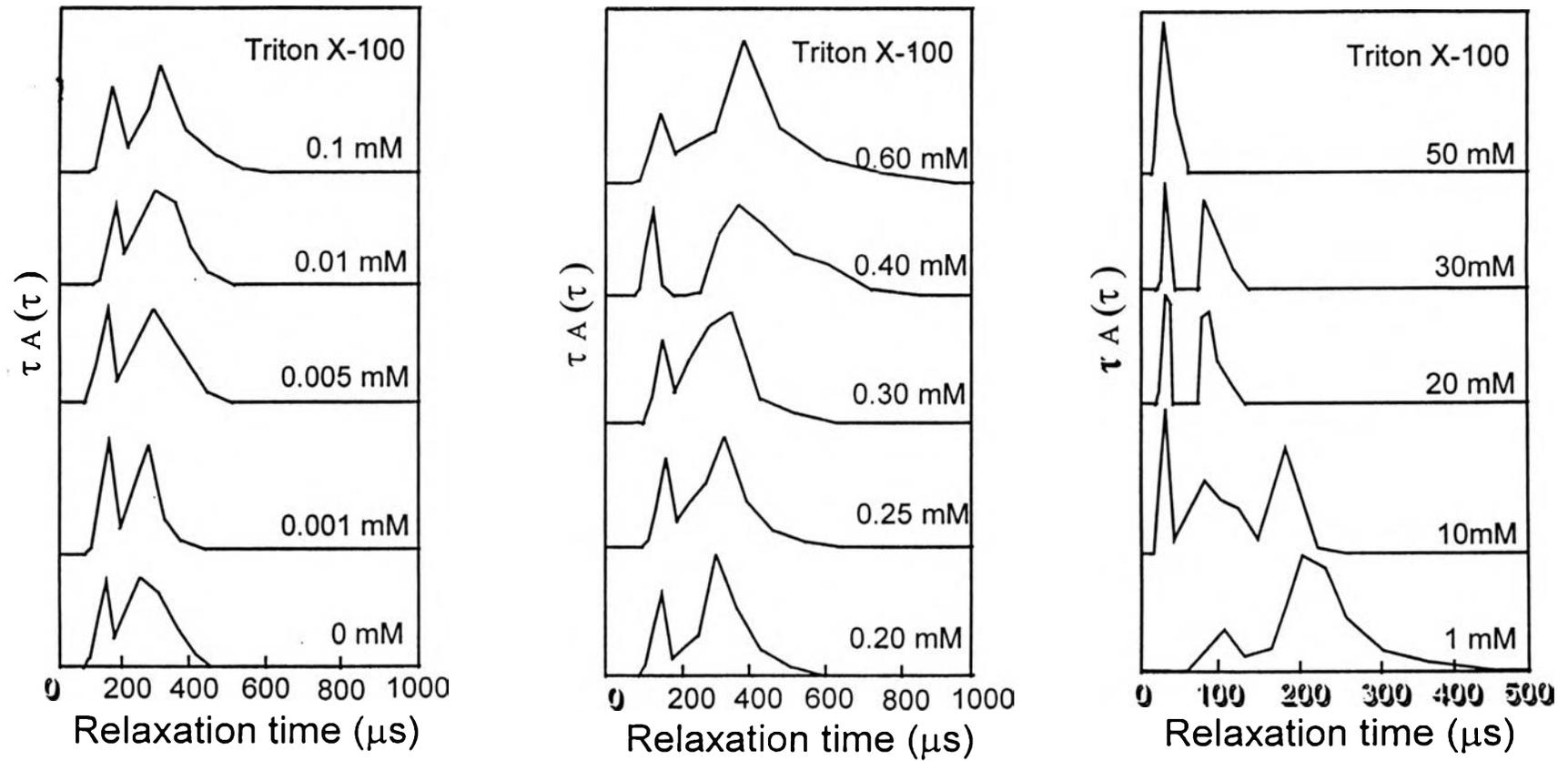


Figure 3.8 Relaxation time distributions for constant PAM concentration (0.4 g/l) with successive increase of TX - 100 concentration.

The increase in the slow mode relaxation times with the increase of the surfactant concentration is clearly evident in figure 3.8.

