CHAPTER I

INTRODUCTION

1.1 Background

1.1.1 Definitions and Significant Behavior
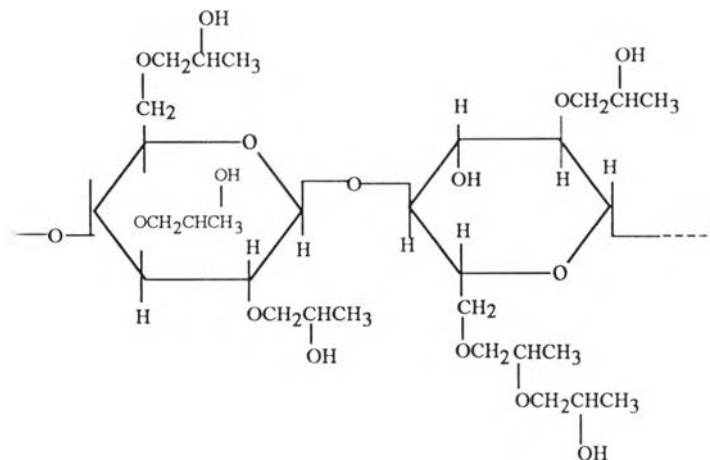
Hydroxypropylcellulose

Hydroxypropylcellulose (HPC) is a thermoplastic, nonionic cellulose ether, soluble in water and in a number of organic solvents. It can be prepared by the base catalyzed reaction of propylene oxide with alkalicellulose slurried with an aliphatic hydrocarbon and alcohol or propylene oxide as shown in fig. 1-1.

$$R_{cell}OH\ NaOH + n\ CH_3\text{-}CH\text{-}CH_2 \longrightarrow R_{cell}(OCH_2CHCH_3)_nOH + NaOH$$

Figure 1.1 The preparation of hydroxypropylcellulose (HPC).

An idealized structure is shown in fig. 1.2. The polymer is soluble in cold water, but when aqueous solution of HPC is warmed to about 40 °C, a phase separation occurs with a sharp increase in turbidity and a decrease in viscosity (Klug, 1971). HPC forms an ordered liquid-crystalline phase with cholesteric structure in concentrated aqueous solutions.

Figure 1.2 The idealized structure of hydroxypropylcellulose.

Latex

A latex is conveniently defined as a stable colloid dispersion of a polymeric substance in an aqueous system. Polymer chains form approximately a spherical particle, with a diameter ranging from 10 to 1000 nm. The dispersion medium is usually a dilute aqueous solution containing substances such as electrolytes, surface-active compounds, hydrophilic polymers, and initiator residues.

Latex is usually synthesized by emulsion polymerization of olefinic monomer, involving a free-radical propagation mechanism.

Stability of latex

The latex stability is determined by the balance between attractive and repulsive forces. The origin of the attractive forces is usually presumed to be quantum-wave-mechanical interactions of the London-Van der Waals type which occurs between all pairs of atoms contained in the two particles. These forces tend to encourage flocculation and coagulation of the

latex particles. The stable latex does not aggregate because of the repulsive forces between the particles. These forces can be distinguished into 4 types.

1. Electrostatic forces arise when there are ionic groups at the particle surface, and the counter ions clouds surrounding two electrically charged particles interpenetrate, as the particles approach each other. The system may be irreversible aggregation or reversible aggregation of flocculation depends on the kinetic energy to overcome electrostatic barrier which is based on the DLVO theory. This has been termed *electrostatic stabilization.*

2. Steric forces arise when lyophilic macromolecules adsorb onto the surface of the particles, Thus, two particles coated in this manner, upon a Brownian collision, repel each other strongly because of the solvation forces of the continuous medium for the adsorbed polymer. When the adsorbed polymer molecules on two colloiding particles overlap, an osmotic pressure is developed in such a way that the solvent tends to enter the region between the particles and force them apart. This phenomena is known as *steric stabilization.*

3. The force that arises from the layer of a solvation layer surrounding the particles.

4. Exclusion or depletion forces arise because of changes in entropy and enthalpy associated with the presence of lyophilic macromolecules dissolved in the dispersion medium.

Advantages of steric stabilization

Steric stabilization is widely used in industry because it offers several distinct advantages over electrostatic stabilization. These are summarized in table 1.1 (Hunter, 1986).

