ADSORPTION OF HYDROXYPROPYLCELLULOSE AT THE SOLID/WATER INTERFACE

BY

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(Under the supervision of Professor George Zografi)

A thesis submitted in partial fulfillment of

the requirements for the degree of

MASTER OF SCIENCE

(Pharmacy)

at the

UNIVERSITY OF WISCONSIN-MADISON

1987

ACKNOWLEDGEMENTS

First and foremost I thank my fiancee Jan for her love, support and understanding.

I wish to express my sincere appreciation to Professor Zografi for his guidance and leadership in the course of this study.

I thank my friends Paul Bummer, George Grandolfi and Jayne Hastedt, for the stimulating discusions, valuable suggestions and their friendship.

To my parents, I express my utmost appreciation. For through their example I have learned the importance and value of education.

Thanks are extended to Dr. Stuart Porter and Colorcon, Inc. for partial financial support of this project.

Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the ACS, for partial support of this research.

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I. Introduction

Cellulose derived polymers are widely used in pharmaceutical systems as binders, coatings, emulsifiers, film forming aids, stabilizers, suspending agents and thickeners (1). Examples of these semi-synthetic polymers are hydroxypropylcellulose (HPC), hydroxyethylcellulose (HEC), hydroxypropylmethylcellulose (HPMC), methylcellulose (MC), carboxymethylcellulose (CMC), and ethylcellulose (EC). For film coating, HPC, HPMC, and EC are useful in both nonaqueous and aqueous processes. The use of cellulose derived polymers in the aqueous film coating of pharmaceutical tablets has recently attracted a great deal of attention due to governmental regulations on the use and recovery of organic solvents (2-4), as well as to the greater costs accrued in using organic solvents. This has created the need for a better understanding of the various interactions which occur between these polymers and solid surfaces in aqueous systems. Of primary interest is the interaction between polymer and the solid substrate being coated. The interaction between the polymer and the various dispersed solid components, (pigments, binders, plasticizers etc.), of a film coating solution is also an important determinant of the mechanical properties of the film. In the manufacture of paints, plastics, and coating solutions, the degree of pigment dispersion is essential to producing a quality product (5); e.g. the mechanical properties of films are dependent upon good dispersion of the pigment, therefore knowledge of polymer-pigment interactions would allow for optimization of the film coating process.

Little conclusive work concerning the interaction between water-soluble cellulosics and pigments, in particular, has been reported (6-7). Insight into the possible interaction between these polymers and solids can be gained by measuring the tendency of these polymers to adsorb at the solid/liquid interface. Such adsorption is conveniently described by adsorption isotherms; measuring the affinity of the polymer for the solid surface and vica versa. The major long-range goal of this study is to look at such a system, in order to discern the mode of attachment between polymer and pigment and the conformation of the adsorbed polymer molecule at the interface.

Since the focus of this study is on the adsorptive properties of a representative cellulosic polymer, HPC, on solid surfaces, this introduction will consist of a brief general discussion of some relevant polymer characteristics, including molecular weight distribution and the solution and interfacial properties of polymers. Major emphasis will be on the adsorptive properties of water-soluble cellulosic polymers at the solid/liquid interface. Other polymers will be mentioned where deemed appropriate for this study.

A. General Characteristics of Polymers

Polymers can be defined as large molecules composed of smaller repeating units known as monomers. These monomers covalently bond to form long chains that can be linear, branched or cross-linked. The manner in which these monomers link together determines the molecular configuration of the polymer molecule. In addition to the covalent bonds between monomers, intermolecular bonds also exist. The

intermolecular interaction between these long chain molecules gives rise to multidimensional polymer networks. Because of the rotation of the atoms in a molecule around single bonds, many different geometrical arrangements of the atoms are possible. Each arrangement represents a different molecular conformation. Due to the size of polymer molecules a large number of different conformations are possible. In solution, in turn, the conformation of the polymer (solute) is highly dependent upon the interactions between the solute and solvent molecules. In good solvents, a high degree of interaction between polymer and solvent occurs and the polymer chains stretch-out, assuming conformations that maximize these interactions. In poor solvents the polymer chains have a greater affinity for each other than for solvent molecules and take on a more coiled conformation, thus reducing solute/solvent interactions. The temperature at which monomer/monomer and solvent/monomer interaction energies are equal is known as the theta temperature. These different conformations and configurations exert a marked effect on the physical properties of polymer solutions in that both affect the proximity of one chain relative to another.

In order to characterize a polymer sample it is helpful to determine the "size" of the molecules. The word "size" is a very vague term and thus a definition of "size" is needed. In most polymer work size is described by the "radius of gyration". Consider the skeleton atoms of a polymer chain connected by bonds which can be represented by vectors (l_i) as pictured in Figure 1 (8). $(S)_i$ is the distance from atom (i) to the center of gravity (cg), and (n) is the number of bonds in the polymer molecule. If

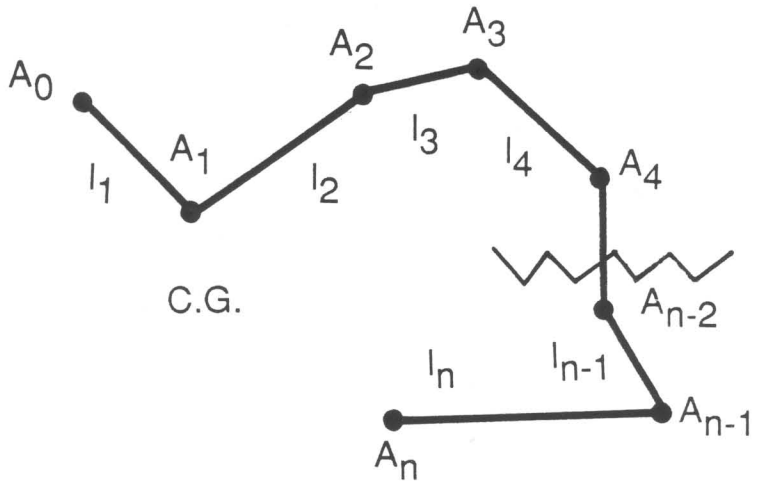


Figure 1. A skeletal representation of a polymer chain used for calculating radius of gyration (ref. 8)

bond angles and bond lengths are neglected for simplicity, the radius of gyration (S) is described by the root mean square distance of the collection of atoms from their common center of gravity

$$S^2 = \Sigma_i^n{}_{=1} \, (Si^2/n) \qquad (1)$$

Another important property of polymers is molecular weight or molar mass. The number of monomer units in each polymer chain, or the degree of polymerization, can often vary randomly. This necessitates speaking in terms of distributions and statistical averages of molecular weight. Three molecular weight averages commonly used, are 1) the number average molecular weight (Mn); 2) the weight average molecular weight (Mw); 3) and the viscosity average molecular weight (Mv). Mn, Mw, and Mv are defined as

$$Mn = \Sigma N_i M_i / \Sigma N_i \qquad (2)$$

$$Mw = \Sigma N_i M_i^2 / \Sigma N_i M_i \qquad (3)$$

$$Mv = (\Sigma N_i M_i^{1+a} / \Sigma N_i M_i)^{1/a} \qquad (4)$$

where N_i is the number of molecules with molecular weight M_i and a is a constant which is a function of solvent and polymer type (9).

A typical molecular weight distribution is schematically pictured in Figure 2 (9).