The fast mode has an approximately constant relaxation times while the slow mode is displaced to longer relaxation times. The similar situation was recently observed in the work of Feitosa and Brown [1996]. They reported the relaxation time distributions for PEO and dodecyl pentaethylene oxide (C<sub>12</sub>E<sub>5</sub>) systems. These authors attributed the relaxation time of the fast mode to be almost constant with the change in the surfactant concentration, and the concentration dependence is small. From the infinite dilution value, it was estimated that the hydrodynamic size of surfactant micelle agrees well with the value for the surfactant in binary solution. It was also found that the relaxation time for the slow mode increases with increasing surfactant concentration.

Addition of Triton X - 100 has a little effect on the slow mode relaxation times until its concentration exceeds 0.1 mM. Then it induced a shift to longer relaxation times until reaching the concentration of 1 mM. These changes occur very clearly over the narrow Triton X-100 concentration range of 0.1 to 1 mM, that is, near and just above the cmc of Triton X-100 (0.18 mM). The similar phenomena was found in the interaction of fluorescent dye labeled HPC with nonionic surfactant n-octyl  $\beta$ -D-glucopyranoside (OG) reported by Francoise M. Winnik [1990]. He showed that the interaction occurred over the narrow OG concentration range of  $2.5 \times 10^{-2}$  to  $4 \times 10^{-2}$  M (just above the cmc of OG).

Above 1 mM, the slow mode relaxation times decrease with increasing surfactant concentration. At a certain concentration range (10 mM of surfactant), one additional mode is observed. In this case, the fast mode comes from the pure surfactant micelle and the intermediate mode corresponds to the internal relaxation of polymer chains. The slow mode attributes to the complexes which are made up of surfactant micelles residing at the surface of the polymer coil. This suggestion is similar to the interpretation of reported

data for polyethylene oxide - octyl thioglucoside (OTG) systems [Brackman, 1988]. They reported the hydrophilic PEO is insoluble in hydrocarbons, and PEO-OTG interaction would force the polymer to reside at the surface of the micelle. The internal relaxation modes are disappeared at 20 and 30 mM of surfactants because of the high surfactant concentration. At very high surfactant concentration of 50 mM, one mode is only observed. This mode relaxation time is identical with the pure surfactant micelle.

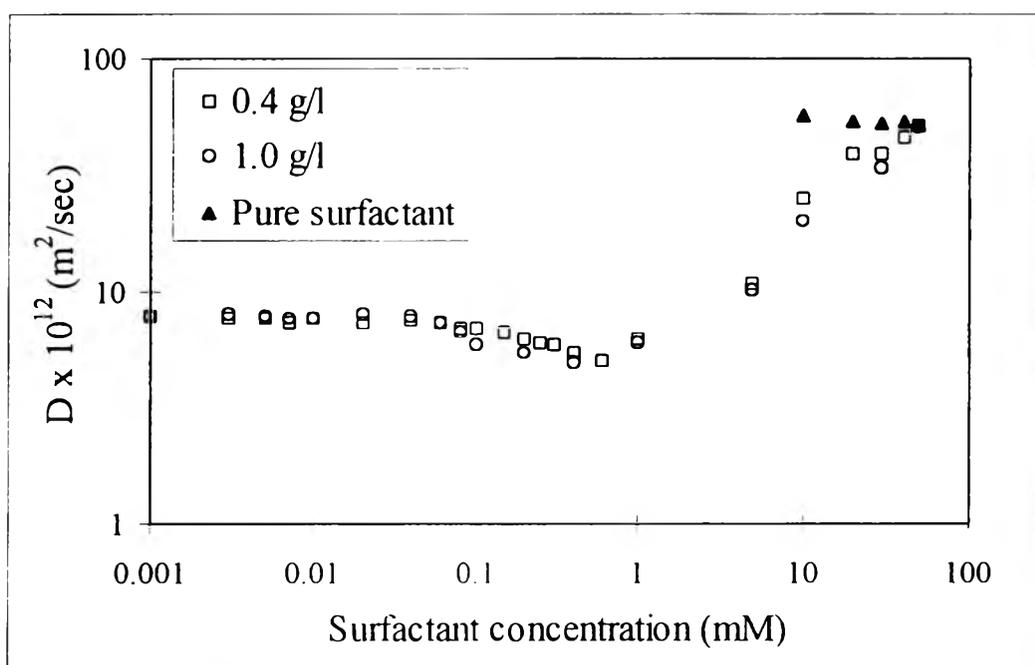


Figure 3.9 Diffusion coefficient vs. concentration for PAM and TX - 100.

