

CHAPTER IV

DISCUSSION

4.1 Γ Dependence on q^2

Dynamic light scattering theory relates the relaxation rate of the correlation function and the diffusion coefficient of the solution. In the dilute solution, there are two regimes:

1. $qR_g \ll 1$, the polymer coil size is much smaller than the probing wavelength, the polymer chain is “ seen “ as a dot. In this case, the relaxation rate is related to the diffusion coefficient and q as,

$$\Gamma = Dq^2 \quad (4.1)$$

where Γ is the relaxation rate, D is the centre of mass diffusive constant and q is the magnitude of the scattering vector. This result is rigorous and exact [Berne and Pecora, 1976].

2. $qR_g \gg 1$, the polymer coil size is much larger than the probing wavelength, individual monomers are seen. The relaxation rate is related to the diffusion coefficient and q as

$$\Gamma = Dq^3R_g. \quad (4.2)$$

In this limit, D is the diffusion coefficient resulting from internal motion of the polymer chain. This result can be obtained by a scaling argument [Han and Schafer, 1985]. The q^3 dependence arises partially from the effect of

hydrodynamic interaction; the fact that the solvent flowing around one segment is altered by the wakes arising from flow around neighboring segments.

In the intermediate regime, $qR_g \approx 1$, it can be expected that both diffusive characters can be observed. This is indicated by varying q , one moves smoothly from probing the centre of mass diffusion to probing the internal dynamics [Goddard, 1993].

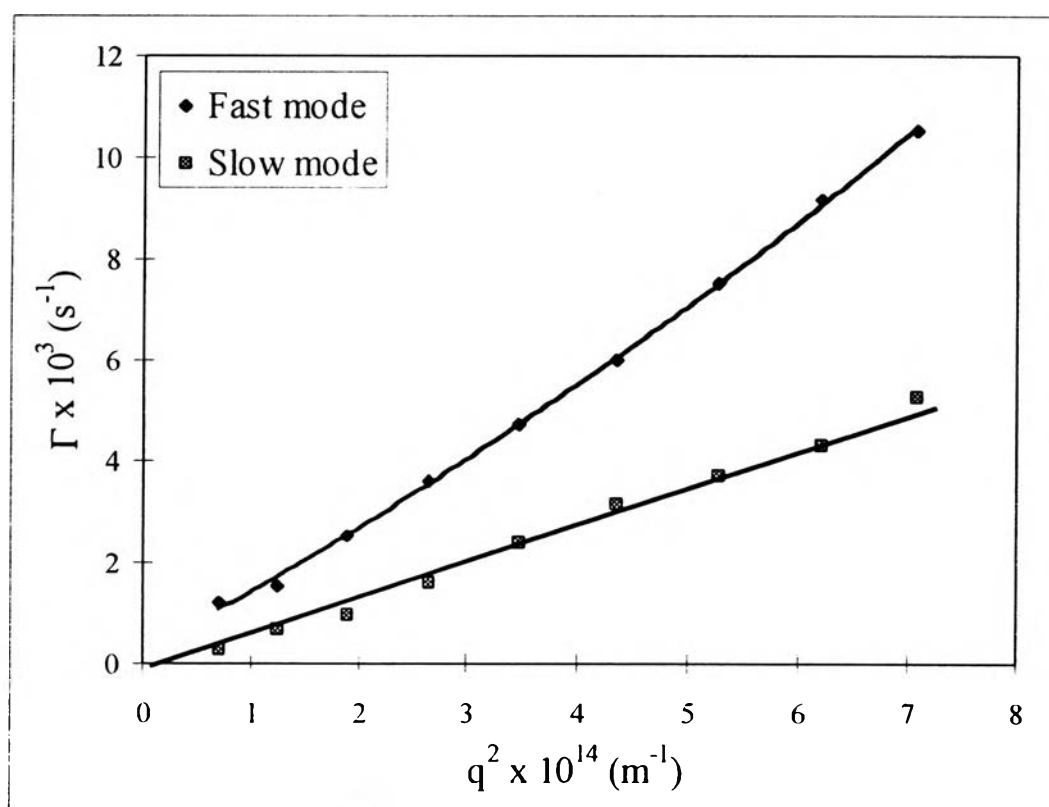


Figure 4.1 Dependence of the relaxation rate vs. the square of the scattering vector for the ternary system (0.4 g/l PAM + 0.4 mM TX - 100).

Figure 4.1 shows the dependence of the relaxation rate on the scattering vector. The slow mode clearly shows the linear dependence and therefore this mode is the center of mass diffusion. The fast mode shows a deviation from the linearity. In the limit of $qR_g \approx 1$, we conclude that this mode comes mainly from the internal relaxation of polymer chains.