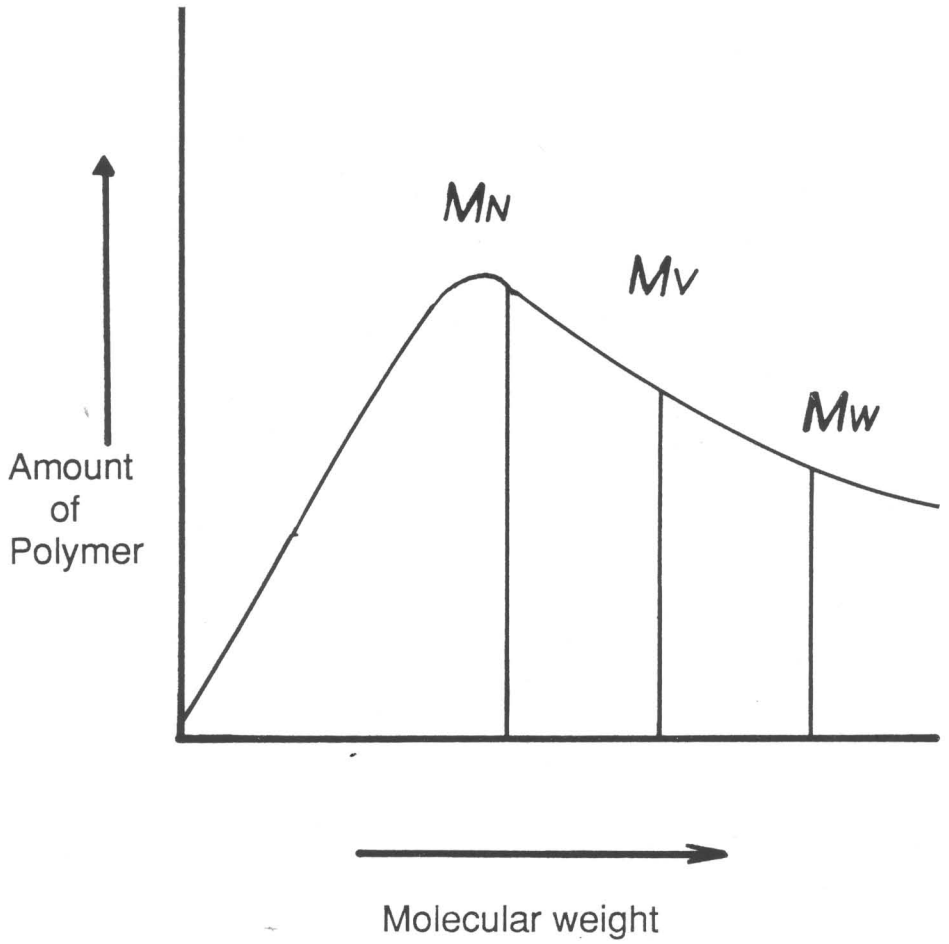


Figure 2. A typical polymer molecular weight distribution showing the relative magnitudes of the common molecular weight averages (ref. 9).

The degree of dispersity of molecular weights is given by the polydispersity index (Mw/Mn). The magnitude of this index is equal to one for monodisperse polymers (i.e. Mw = Mn), and greater than one for polydisperse materials (i.e. Mw>Mn), the extent of deviation from unity reflecting the degree of dispersity. The weight average molecular weight is always greater than the number average molecular weight for polydisperse systems due to differences in contribution given to each size. Mn simply counts the number of molecules with mass $(M)_i$ while Mw weighs their contribution on a mass basis. The third common average molecular weight, Mv, stems from the empirical dependence of a solution's viscosity on the molecular weight of the dissolved polymer. The viscosity average molecular weight has a magnitude intermediate to the weight average and number average molecular weights so that Mw > Mv > Mn. Methods for experimentally determining these various averages generally depend on the effect of molecular weight on different physical properties. Estimates for the number average molecular weight are usually obtained from colligative properties such as osmotic pressure. Weight average molecular weights frequently are derived from light scattering data, while viscosity average molecular weights are obtained from intrinsic viscosity measurements. While all these methods yield a molecular weight average, none gives information on the extent of the distribution of molecular weights present.

Experimental determination of the molecular weight distribution (MWD) of a polymer was formerly a tedious process accomplished by the addition of a precipitating agent. This precipitating agent decreases the solubility of the polymer,

preferential precipitation of the higher molecular weight species. The molecular weight of the fractions are then determined and the distribution constructed. The technique of choice for determining the MWD is Gel Permeation Chromatography (GPC), a process which separates polymer molecules on the basis of molecular or hydrodynamic volume; hydrodynamic volume is proportional to the cube of the radius of gyration. A solution of the polymer is passed down a chromatographic column containing a highly porous rigid gel, often cross-linked polystyrene (9). The smaller polymer molecules diffuse into the porous gel with greater ease than larger molecules. The larger molecules therefore move down the column faster than the smaller molecules, thus accomplishing separation. The chromatogram serves as a means of visualizing the extent of the MWD.

Polymer solubility is another characteristic worthy of brief discussion. This study will involve work with nonionic water-soluble polymers, so comments on polymer solubility and precipitation will be restricted to such systems. The thermodynamics of polymer systems have been well described in the literature (10), so an in depth discussion will not be undertaken here. Phase separation for nonionic species can be understood by considering the interaction between polymer and solvent

$$MM + SS \rightleftharpoons MS + MS \qquad (5)$$

where M represents a monomer unit, and S a solvent molecule (11). MM stands for any interaction between two monomer units on the same or different molecules; SS is the interaction between two solvent molecules. The balance of this equilibrium, and thus polymer solubility and precipitation, is dependent on temperature, and the

presence of other materials; i.e. solvents, non-solvents, electrolytes, etc. If dissolution is exothermic, such a system will generally be reversed by a rise in temperature, leading to an increase in the number of MM and SS species and possible phase separation. The converse is true for endothermic systems. This point of phase separation as temperature is elevated, called the cloud point, is often accompanied by a decrease in solution viscosity. Polymers which exhibit a cloud point upon heating are said to exhibit a lower critical solution temperature, while those showing phase separation upon a lowering of the temperature are said to possess an upper critical solution temperature.

B. Polymer Adsorption

The objective of many adsorption studies is to measure the amount of polymer adsorbed per unit area and to gain insight into the average conformation of the polymer molecules at an interface. Adsorption of polymers at interfaces is complicated by the numerous conformations of the polymer molecule caused by the capacity to form multiple points of attachment to the solid. Points of direct attachment to the solid are referred to as trains, while those portions of the polymer molecule that extend into solution are called loops or tails (Figure 3) (12). As the amount of polymer in solution increases the polymer chains begin to interact with each other. This results in changes in the area occupied by each molecule, the fraction of segments in contact with the solid, and the thickness of the adsorbed layer. Information about these three quantities enables prediction of the conformation of the adsorbed molecule (13). Experimental methods for measuring these parameters

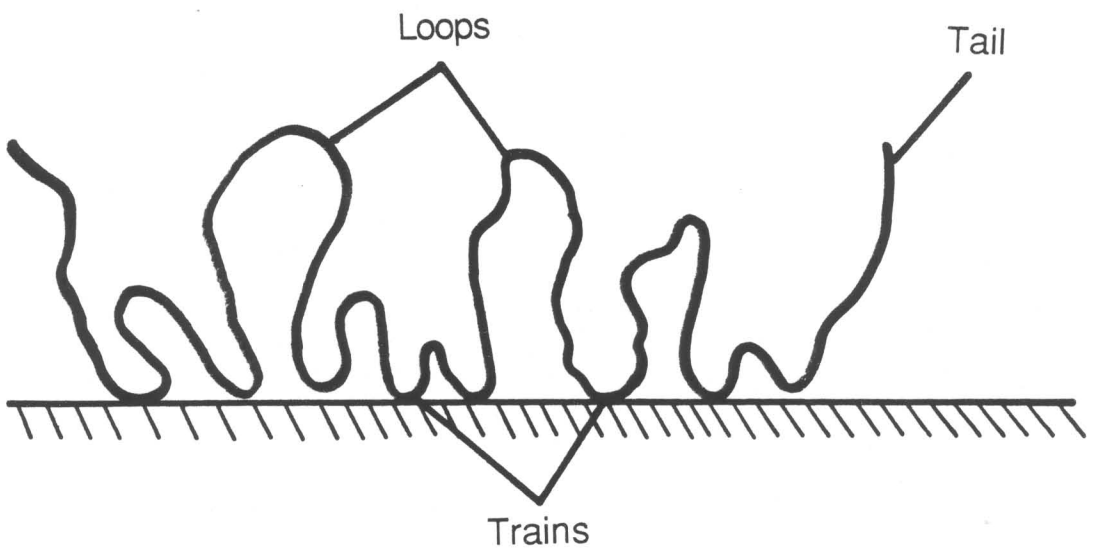


Figure 3. Schematic representation of an adsorbed polymer molecule at an interface (ref. 12).

have been covered in the literature (14-21).