Figure 3.9 shows the diffusion coefficients obtained from the distributions in Figure 3.8 as a function of surfactant concentration at two PAM concentrations and the diffusion coefficient of the pure surfactant. In the binary system, the chains were expanded by the influence of a good solvent, water. Adding the surfactant to the polymer solution, adsorption of the surfactant molecules to the polymer chain occurred. Near cmc value, the binding of the surfactant molecules to the polymer chain induced a slight chain expansion or a slow diffusion of polymer chains. The reason is that, at this concentration

range, the individual surfactant molecules and a small number of pre-micellar structures dispersed in the solution and therefore they can inhibit the diffusion of polymer chains.

Above cmc, the chains contracted and wrapped around the surface of the micelles. Therefore, the chains might fold itself around the micelles and which would correspond to a strong reduction in the hydrodynamic size of the polymer chains. The similar situation was observed for the system of PEO and nonylphenol polyglycol ether (slovafo 909) by GPC measurement [Szmerekova and Kralik, 1984]. They reported a decrease in dimensions of macromolecules with increasing surfactant concentration as due to polymer - surfactant interaction. At very high surfactant concentration the diffusion coefficient is identical to that of a single surfactant micelle. In this concentration range the number of micelles is sufficient enough in the solution and therefore light scattered was dominated by the surfactant micelles.

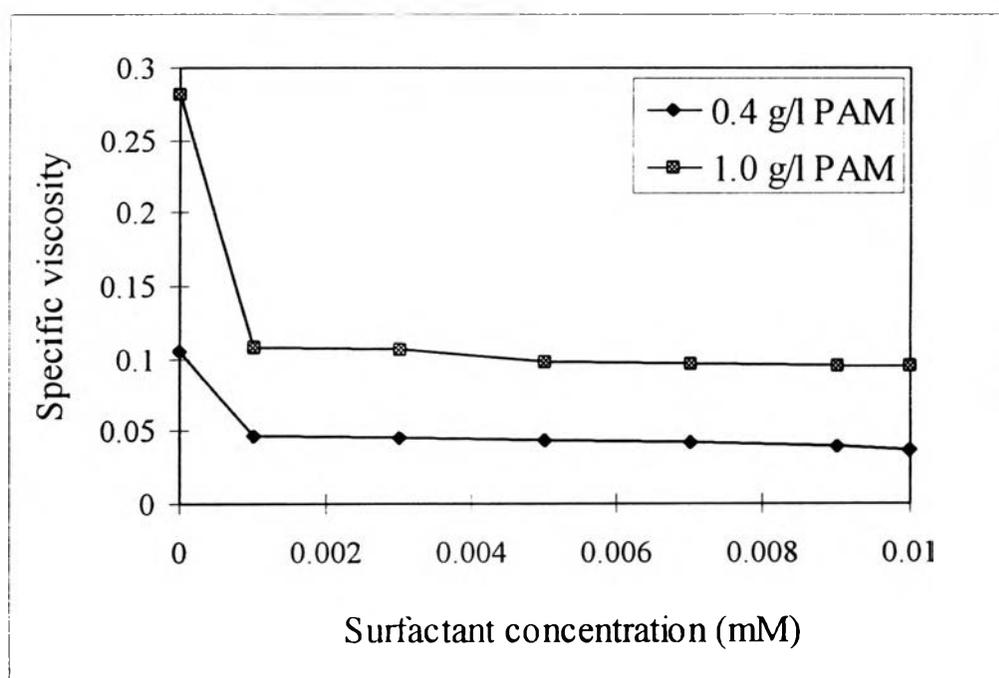


Figure 3.10 (a) Dependence of specific viscosity on surfactant concentration.

The specific viscosity is used here rather than the reduced viscosity ( $\eta_{sp}/c$ ) since the concentration of the complex solution is not known. The specific viscosity is determined at a fixed PAM concentration of 0.4 and 1 g/l as a function of surfactant concentration. The data shown in figure 3.10 (a) indicates that the specific viscosity of the polymer solution decreases remarkably upon addition of surfactant. Further addition of surfactant shows no change in the viscosity. Obviously, the surfactants disrupt the interchain association. This is in agreement with the work of McCormick et al., [1988]. They studied the effect of nonionic and anionic surfactants on the viscosity of PAM and PAM / N-alkyl acrylamide copolymer solutions.