Table 1.1   Comparison of the properties of sterically and electrostatically stabilized dispersions.

Steric stabilization	Electrostatic stabilization
1. Insensitive to electrolyte	1. Coagulation on addition of electrolyte
2. Equally effective in aqueous and non-aqueous dispersion media	2. Mainly effective in aqueous dispersion media
3. Equally effective at high and low volume fractions of particles	3. More effective at low volume fractions
4. Reversible flocculation	4. Coagulation often irreversible
5. Good freeze-thaw stability	5. Freezing often induces irreversible coagulation

### 1.1.2   The Structure of Stabilized Latex

Adsorbing polymer (isolated layers)

In steric stabilization, the adsorbed polymer on a solid surface has been considered in its configuration. Generally, polymers adsorb at random points along their backbone to a degree that depends on the nature of the polymer, the solvent, and the surface. An interaction energy of less than 1

kT per segment suffices to generate significant adsorption (Russel et. al, 1989).

The adsorbed chain consists of a collection of trains, loops and tails, which are illustrated in fig. 1.3. The attached segments are called *trains* and the remaining, unattached segments extend away from the surface in the form of *loops*, in which only the initial and final segments contact the surface, and *tails* which begin at the surface but terminate in the solution. Such configurations minimize the entropy loss. While maintaining enough segments on the surface to achieve an adsorption energy large relative to 1 kT for the polymer molecule as a whole.
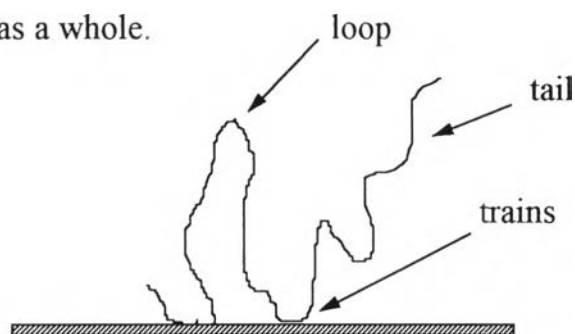
Figure 1.3 Structure of adsorbing polymer on the surface

Terminally anchored polymer (isolated layers)

The soluble polymers are attached by one end to a surface, their conformation depends on the surface density of the chain and the excluded volume (de Gennes, 1980). The structures of terminally anchored polymer on the surface are shown in fig. 1.4.
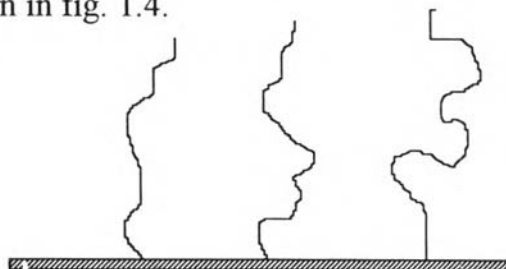
Figure 1.4 Terminally anchored polymer on the surface.

An important aspect of adsorbed chain is that the adsorption process has appeared to be essentially *irreversible*. Since each segment is not tightly bound, the equilibrium is dynamic with continuous exchange of adsorbed and free segments. However, the probabilities of all adsorbed segments of a chain leaving the surface simultaneously is small, so desorption may be quite slow. Anyway, predicting the exact structure of the adsorbed layer is difficult because the segments densities can vary from highly concentrated at the surface to infinitely dilute in the bulk solution. A complete theory does not exist. (Russel et. al, 1989)

1.2   **Applications**

Polymeric stabilization is exploited in a diverse range of industries products: paints, glues, inks, pharmaceutical and food, emulsions, detergents, lubricants, etc.

Hydroxypropylcelllulose (HPC) is a surface active agent capable of thickening and stabilizing aqueous systems. So it may be used in the latex-paint application by adsorption of polymer onto the latex particles, in the paint removers as the acid-resistant thickener for acid-based, scrape-off or flush-off removers.

Food grade HPC is also used in pharmaceutical and cosmetics. In pharmaceutical, HPC is the alcohol-soluble coating and binder for tablets. It is also used as the stabilizer, thickener, alcohol-soluble suspending agents for medicals. In cosmetics industries, HPC is used as the alcohol-soluble thickener and film former for hair dressings, grooming, aids, perfumes, and colognes. In addition to the food industries, HPC is used as the stabilizer and whipping aid in whipped toppings, as the oil barrier for nut and candy coating and as the binder for molding and extrusion of fabricated foods.