Several factors have been identified as having a significant effect on the conformation of the polymer molecule in bulk solution and at the interface. These include the molecular weight and degree of dispersity of the polymer,the nature of the solvent and the adsorbent, and the temperature at which the adsorption isotherm is measured (14). We will consider each in order. The molecular weight and dispersity of the polymer greatly affect the types of conclusions that can be drawn from adsorption data. For example, in working with semi-synthetic polymers, such as the cellulosics, a wide distribution of molecular weights is generally encountered within a given sample. In order to determine the effect of molecular weight on adsorption, however, it is necessary to work with polymers that have relatively narrow molecular weight distributions. When evaluating the effect of molecular weight on adsorption two extremes can be considered: one where adsorption is totally independent of molecular weight and the other where adsorption is linearly dependent on molecular weight. The first is consistent with the situation where the polymer molecules adsorb lying flat on the surface with all segments attached to the surface. The latter case is represented by a polymer molecule standing "on-end" with a single point of attachment to the surface. It has been shown that adsorption on nonporous solids often follows the empirical relationship

$$A_S = K M^a \qquad (6)$$

where A_S is the amount of material adsorbed at the plateau of the isotherm, M is

molecular weight, and K and a are constants for a particular polymer/solvent system (22). For the situation where there is no molecular weight dependence, (molecules lying flat on the surface), a is equal to zero. If however, the polymer were to adsorb via a single attachment a would be equal to one. Adsorption studies of several water soluble polymers report values between 0.1 and 0.5 (23-24), representative of an intermediate state of adsorption. In speaking of the effect of solvent on adsorption three types of interactions must be considered: solvent-solute, solvent-solid, and solid-solute. The nature of the solvent influences the conformation of the polymer chains, as previously discussed, as well as the "escaping tendency" of the polymer. The possibility of solvent adsorption to the solid is also important. Depending on the extent of competition for the solid, an increase in the concentration of polymer in solution may be seen. The relationship between temperature and adsorption is complicated and dependent on several variables. A major one, changes in solvent power, is best demonstrated by polymers that precipitate near the temperature at which adsorption is being studied, i.e. adsorption is enhanced as the temperature approaches the cloud point. This has been demonstrated experimentally for HPC from water (25). The last factor affecting adsorption, the nature of the adsorbent, can be discussed in terms of three parameters: specific surface area, the chemical nature of the surface, and degree of porosity (14). The specific surface area available for adsorption should be sufficient to allow a detectable change in solution concentration of the polymer using a reasonable amount of solid. Until the advent of polymer latex systems, such as poly(styrene) latex beads, the choice of solids with sufficient

surface area was limited. The chemical nature of the surface (i.e. energy of exposed groups) dictates the type of polymers capable of adsorbing and also determines the extent of solvent adsorption. The porosity of a solid not only affects the specific surface area of a solid, but it also can selectively exclude different size molecules. For example, highly porous solids will exhibit different effective surface areas with different probe molecules. Therefore a technique for measuring surface area should reflect the surface area available to the polymer for adsorption.

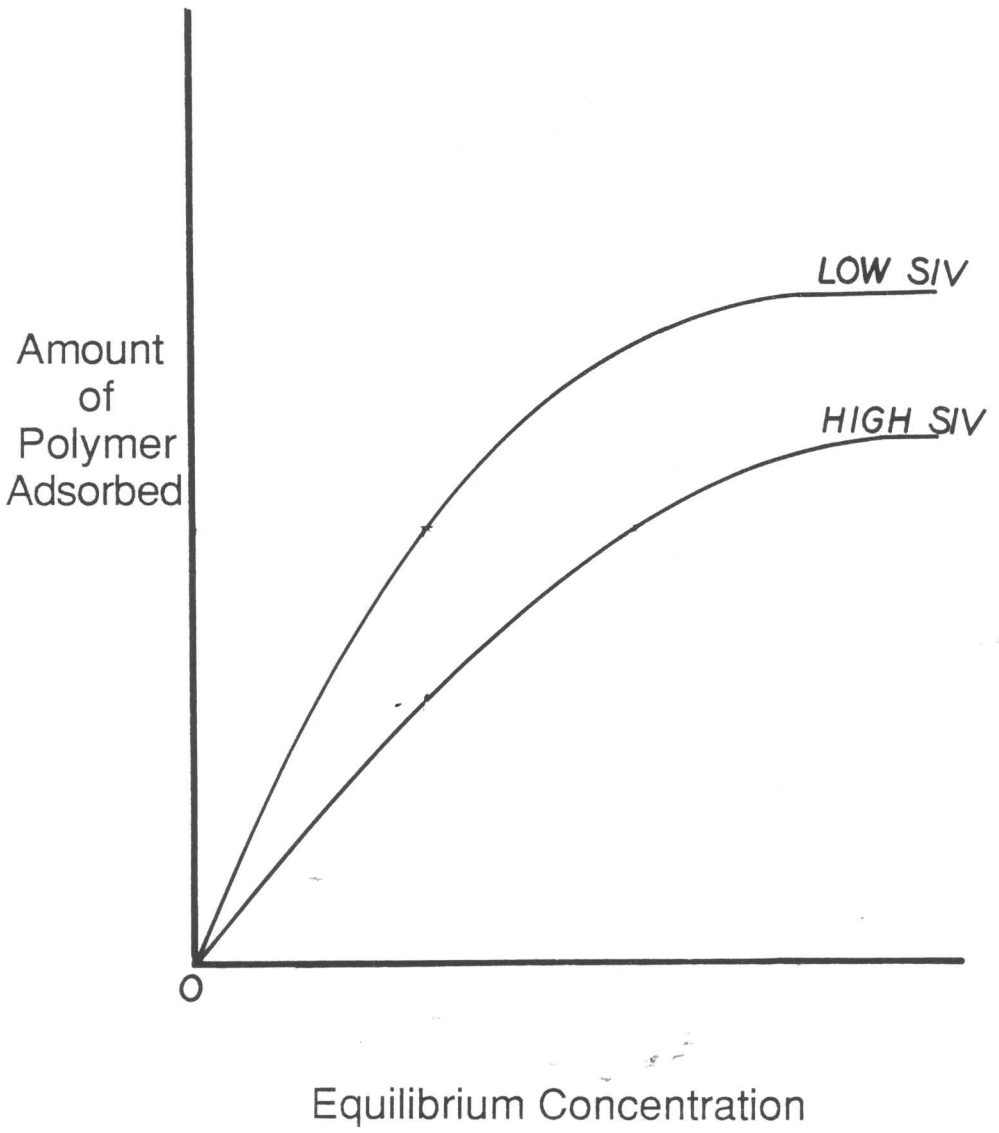
When discussing variables that affect the adsorption isotherm it is important to realize that the ratio of solid surface to solution volume (S/V) used in an adsorption study can affect the shape of the isotherm obtained and the amount adsorbed. Most adsorption studies are performed with a constant amount of solid, though a few studies have been carried out where this effect has been taken into consideration (26). These latter studies have shown that the effect of S/V on the shape of the isotherm can be explained by considering the degree of polymer polydispersity. It has been well demonstrated that long chain polymer molecules generally adsorb preferentially over shorter molecules (26). This preferential adsorption of longer chains leads to a fractionation in solution if the amount of surface available for adsorption is small; only the high molecular weight molecules will adsorb leading to a high amount of polymer adsorption. If a greater amount of surface is available for adsorption, (higher S/V ratio), some of the lower molecular weight molecules could also be adsorbed, resulting in a smaller amount of polymer adsorbed per unit area. Adsorption isotherms for low S/V ratios lie above those for high S/V as illustrated in

Figure 4 (26). To account for this effect, it has been suggested that adsorption isotherms be plotted as A versus A^*, where A^* is simply the equilibrium concentration divided by the surface to volume ratio (S/V). Now A^* has the same units as A and the curves shown in Figure 4 should collapse into one, independent of S/V.