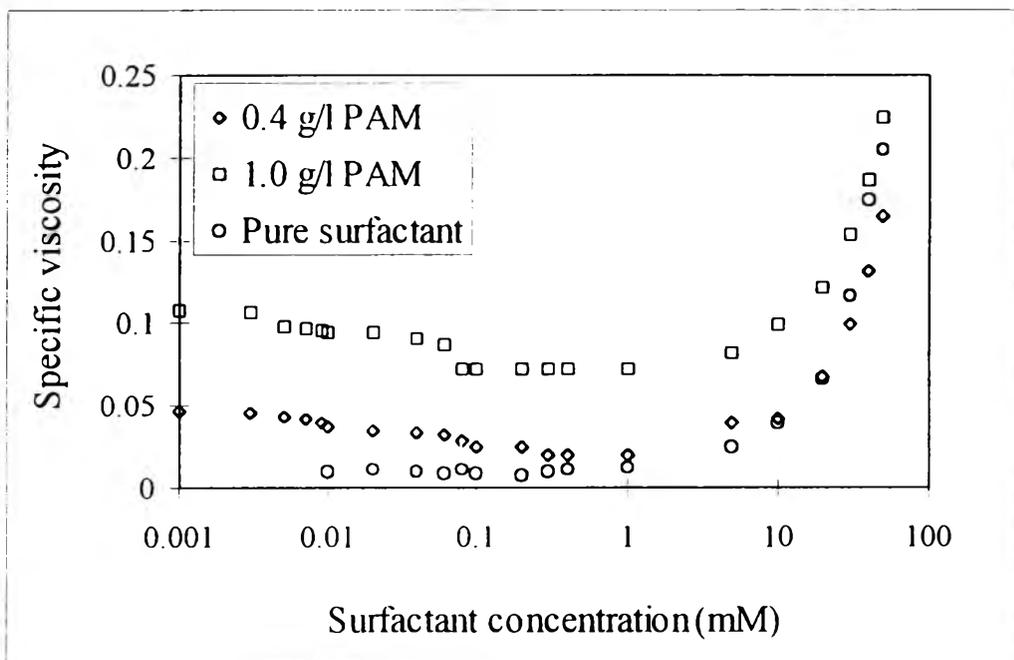


Figure 3.10 (b) Semi-logarithmic plot of the dependence of specific viscosity on concentration.

Figure 3.10 (b) shows a wider range of surfactant concentration. As more surfactants are added to the solution, the viscosity slightly decreases until reaching a minimum value. Physically, we can write the following equation [Tanford, 1961].

$$\eta_{sp} = 2.5 NVc / M \quad (3.3)$$

where  $N$  is the Avogadro's number,  $V$  is the hydrodynamic volume of polymer complex,  $c$  is the polymer + surfactant concentration in g / ml, and  $M$  is the molecular weight of polymer complex. Since the polymer concentration ( $c_p$ ) is constant,  $c = c_p + c_s$  increases as  $c_s$  increases. In figure 3.10 (b), specific viscosity decreases initially, it follows that either molecular weight increases with surfactant concentration or hydrodynamic volume decreases with surfactant concentration. Apparently, from the diffusion data in Figure 3.9, hydrodynamic volume increases, this means that the increase in molecular weight outweighs the increase in hydrodynamic volume. Therefore, it can be concluded that the binding of the surfactant molecules to the polymer chains induces a chain expansion and an increase in molecular weight over the range of 0.1 to 1 mM of Triton X-100 concentration.