4.2 Physical Model of Polymer - Surfactant Complex

The physical models for the complex are envisioned as shown below.

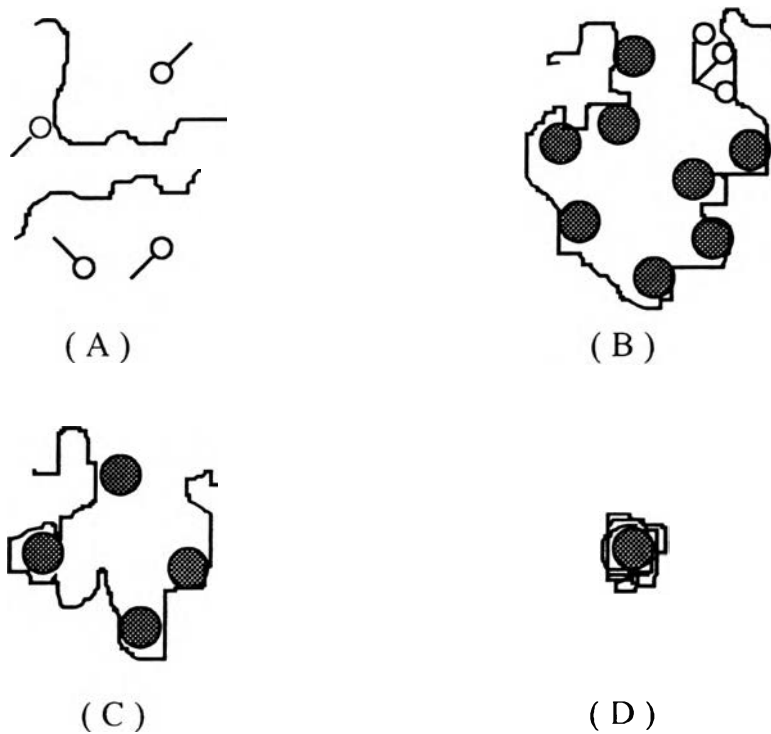


Figure 4.2 Schematic representation of the interaction between PAM and Triton X - 100.

In the solutions of PAM containing sufficiently low concentrations of Triton X - 100, both hydrodynamic radius and specific viscosity are independent of surfactant concentration. R_H is equal to the hydrodynamic size of pure PAM which is about 35 nm for PS - 19901 and 55 nm for PS - 02806 samples. This indicates that no interaction between PAM and Triton X - 100 occurred. Most of the surfactant molecules exist freely in the form of monomers [Figure 4.2 (A)].

When the surfactant concentration is near or above cmc, complex formation occurs. Due to the binding of pre-micellar structure of surfactants and

the surfactant micelles to the polymer chain, an increase in the hydrodynamic size of the polymer takes place [Figure 4.2 (B)].

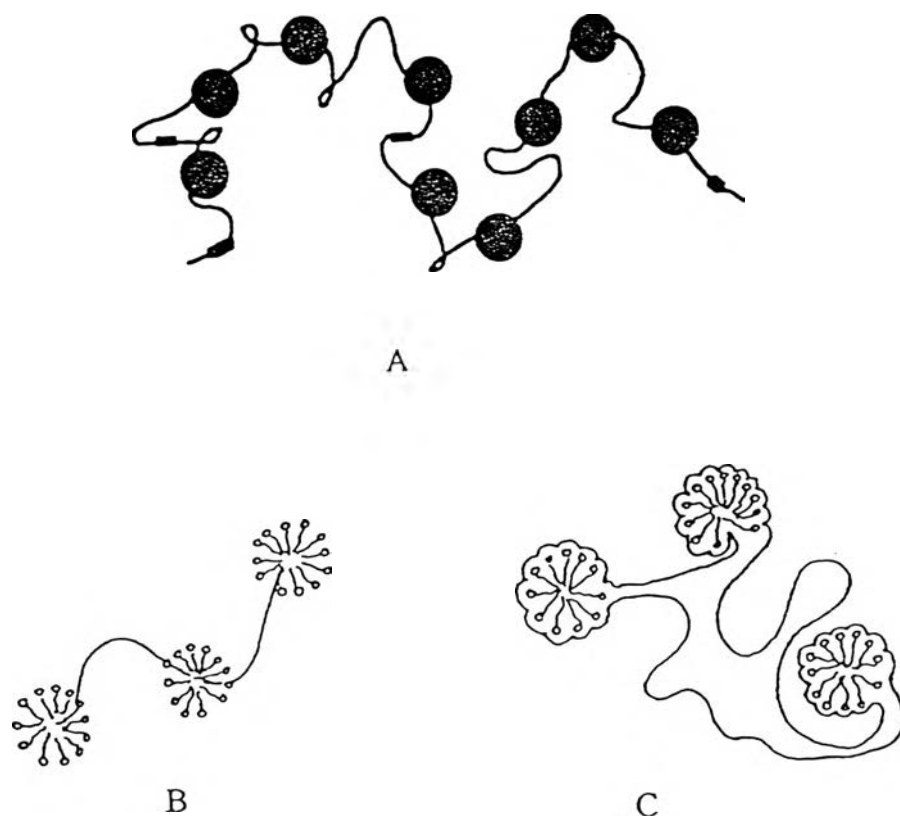


Figure 4.3 Schematic representations of interaction between a nonionic polymer and an ionic surfactant, (A) pearl - necklace model, (B) site clustering model, and (C) mixed micelle type.