C. Chemical and Physical Properties of Hydroxypropylcellulose

Hydroxypropylcellulose (HPC) (Figure 5) is a semi-synthetic nonionic polymer derived from cellulose. It is manufactured by reacting alkali cellulose and propylene oxide at elevated temperature and pressure. The propylene oxide substitutes on the cellulose through an ether linkage at the three reactive hydroxyls of the anhydroglucose monomer. The secondary hydroxyl group in the hydroxypropyl side chain is also capable of hydroxypropylation, yielding side chains of varying length. The degree of substitution is expressed in terms of the average number of moles of propylene oxide per anhydroglucose unit (M.S.). For HPC typical M.S. values obtained are between 3.0 and 4.5. The value of 4.0 will be used in later calculations. The degree of polymerization varies randomly in the range of 150 to 3000. Thus the molecular weight can range between 60,000 and 1,200,000 (1). HPC is available commercially in a variety of molecular weight grades and viscosity ranges (Table 1) (1), with many physical characteristics that make it ideally suited for use in many organic and aqueous systems. It is freely soluble in water below 40 degrees centigrade, and in many organic solvents. It is highly insoluble in water above 45

Figure 4. Effect of surface to volume (S/V) ratio on the adsorption isotherm (ref. 26).



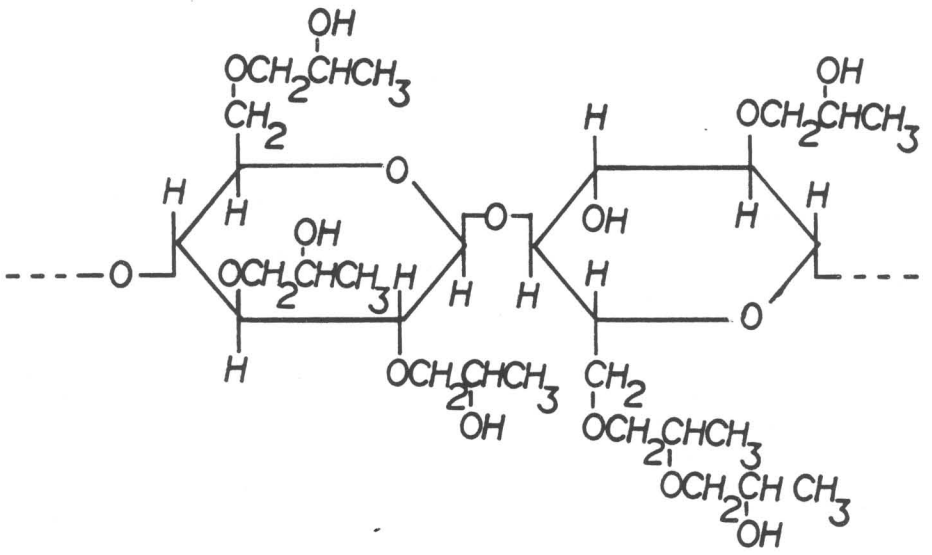


Figure 5. Repeat unit structure of hydroxypropylcellulose

Table 1. Typical viscosity and molecular weight data for various commercial grades of hydroxypropylcellulose (1).

Grade	% Concentration	Viscosity (cP)*	Molecular Weight, Mw
H	1	1,500 - 2,500	1,000,000
M	2	4,000 - 6,500	800,000
G	2	150 - 400	300,000
J	5	150 - 400	150,000
L	5	75 - 150	100,000
E	10	300 - 700	60,000

* Measured with a Brookfield viscometer

degrees (27); the actual temperature of phase separation is dependent upon the molecular weight grade of HPC. The precipitation of HPC from aqueous solution upon heating is completely reversible upon cooling, and the original viscosity of the solution is restored. The cloud point temperature is increased by the addition of organic liquids that act as solvents and decreased in the presence of high concentrations of other dissolved materials that compete with the polymer for water e.g. inorganic electrolytes. Aqueous solutions of HPC are susceptible to microbial growth and should be prepared just prior to use. Moisture content of the polymer exposed to ambient conditions is generally below five percent. HPC is appreciably surface active and is capable of lowering the surface tension of water to 42.2 dynes/cm. (0.1% solution) (28). The surface tension of various grades of HPC has been found to be independent of solution concentration and molecular weight. Time dependence of surface tension due to reduced diffusion rates has been reported for various solution concentrations (28). Solutions of HPC exhibit a pH range of between 5.0 and 8.8 (1).

D. Adsorption Theory

The last few decades have seen an increased interest in the development of theoretical models to describe polymer adsorption. A number of different approaches have been attempted, the first of which considered the adsorption of polymers at an interface as a random walk process, as described by Flory (10) and Simha, Frisch and Eirich (29-33). Later attempts at modeling adsorption took a statistical mechanical

approach (34-36). These theories considered polymer in the adsorbed state in terms of trains, loops and tails, describing the probability of finding segments in each of these conformations. In addition such parameters as the energy of adsorption and the conformation of the molecule in solution were included. All of these early attempts at modeling assumed the polymer solution to be infinitely dilute and thus neglected intra and intermolecular interactions between polymer and solvent molecules. At low polymer concentrations often the interface is saturated and therefore it is essential to take these interactions between segments into account (13). This oversimplification on the part of these investigators has tended to negate the practical use of these earlier theoretical descriptions of adsorption. Later theories put forth by Hoeve (37-39), Silberg (40), Roe (41) and Scheutjens and Fleer (42) included parameters in their equations to take these molecular interactions into account. In spite of the significant advances in the understanding of polymers at interfaces many of the proposed theories still have not been verified experimentally. This is so, most likely, because many of the theoretical treatments contain parameters not readily obtained by experiment. However, some models have been examined systematically in nonaqueous systems (43-49).

E. Adsorption of Water-Soluble Polymers

Little work has been reported in the literature regarding the adsorption of water-soluble polymers. For convenience, this discussion of previous work will be divided into the adsorption of nonionized and ionized polymers. The focus of this

review will be on attempts made to determine the amount of polymer adsorbed and the conformation of the adsorbed layer at the solid/liquid interface.

Saunders (50) has reported the adsorption of methylcellulose (MC) in the presence of sodium lauryl sulfate (SLS) and has determined the effect of surfactant coverage on polymer adsorption. He found that the amount of MC adsorbed depended on the available free area on the surface; no adsorption took place when the surface was completely covered by SLS. From calculations of the area occupied by an adsorbed polymer molecule the author speculated that MC was not adsorbed parallel to the surface as a monolayer, but instead was adsorbed with some of its chains extended into the bulk solution. This idea of a polymer adsorbing with some of its chains perpendicular to the surface also was suggested by the work of Jenkel and Rumbach (51). Here, each molecule is anchored on the surface by one or more attachments. The number of attachment sites is felt to be related to the flexibility of the polymer chains, more points of attachment being associated with chains of greater flexibility. Adsorption of polyvinylpyrrolidine (PVP), and sodium carboxymethylcellulose (SCMC) on a polystyrene latex was examined in an effort to determine the conformation of the adsorbed molecules (52). All isotherms were of the Langmuir type and were found to be molecular weight dependent. Adsorption was studied as a function of molecular weight according to the empirical relationship of Perkell and Ullmann (22) discussed earlier. It was proposed that PVP adsorbs in a random coil conformation while SCMC adsorbs via a one point attachment. This would be consistent with the SCMC molecule trying to minimize its electrostatic intramolecular

interactions due to the charged carboxyl groups in its repeating structure. The first extensive study of the adsorption of nonionic cellulosic polymers was performed by Hsia et. al. in 1978 (53), who studied the adsorption of MC, HPMC and poly (vinylalcohol) (PVA) on poly (methylmethacrylate) (PMMA) powder. The amount of polymer adsorbed was ranked as MC>PVA>HPMC. All isotherms exhibited Langmuir behavior showing level plateaus consistent with monolayer coverage. The order of the amount of polymer adsorbed was attributed to the conformation of the adsorbed molecule and chain flexibility. The flexibility of PVA molecules was purported to be much greater than that of MC molecules owing to the inflexible anhydroglucose ring and ether links of MC. The greater flexibility of the PVA molecule was believed to allow for a greater number of attachment points and, hence, less polymer adsorption. HPMC and its extra hydroxypropyl groups would be expected to take up a greater percentage of the surface as compared to MC, leading to a smaller amount of HPMC adsorbed.