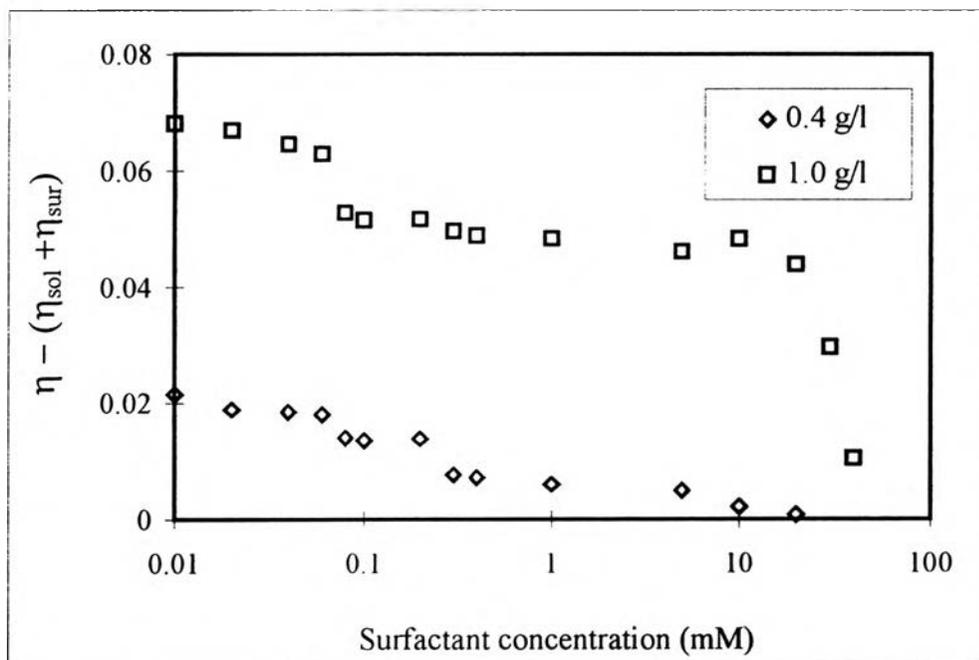


Figure 3.11 Apparent viscosity of complex solution as a function of surfactant concentration.

The subsequent increase in viscosity at very high surfactant concentration is suggested to be due to the formation of the micelle-type structure.

The viscosity of the solution is described as follows:

$$\eta = \eta_{\text{polymer}} + \eta_{\text{surfactant}} + \eta_{\text{solvent}} + \eta_{\text{interaction}} \quad (3.4)$$

Therefore the viscosity of interaction can be obtained by the subtraction of the solution viscosity from the viscosity of other three terms. At a constant polymer concentration, the viscosity of interaction is;

$$\eta_{\text{interaction}} = \eta - ( \eta_{\text{surfactant}} + \eta_{\text{solvent}} ). \quad (3.5)$$

By the subtraction of the surfactant viscosity, the viscosity of the complex solution decreases as shown in figure 3.11. This result is consistent with the dynamic light scattering. At high concentration range the chains contracted and wrapped around the surfactant micelles. This would induce a strong reduction in the hydrodynamic size of the polymer chains and at the same time reduces the viscosity.

### 3.3.2 Effect of Polymer Concentration

Figure 3.12 shows the relaxation time distributions for various concentrations of PAM at a fixed surfactant concentration (5 mM). As shown in this figure, peaks are determined by free surfactant micelles, internal relaxation of polymer chains and polymer - surfactant complex. The shortest relaxation time represents free surfactant micelles. The micelle mode intensities decrease with increasing polymer concentration. The intensities of intermediate mode, which refers to the polymer - polymer interaction, increase as increasing polymer concentration but their relaxation times are approximately constant.