At higher surfactant concentrations, the chain contracts as the number of surfactant micelles per chain decreases and therefore a marked decrease in the size of the polymer chain occurs [Figure 4.2 (C)]. The reduction of the number of surfactant micelles per chain occurs due to the high surfactant content. At very high surfactant concentration (50 mM), the micelles are sufficient enough in the solution and therefore light is scattered by the dominant surfactant

micelles and the chains may be wrapped around the surfactant micelles [Figure 4.2 (D)].

The schematic interpretations for neutral polymer with nonionic surfactant are different from the interaction between a nonionic polymer and an ionic surfactant. Shirahama et al [1974] proposed an alternative model of the neutral polymer with ionic surfactant complex according to which micelle - like aggregates are decorated along the polymer chain. This model, called the pearl - necklace model, consists of a flexible chain which is freely draining with respect to the solvent [Figure 4.3 (A)].

Holmberg et al. [1992] also proposed the site clustering model [Figure 4.3 (B)] where the surfactant molecules clustered around the hydrophobic sites of the polymer. Another model is the polymer segments partially penetrate and wrap around the hydrophilic micellar surfaces which is called the mixed-micelle type structure [Figure 4.3 (C)].

These models are represented by the cooperative binding of the polymer-surfactant complex which are different from the non - cooperative binding of the neutral polymer with nonionic surfactant system. The latter interaction would force the polymer to reside at the surface of the surfactant micelles.

4.3 Mechanisms of Interaction

The reduction of the interface between the hydrophobic core and water is considered to be a major driving force for polymer - micelle interaction. For polymers with surfactants system several modes of interaction (hydrophobic interaction, hydrogen bonding, steric repulsion between hydrated headgroups, electrostatic interaction, and non - hydrophobic interaction) may contribute in the same order of magnitude to the total free energy of the systems.

Hydrophobic interaction is the interaction between the hydrophobic segments in order to minimize their exposure to water. Cabane [1977] investigated that the nature of interaction in the PEO - SDS system arises mainly from the hydrophobic interaction between the surfactant tail and the methylene group of PEO. The PEO chain is wrapped around the SDS micelle with some of the segments of PEO adsorbed at the hydrocarbon / water interface, while most of them form loops in the surrounding water.

The bulky polar head groups of surfactant might have some steric repulsion between each other. Therefore, the hydrophobic segments of polymer can enter easily to the hydrophobic core of the surfactant. Winnik [1990] proposed the association between OTG / PPO system. He considered that upon association two factors, namely the unfavorable steric repulsion between hydrated headgroups and polymer segments and the favorable transfer of the hydrophobic polymer to the micellar environment, compensate each other resulting in a negligible change in total Gibbs free energy. Therefore, the cmc, which is determined by the total Gibbs free energy for the formation of polymer - bound micelles, is not affected.

The interaction between polyelectrolytes and oppositely charged surfactants is dominated by electrostatic forces. Wu, et al., [1996] proposed for the interaction between highly branched polyelectrolytes (HBNP) and cetyl trimethylammonium bromide (CTAB) in aqueous solution. Their model showed a number of the HBNP clusters are attracted to one CTAB micelle by electrostatic interaction. This interaction is stronger than the hydrophobic interaction.

Moroi et al., [1977] suggested that the complex formation between PEO - SDS system arises mainly from the interaction between the ionic head group of surfactant and the $-\text{CH}_2\text{O}-$ group of polymer and is hardly affected by hydrophobic interaction between the surfactant tail and $-\text{CH}_2\text{O}-$ group. The head group of surfactant is the hydrophilic group and therefore this interaction

is called the hydrophilic interaction. However, this mode of interaction can change depending on the conditions, such as polymer molecular weight, concentration of polymer and surfactant, and presence or absence of supporting electrolyte.

In the case of PAM and Triton X - 100, a possible interaction is the hydrogen bonding between the polar group of the surfactant micelles and the hydrophilic part of the polymer. Another possible interaction is the non - hydrophobic (hydrophilic) interaction. PAM is the hydrophilic polymer which may adsorb at the surface of the hydrophilic part of the surfactant micelles.