More evidence supporting the idea of partial polymer adsorption, (polymer adsorbing with only a few points of attachment to the solid), was shown by Law and Kayes (54) from the adsorption behavior of HEC, HPC, and HPMC on polystyrene latex beads. Contrary to the work of Hsia, the adsorption isotherms all showed the plateau characteristic of monolayer adsorption followed by an inflection point at higher concentrations, apparently indicative of multilayer adsorption. Using viscosity measurements, the molecular dimensions of the polymer molecule in the bulk were determined. The size of the various molecules in the bulk was found to be much

greater than that of the molecule adsorbed at the surface of the latex, again suggesting only a few points of attachment between polymer and surface. Adsorption experiments were performed with various molecular weight grades of each polymer. Calculation of the area occupied by a molecule for each of the molecular weight grades showed that this area increased with molecular weight for HEC and HPC. This was thought to indicate a change in the conformation of the adsorbed molecule. As the molecular weight increased the molecule was thought to assume a flatter conformation. The authors suggested that data showing a decrease in layer thickness with increasing molecular weight confirmed this conclusion. For HPMC, the calculated area occupied by an adsorbed molecule was constant with increasing molecular weight. It was postulated that an HPMC molecule adopts an "on-end" conformation, which would be consistent with measurements that show the layer thickness increasing with molecular weight. Furusawa (25), in a recent study, examined the adsorption of HPC, ethyl hydroxyethylcellulose (EHEC), and PVP on several latexes. The adsorption temperature and nature of the latex surface was found to have a significant effect on the amount of polymer adsorbed. At temperatures near the cloud point, adsorption was reported to be 1.5 times greater than at room temperature, which is not unexpected in light of the earlier discussion of polymer behavior near the precipitation point. Consideration of the effect of the nature of the polystyrene latex surface on adsorption showed that the greater the surface charge, the lower the amount of polymer adsorbed. The authors pointed out that these results indicate that hydrophobic interaction between the polymer and adsorbent is a major determinant of the extent to which

adsorption will occur.

Studies on the wetting of PMMA, poly (ethyleneterephthalate) (PET), and polyethylene (PE) by HPC and HPMC solutions have shown that these hydrophobic polymers are less effective in reducing contact angle than a pure liquid with an equivalent surface tension. Receding contact angle measurements indicated that HPC and HPMC are strongly adsorbed in an apparently irreversible manner, exhibiting a zero degree receding angle. Such effects were not noted for wetting of paraffin or for wetting of PMMA or PET using less hydrophobic polymers such as poly (ethylene glycol), HEC or PVP. Such studies suggest a strong interaction between HPC and HPMC and the more polar solid surfaces (55).

II. Statement of the Problem

The intent of this thesis is to study the adsorption of hydroxypropylcellulose (HPC) on two well-defined solid surfaces, titanium dioxide and polystyrene. The solids were chosen so as to allow comparison of adsorption on surfaces of widely divergent polarities.

The first series of experiments will be aimed at determining the surface area of the two solids. The most frequently used method of measuring solid surface area is B.E.T. gas adsorption. However, adsorption experiments require that the solid be dispersed in a liquid thus raising an important question, i.e. does the surface area of the solid in the dry state change when dispersed in the liquid medium for which adsorption is to be measured? To address this concern with titanium dioxide, a variety of surface area techniques in both the dry and wet state will be investigated.

Previous studies with cellulosic polymers suffer from having used unfractionated samples of unknown molecular weight. Consequently, uncertainties due to polydispersity exist. In this regard the second set of experiments will be directed at determining the degree of polydispersity of unfractionated and fractionated samples of hydroxypropylcellulose. Working with a polymer having a well defined molecular weight distribution would enable us eventually to establish the importance of molecular weight on adsorption.

The planned adsorption studies, which compose the third series of experimental measurements in this study, will attempt to answer a number of questions: 1) How

do adsorption isotherms for the unfractionated and fractionated polymer samples compare? 2) To what extent does polymer polydispersity affect the shape of the adsorption isotherm and the amount of polymer adsorbed at various slurry densities? 3) How does the polarity of the solid surface affect the amount of polymer adsorbed?

III. Experimental

A. Materials

1. Titanium dioxide (Colorcon Inc., West Point, P.A.) was identified as being composed of greater than 95% Anatase and small traces of Rutile, using an x-ray powder diffractometer (Phillips Instruments) and scanning 2Ø from 0 to 90 degrees. The material was subjected to a cleaning procedure, described by Busca et. al. (56), prior to use to remove any impurities, i.e. hydrocarbon and chloride ion (57). A schematic diagram of the cleaning apparatus is shown in Figure 6. The cleaning procedure, which entails heating the titanium dioxide in oxygenated water vapor at 425^{o} C for twelve hours, has been shown to be as effective as repetitive washing and centrifugation of the solid with water (58). The density of the solid titanium dioxide was measured using a modified liquid pycnometric technique (59). Heptane was chosen as the solvent, this being a solvent in which titanium dioxide is insoluble, nondispersible and which was found to adequately wet the surface of the solid. A 25 ml. pycnometer was weighed empty, and again when filled with solvent; the weight of solvent (A) was determined by difference. One gram of solid (B) was added to the partially filled pycnometer, brought to volume with solvent and again weighed. The weight of solid and solvent (S) was then calculated. The density (p) of the titanium dioxide was calculated using (59)

$$p = (AB)/25(A+B-S) \qquad (7)$$

Upon receipt, the titanium dioxide was subjected to sieve analysis (Arthur La Pine &