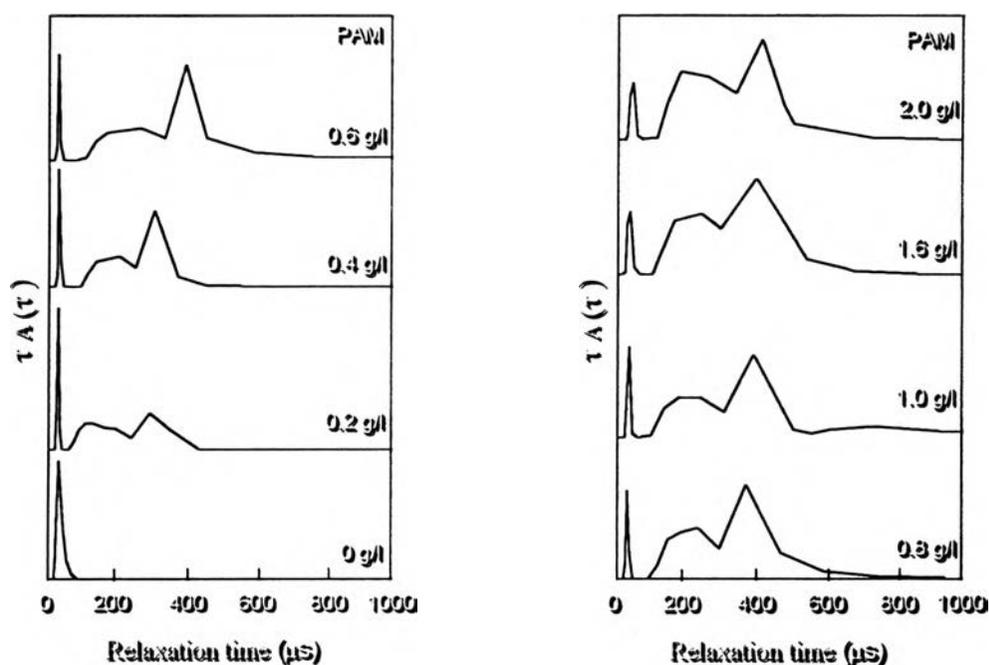


Figure 3.12 Relaxation time distributions for various concentration of PAM.

The slow mode corresponds to the complex made up of polymer resided at the surface of the surfactant micelles. The relaxation times of the slow modes increase gradually but their intensities remain constant. It is found that the polymer segments which are associated with the micelles are much less affected than the polymer - polymer segment interaction.

Figure 3.13 shows the variation of the diffusion coefficients of the slow mode as a function of polymer concentration for various concentrations of surfactant. At 0.1 mM of surfactant, diffusion coefficient is slightly lower than that of pure polymer because of the slight chain expansion. As more surfactants are added to the solution, the chains contracted and wrapped around the surface of the micelles. Therefore, diffusion coefficients are higher than that of a pure polymer. When adding more polymer, diffusion coefficients decrease gradually because of the reduction of the contribution of polymer chains to surfactant micelles. The diffusion coefficients is identical to that of the single micelle at very high surfactant concentration. A similar result was obtained for

hydrophobically end - capped PEO -  $C_{12}E_8$  system reported by Alami, Almgren and Brown [1996].

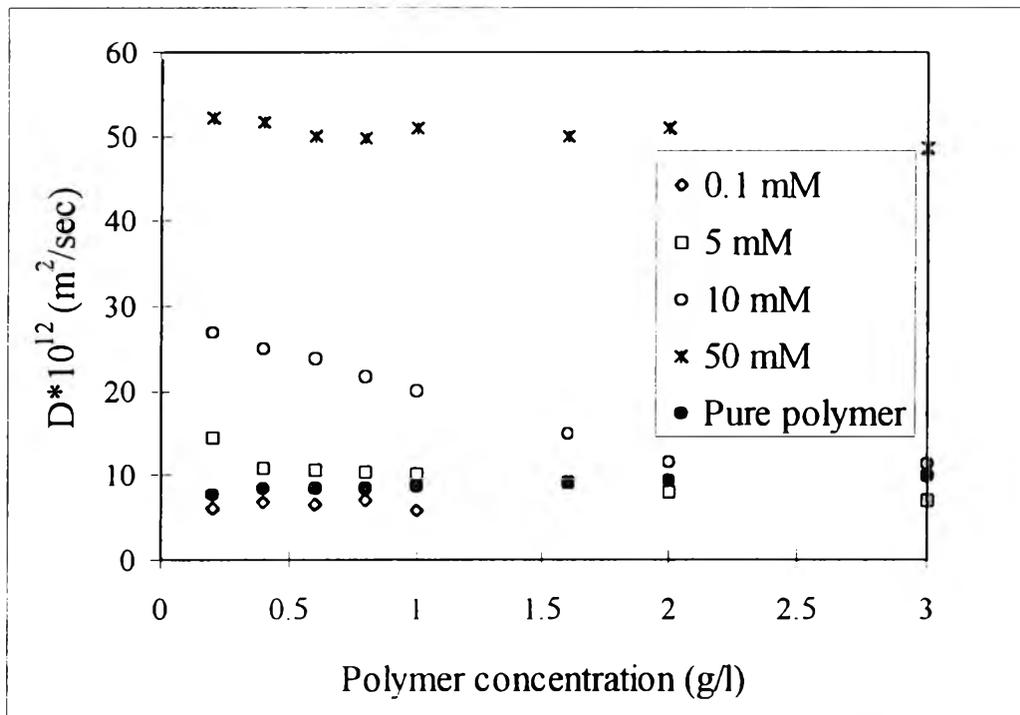


Figure 3.13 Diffusion coefficients for the complex mode as a function of PAM concentration.