Furthermore, polymeric stabilization is operative in many biological systems, such as blood and milk, e.g. protein adsorption in biocompatibility studies of artificial organs. It is also important in a wide range of industrial and agriculture processes e.g. water treatment, soil stability, coal washing, oil recovery, and etc.

1.3   Previous Work

The diffusion of sphere in polymer solution has been the subject of numerous investigations in both the dilute and semidilute regime of polymer concentration. Several experiments found that the Brownian motion of test spheres through an entangled polymer network is best described by a stretched exponential function of matrix concentration, $D/D_0 = \exp(-AC^\delta)$.

There is considerable variation in the behavior of parameters A and δ. Laurent, et al. (1963) and Langevin and Rondelez (1978) found that A is independent of matrix molecular weight, but is proportional to sphere radius. Other experiment demonstrated that A is independent of probe radius but is dependent on molecular weight as $A \propto M^\sigma$ where $\sigma = 0.8\text{-}1.0$. δ value also varied from 0.5 to 1.0 as observed from many experiments (Jamieson,et al. (1987), Phillies, et. al. (1985), Brown and Rymden (1986), and Furukawa and Ware (1987), and etc.)

A theoretical expression was derived by Cukier (1984) in the form of $D/D_0 = \exp(-\kappa R)$ where R is the sphere radius and κ is the screening constant. In the excluded volume limit $\kappa \sim C^{3/4}$ and in the theta condition $\kappa \sim C$ so δ value in his work may be 0.5, 0.75 and 1.0 and A is independent of molecular weight.

Brown and Rymden (1986) investigated the diffusion of polystyrene latex spheres in many kinds of polymer including hydroxyethyl cellulose (HEC), hydroxypropyl cellulose (HPC), carboxymethyl cellulose (CMC) (at pH 4 and pH 9) at different ionic strengths, and nonionized polyacrylic acid (PAA) (pH 3.5) By using multiexponential bimodal fit in very dilute solution, they obtained (a) a polymer concentration independent, fast mode, where D was equal to that of latex monomer at infinite dilution. (b) a slow mode, where D corresponded to aggregate species with apparent radii 2-3 times that of the latex monomer The aggregation behavior is consistent with a bridging mechanism. In semidilute solutions of nonionized CMC at pH 4 (salt free system) D follows $D/D_0 = \exp(-AC^{1/2})$. In HEC, HPC and CMC (at pH 9 with salt free) D does not depend on C as $C^{1/2}$, the interactions in the system follows $D/D_0 = \exp(-AC^{\delta})$ with δ different from 1/2
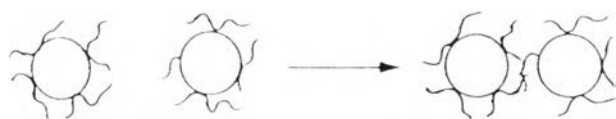
Figure 1.5   Schematic picture of bridging mechanism of absorbed layer on the particles

Yang and Jamieson (1988) studied the diffusion of polystyrene latex spheres in HPC using DLS At the excess concentration of Triton X-100, the diffusion served to test hydrodynamic theory of the Brownian motion of inert spheres in a matrix of entangled polymers that follow a stretched exponential function of the HPC concentration For low M_w of HPC, the diffusion coefficient (D) follows the Stokes-Einstein (SE) law, determined by the bulk viscosity of HPC solution For the high M_w of HPC, the microviscosity measured by the SE equation is smaller than the bulk viscosity, the data follow

the stretched exponential law of $D/D_o = \exp[-(AC^\delta - C^\delta_+)]$ with $A \propto M^\sigma R^\varepsilon$ where $\sigma = 0.8 \pm 0.1$, $\varepsilon = 0.7 \pm 0.1$ and $\delta = 1.0$. Their results were discussed in terms of different theoretical models.

1.4   Objectives

The propose of this research work is to study the diffusion of the latex particle in hydroxypropylcellulose (HPC) solutions in cases of with (semi-dilute) and without (dilute solution) the obstacle effect. In addition, we will also study the interaction strength between polystyrene latex and the polymer that would be altered when Triton X-100 is added to the system. The effects of the different molecular weights of HPC, latex sizes, concentration of HPC, concentration of latex and concentration of Triton X-100 were investigated by dynamic light scattering and viscometry measurements.