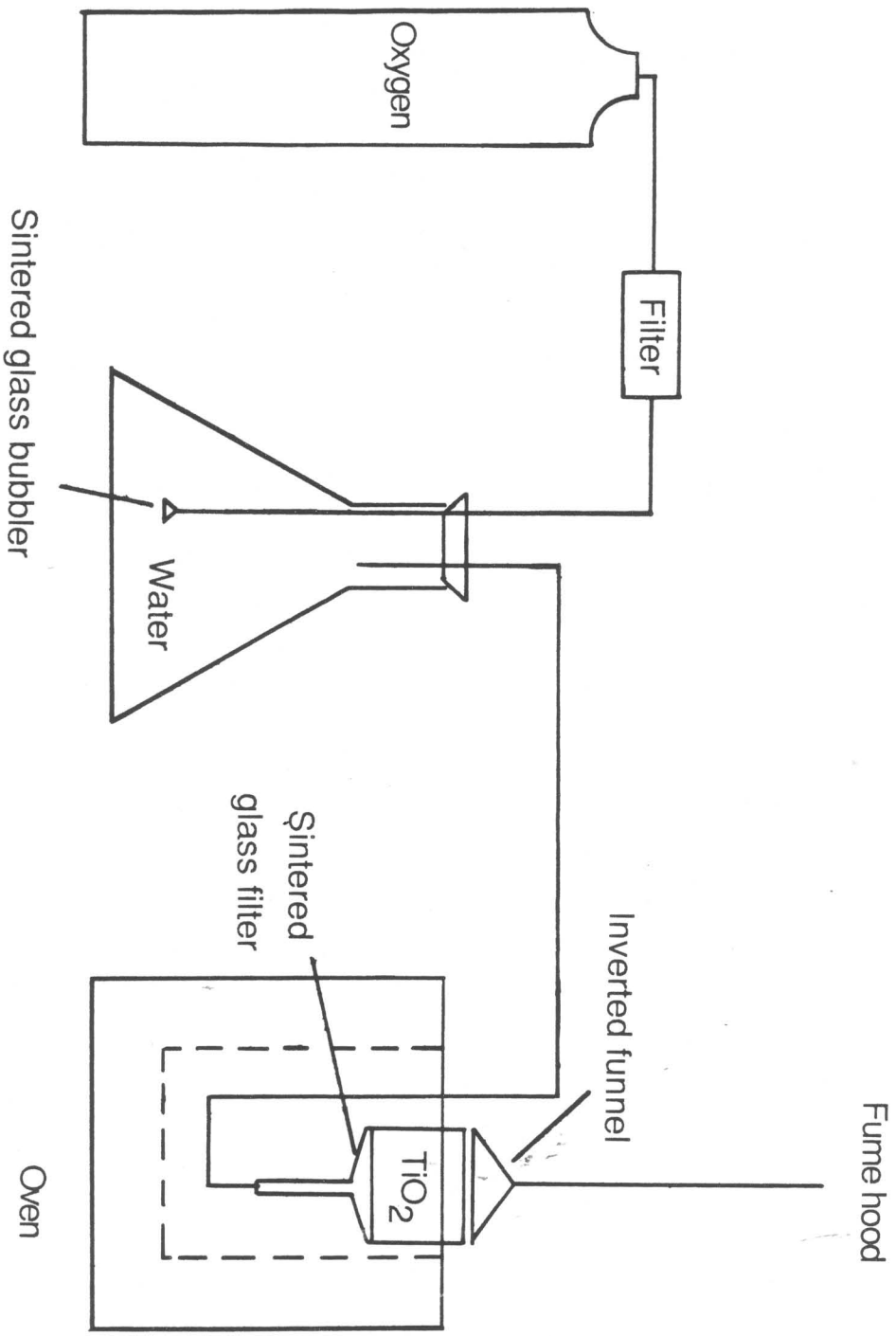


Figure 6. Schematic of the titanium dioxide cleaning apparatus

Co., Chicago, Ill.) to ascertain the degree of primary particle aggregation. U.S. standard sieve screens (American Scientific Products, McGaw Park, Ill.) of 20, 30, 50, 70, 100, and 170 mesh were used. Results indicate a log normal distribution of particle aggregates. The fraction of particles collected on the 170 mesh screen (90 - 150 microns in size) was used in all subsequent experiments.

Particle sizes of the primary titanium dioxide particles were determined using a scanning electron microscope (SEM) (JOEL Model JSM-35C) at magnifications of 10,000X and 20,000X. Photographic enlargements were made of the SEM pictures and the particle diameters were measured to the nearest millimeter. The microscope was calibrated with a diffraction grating that contained 2160 lines per millimeter. Figure 7 shows that the high degree of particle aggregation and nonspherical nature of the particles make accurate diameter measurements very difficult. The micrograph, however, does show that the diameter of the primary particle is approximately 0.30 microns and that the particles are fairly uniform in size. An average particle diameter for titanium dioxide was also obtained using a dynamic light scattering technique (performed by Vincent Hackly, Dept. Water Chem., U.W.-Madison) with a dilute aqueous dispersion. The instrument (Brookhaven Instruments) measures the intensity of laser light scattered by the sample at an angle 90 degrees to the direction of the helium-neon laser beam. The light scattering technique yielded a mean diameter of 0.336 microns, in good agreement with the SEM measurements.

2. Polystyrene latex beads were prepared by an emulsion polymerization procedure previously described (12). The beads were purified by exhaustive dialysis to

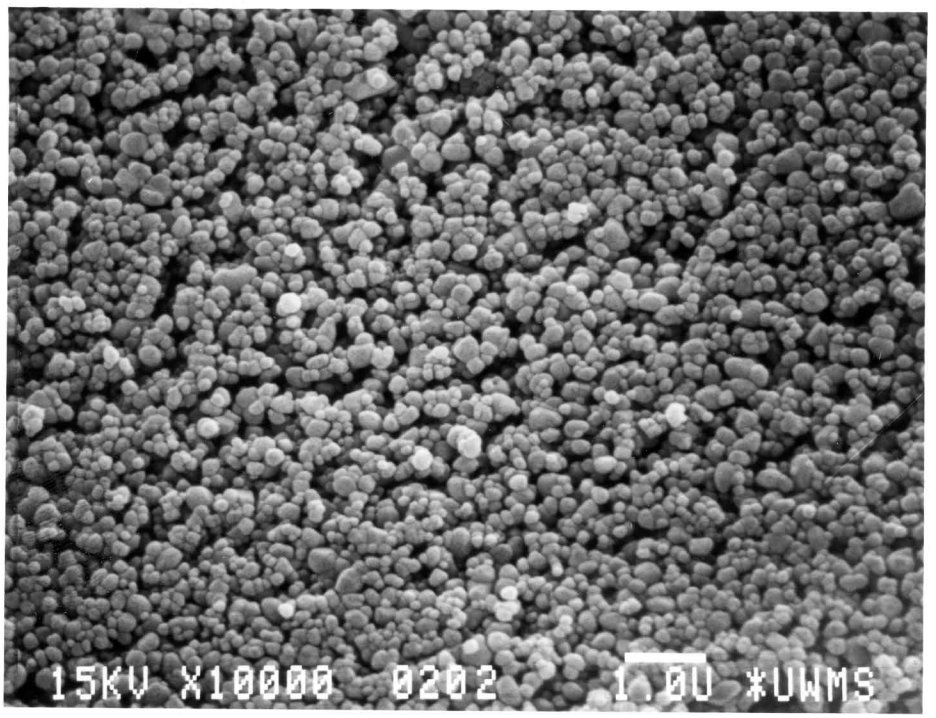


Figure 7. Scanning electron micrograph of titanium dioxide particles

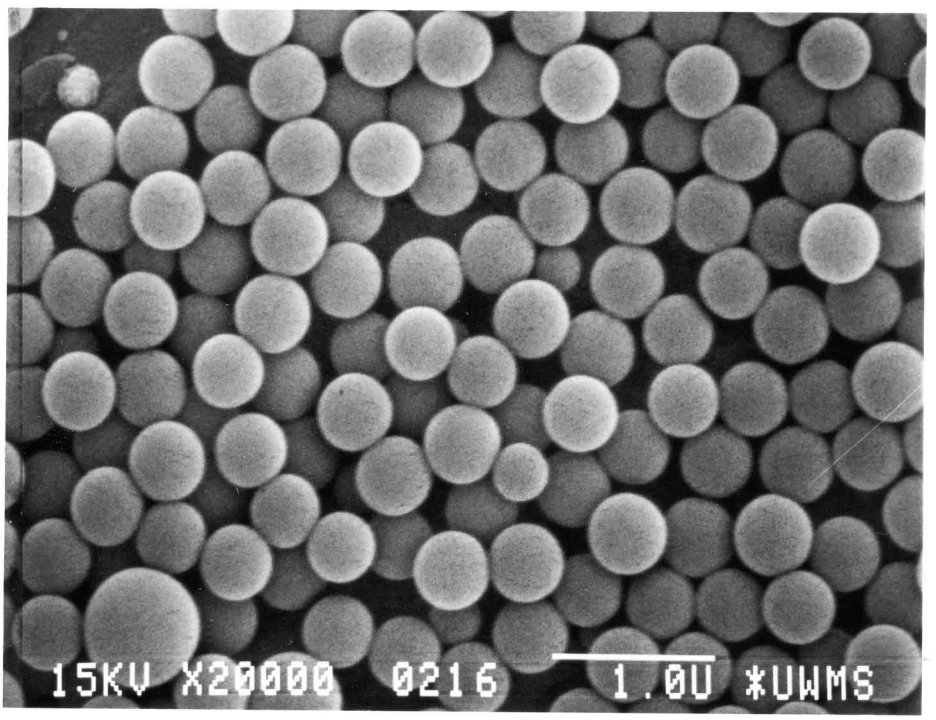


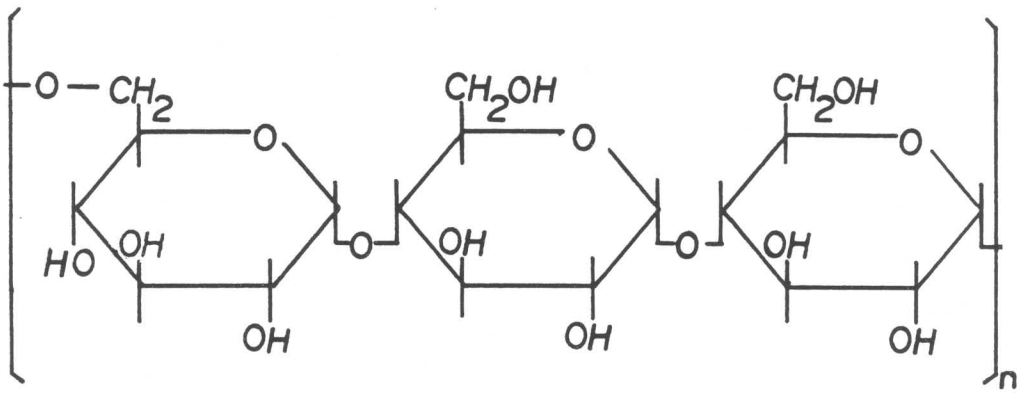
Figure 8. Scanning electron micrograph of polystyrene latex particles