Figure 3.14 shows the specific viscosity versus PAM concentration for various surfactant concentrations. The specific viscosity does not change upon the variation of surfactant except at very high surfactant concentration. The micelles are sufficient enough at high concentration range and therefore the solution is massive with surfactant micelles and the solution viscosity will be increased. The specific viscosity of the complex solutions increases upon the addition of more polymer due to the presence of the polymer chains.

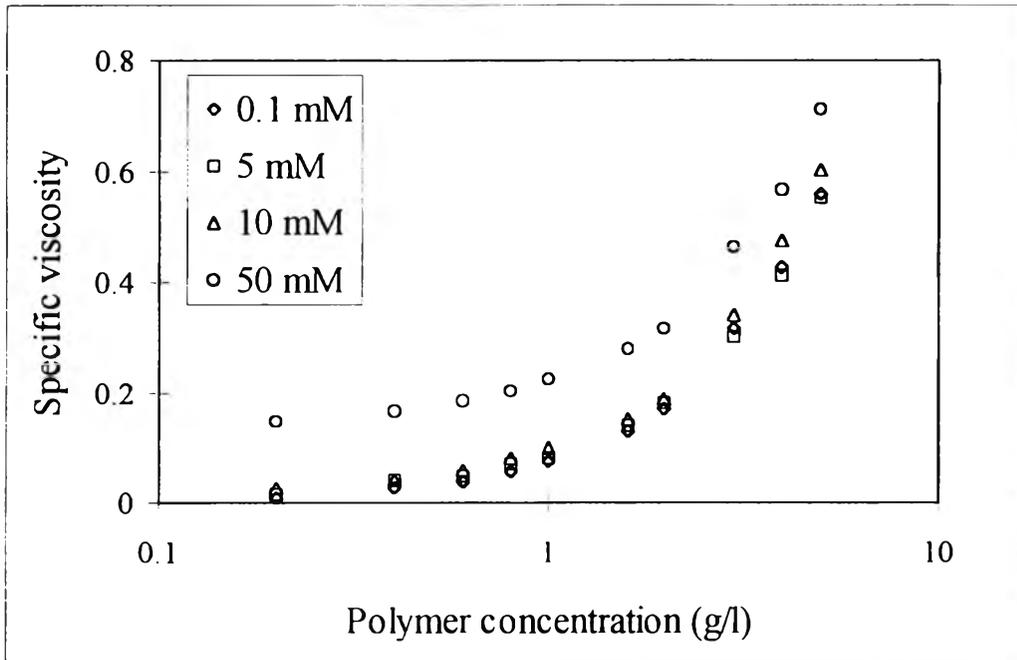


Figure 3.14 Specific viscosity vs. polymer concentration at different surfactant concentrations.