remove any unreacted monomer. A scanning electron micrograph of the polystyrene latex is shown in Figure 8. The mean particle diameter was obtained from measurements of more than 300 particle diameters, and found to be 0.70 microns (S.D. 0.06). The particles were found to be very monodisperse.

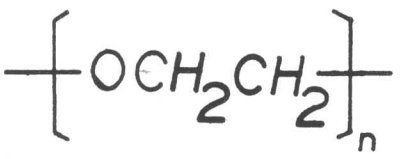
3. Hydroxypropylcellulose, the polymer chosen for use in the adsorption studies,was a grade referred to as HPC-H (Hercules Inc. Willmington, DE). It was used in two forms: as received; and after being subjected to a solvent extraction technique (60) aimed at obtaining a polymer fraction with a narrower distribution of molecular weights. (To be discussed). Aqueous solutions of the polymer were prepared according to the manufacturer's recommendation to preslurry the polymer in hot water to avoid agglomeration and to enhance the dissolution rate (27).

4. Molecular Weight Standards. Two polymers, of known molecular weight and narrow molecular weight distribution, were used as standards to estimate molecular weights of HPC-H from gel permeation chromatographic analysis, (to be discussed later). These were: 1) Pullulan (MW- 5,800 - 853,000), a synthetic polysaccharide; and 2) Polyethylene oxide (MW- 18,000 - 990,000) (Figure 9) (Phenomenx, Rancho Palos Verdes, CA). Both standards were dissolved in triple distilled water according to the manufacturer's directions.

5. Miscellaneous Materials. Orange-II (Aldrich Chemical Co., Milwaukee, WI), 4-(2-hydroxy-1-naphthylazo) benzenesulfonic acid, sodium salt, a dye used in surface area experiments, was twice recrystallized from absolute ethanol, yielding a molar absorptivity of 2.0750×10^4 at 485 nm, in agreement



Pullulan



Poly (ethylene oxide)

Figure 9. Repeat unit structures of the polymers used for Gel Permeation Chromatography (GPC) standardization

with the literature (61). Further recrystallization did not significantly change this value. Methylene blue Injection U.S.P. 1% (Elkins-Sinn, Cherry Hill, NJ) and Stearic Acid (>99+%) (Aldrich Chemical Co., Milwaukee, WI) were used as received. Solvents and other reagents used in all experiments are listed in Table 2.

B. Procedures

1. Determination of Specific Surface Area of Solids. Several techniques have been used to determine the specific surface area of the two solids used in this study. These techniques can be divided into three catagories: 1) particle size (SEM and Light scattering); 2) vapor phase adsorption of nitrogen and krypton at low temperature, and; 3) adsorption of stearic acid and some dyes from solution.

Estimates of the specific surface area (S) of the solids, from particle size measurements, were obtained using the relationship (62)

$$S = 6/pd \qquad (8)$$

where p is the density of the solid in g/cm^3 and d the average particle diameter in centimeters. This assumes monodisperse spherical particles, which is correct for the polystyrene latex but not for the titanium dioxide samples used.

Vapor phase adsorption measurements were performed on titanium dioxide with the Quantasorb Sorption System (Quantachrome Corp., Syossett, NY) using nitrogen and krypton gases mixed with helium as a carrier gas (Matheson, Joliet, IL). The Quantasorb system quantitates the mass of gas adsorbed to the solid by monitoring changes in the gas composition, via thermal conductivity measurements, before and

Table 2. Solvents and other reagents used.

Absolute ethanol,reagent grade, Aaper Alcohol and Chemical Co. (Shelbyville, KY)

Acetic acid, reagent grade, J.T. Baker Chemical Co. (Phillipsburg, NJ)

Chloroform, reagent grade, Mallinckrodt Inc. (Paris, KY)

Dimethyldichlorosilane, Sigma Chemical Co. (St. Louis, MO)

Hydrochloric acid, reagent grade, Hi-Pure Chemicals Inc. (Nazareth, PA)

Methanol, HPLC grade, Aldrich Chemical Company (Milwaukee, WI)

Methylene chloride, HPLC grade, Burdick & Jackson (Muskegon, MI)

n-Heptane, reagent grade, Columbus Chemical Industries Inc. (Columbus, WI.)

Water- triply distilled from alkaline permanganate and acidic solutions

after the gas mixture passes over the sample. Application of the B.E.T. equation (63),

$$1/X(P_0/P - 1) = (C-1)/X_mC\,(P/P_0) + 1/X_m \qquad (9)$$

where X is the weight of adsorbate adsorbed at relative pressure P/P_0, X_m is the weight of adsorbate adsorbed at a coverage of one monolayer, and C is a constant related to the heat of adsorption, enables calculation of the amount of gas required for monolayer coverage of the solid surface. Knowledge of X_m allows calculation of the total surface area by the equation (64)

$$S_t = X_m N A_e /M \qquad (10)$$

where N is Avogadro's number, A_e is the cross sectional area of the adsorbate molecule and M is the molecular weight of the adsorbate. Values of A_e used for nitrogen and krypton were 16.2×10^{-20} m^2 and 19.5×10^{-20} m^2 respectively (64). The specific surface area was obtained by dividing the total surface area by the weight of the solid (m) being analyzed.

$$S = S_t/m \qquad (11)$$

Solute adsorption from solution, the third technique, was measured using stearic acid, and two dyes, methylene blue and orange-II. The fatty acid adsorption technique described in the literature (65) was modified for use with titanium dioxide. Three grams of solid were placed in 50ml. ground glass ehrlenmeyer flasks and oven dried for 12 hours at 120^o F to remove any residual water. This was important since residual water has been reported to reduce the amount of stearic acid adsorbed (65).

The flasks were then stoppered and the dry weight determined. Initial experiments using methanol as the solvent showed preferential adsorption of the solvent, consistent with results in the literature (57). Methylene chloride was ultimately the solvent of choice and a range of stearic acid solutions (4-20mg/ml) were prepared. Twenty (20) mls. of stearic acid solution were added to each flask containing dried titanium dioxide, the flasks were sealed with Parafilm, (American Can Co., Greenwich, CT) and allowed to equilibrate in a shaking water bath (Forma Scientific, Marietta, OH) at 25^{o} C for one hour. The mass of solid was chosen so as to maximize the change in stearic acid concentration; a 50% change has been reported to give the best results (65). Solutions were centrifuged (Model TJ-6, Beckman Instruments, Arlington Heights, IL) at 4,000 r.p.m. for ten minutes, and the supernatant was assayed by reverse phase high pressure liquid chromatography (HPLC). Six (6) µl. (microliter) injections of stearic acid solution were made on a Nova Pak C-18 column (Waters Chromatography, Milford, MA) using a mobile phase of 90% methanol, 9% water and 1% acetic acid. The flow rate was set at 1ml. per minute. The amount of stearic acid eluted from the column was determined using a refractive index detector (Model 410, Waters Chromatography, Milford, MA) operated at 40^{o} C. Quantitation by HPLC was chosen due to ease of measurement, lack of sample preparation, such as dilutions, reliability and reproducibility. Adsorption experiments were analyzed by measuring the refractive index of the stearic acid solution before and after exposure to the solid. Initial solution concentrations were used to construct a calibration curve obtained by plotting the refractive index signal height against concentration. The

calibration curve was linear in the concentration range studied. The amount of acid adsorbed was calculated by subtracting the concentration in the supernatant from the initial solution concentration.