### 3.3.3 Effect of Polymer Molecular Weight

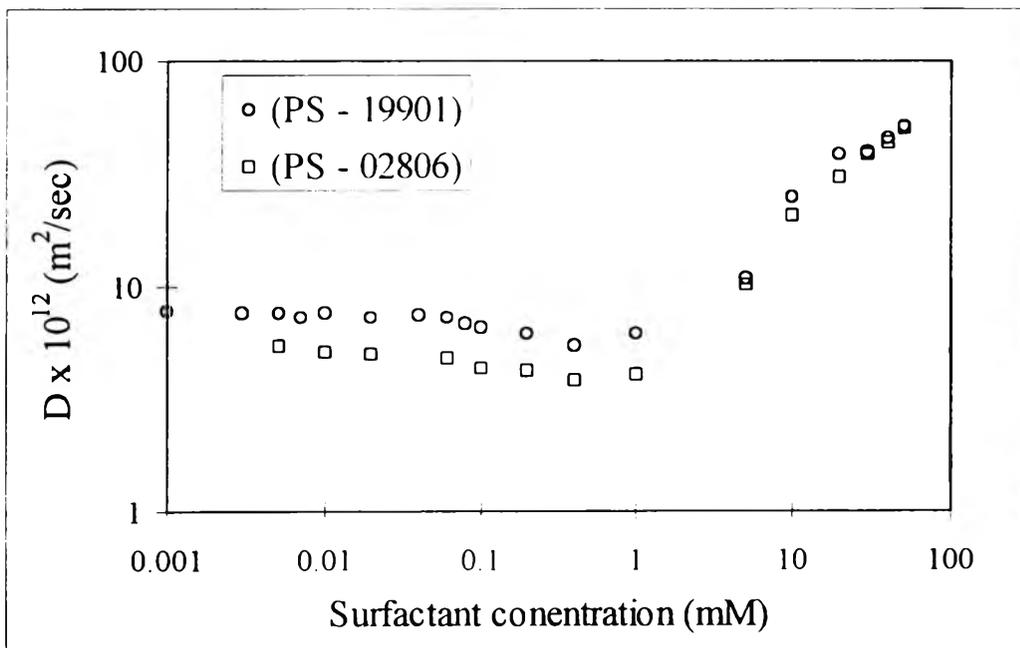


Figure 3.15 Dependence of diffusion coefficient on surfactant concentration at different Molecular weights.

Figure 3.15 shows the dependence of diffusion coefficient on surfactant concentration for two different molecular weights of polymer. This graph indicates that the higher molecular weight polymer (PS-02806) has lower diffusion coefficient which means that the size is bigger in high molecular weight. This graph also shows the same trend for two different molecular weights. Therefore, polymer - surfactant interaction would appear to be the same for both different molecular weights.

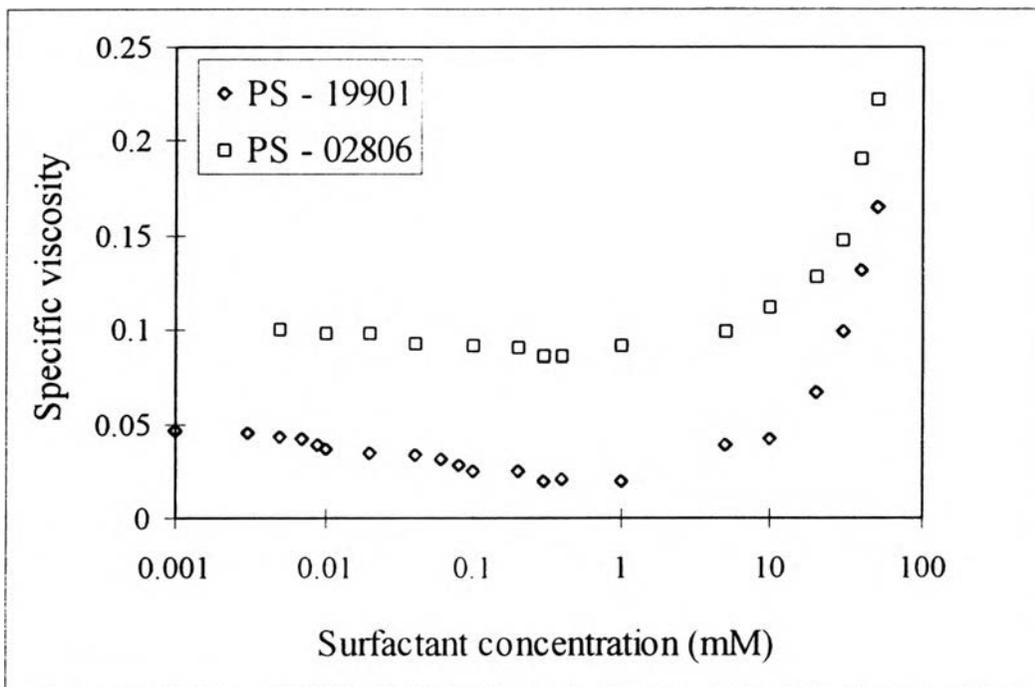


Figure 3.16 Specific viscosity of 0.4 g/l PAM + TX - 100.

Figure 3.16 shows the specific viscosity of the complex solution for different molecular weights of polymer as a function of surfactant concentration. This figure also shows the same trend for different molecular weights. It is concluded that the same interaction occurred for both polymers of different molecular weights..