Surface area measurements from methylene blue were made following a procedure described by Giles and Trivedi (66). A stock solution of 0.8 mmol./l. of methylene blue in water was prepared, from which subsequent dilutions were made. All glassware was silated prior to use to avoid staining and experimental error due to dye adsorption to the glass. One hundred (100) mg. aliquots of titanium dioxide or latex were placed in 16 X 100 mm. test tubes. The titanium dioxide was dried at 120^{o} F for 12 hours and the dry weight was recorded. Five (5) ml. of dye solution (0.8, 0.64, 0.48, 0.32, and 0.16 mmol/l) were added to the tubes and shaken in a 25^{o} C waterbath for 30 minutes. Titanium dioxide dispersions were centrifuged at 4,000 r.p.m. for 10 minutes in a desktop centrifuge, while latexes were centrifuged at 20,000g. for 30 minutes in a high speed ultracentrifuge (Model LM-8, Beckman Instruments, Arlington Heights, IL). Dilutions of 100µl. of dye solution to 5 mls. of water were made on samples of the dye before and after exposure to the solid. A standard curve was constructed using the absorbance of the initial solutions, read against a water blank at 665 nm on a spectrophotometer (Model 2200, Varian, Palo Alto, CA).

The procedure (67) for measuring the adsorption of orange-II was similar to that used for the adsorption of methylene blue. A 2%(w/v) stock solution was prepared from which dilutions were made to give concentrations of 1%, 0.5%, and 0.25%. The

exact concentration of the stock solution was determined by evaporation of 10 ml. aliquots to dryness. Five (5) grams of titanium dioxide were weighed into 50 ml. ground glass ehrlenmeyer flasks to which 25ml. of orange-II solution were added. Solutions were allowed to shake for 24 hours in a 25^{0} C temperature controlled water bath. Upon equilibration, the dispersion was centrifuged and the supernatant assayed for concentration. A calibration curve was prepared by diluting the stock solution to concentrations on the order of 10^{-5} molar and measuring the absorbance on a spectrophotometer at 485 nm. against a water blank. Aliquots of the supernatant were diluted in a similar manner, and their absorbances measured and compared to the standard curve. Estimates of the surface area from orange-II were made by fitting the data to a modified B.E.T. equation as suggested in the literature (67).

2. Fractionation of HPC-H. The fractionation procedure (60) used is based on the solubility differences which arise because of variations in molecular chain length; as the concentration of ethanol in the extractant is increased the solubility of the higher molecular weight components increases. The HPC was sieved through a 35 mesh screen and an eight gram sample was extracted in subsequent mixtures of anhydrous ethanol (solvent) and n-heptane (nonsolvent) at 30^{0} C for 16 hours with continous shaking. The extraction scheme consisted of the following mixtures: 35.8, 39.5,40.2, 40.8,41.6, 42.3 and 100% (w/w) ethanol/heptane. At the completion of each extraction the undissolved gel was separated by centrifugation (International Centrifuge, Boston, MA) 2800 r.p.m., and subjected to extraction with the next richer ethanol mixture. The filtrate was then treated to reclaim the dissolved

polymer by two methods, solvent evaporation and freeze drying. Solvent evaporation under a steady stream of nitrogen yielded a highly viscous gel, which was spread on a Teflon watch glass and dried under vacuum at 60^{o} C for three hours. Freeze drying required prior separation of the ethanol and heptane, which was accomplished by several water washings of the filtrate in a separatory funnel. The polymer, which concentrates in the ethanol/water layer, was freeze dried in large recrystallizing dishes. The polymer solution was initially frozen and freeze dried at -45^{o} C for 24 hours, at which point the temperature of the sample was raised to -5^{o} C to drive off the remaining water and to complete the drying process. Freeze drying was ultimately the procedure used to reclaim the polymer from solution because polymer fractions subjected to solvent evaporation exhibited dissolution problems upon reconstitution. To determine the effectiveness of the fractionation procedure the fractions were subjected to GPC molecular weight analysis (to be discussed).

3. Determination of Solution Surface Tension. Surface tension (S.T.) measurements of the aqueous polymer solutions were made using the Wilhelmy plate technique (68) in a water jacketed beaker to maintain the temperature of the solution at 25^{o} C . This technique of surface tension measurement requires measuring the mass necessary to balance a thin platinum plate at the air-solution interface. Measurement of this required mass was accomplished using a surface tension balance (Federal Pacific Electric Co., Newark, NJ) and the following equation

$$S.T. = (m\ g / 1000\ w\ )\ (\ C) \qquad (12)$$

where m is the mass needed to balance the plate at the interface (mg.), g is the

acceleration of gravity (cm./s^2) and w is the perimeter of the platinum plate (cm.). C is a correction constant for variables not accounted for by the equation, i.e. thickness of the plate and operator to operator variation. This constant was determined by measurement of m for triple distilled water of known surface tension.

4. Cloud Point Measurement. The cloud point of the polymer, fractionated and unfractionated, was measured as a function of polymer concentration. Five (5) ml. of polymer solution were pipetted into glass ampules and placed in a freezer for 6 hours. Once frozen, the ampules were heat sealed and allowed to warm to room temperature. Freezing was performed to guard against the possibility of polymer decomposition during heat sealing. The use of ampules negated the possibility of solvent evaporation over the course of the experiment. The ampules were placed in a shaking water bath initially set at 40^{o} C; the temperature was then increased one-half degree every 30 minutes. The cloud point was detected visually and taken to be the point of first noticeable cloudiness.

5. Determination of Intrinsic Viscosity. Intrinsic viscosity measurements were made of various polymer samples to determine the average molecular weight of HPC. A capillary viscometer (#100, Fisher Scientific, Pittsburgh, PA) was used to measure the time required for polymer solutions to pass between two marks relative to the time required for the solvent to flow the same distance. Such measurements yield a relative viscosity

$$n_{rel} = n / n_0 \qquad (13)$$

where n and n_o are the viscosities of the polymer solution and the solvent, respectively. The specific viscosity is defined as (69)

$$n_{sp} = n_{rel} - 1 \qquad (14)$$

from which the intrinsic viscosity [n] is derived using Martin's equation (60).

$$\log (n_{sp}/C) = \log [n] + K' [n] C \qquad (15)$$

A linear plot of $\log(n_{sp}/C)$ against C (polymer concentration) and extrapolation to zero concentration yields [n]. Intrinsic viscosity measurements give an estimate of the viscosity average molecular weight (M_v) through application of the Mark-Houwink equation (70)

$$[n] = K M^a \qquad (16)$$

where K and a are the Mark-Houwink coefficients. An important consideration with this method of molecular weight determination is that these coefficients must be determined for a particular solvent system by calibration with samples of known molecular weight. These constants, therefore, depend on the nature of the polymer, solvent and temperature. These constants for HPC in various solvents have been tabulated (70) and will be presented later.

6. Determination of Molecular Weight Distribution (MWD). The molecular weight distribution of fractionated and unfractionated samples of HPC was determined by GPC analysis (71-72). Four columns, connected in series, containing a semi-rigid polyether gel swollen in water were employed (TSK-PW 3000, 4000, 5000, 6000,

Toya Soda Mfg. Co., Japan). Columns were coupled in order of descending pore size (i.e. smallest pore size last.) The gels were designated by nominal pore sizes of 200 to greater than 1000 angstroms (Å) (73). Flow rate was set at 1 ml./minute and columns were used at room temperature. Solutions having a concentration of 0.2%(w/v) of HPC-H and the polymer standards, pullulan and poly(ethylene oxide) were prepared in triple distilled water. Injections of100 µl. were made into the first column and flushed through with an aqueous mobile phase which had been subjected to degassing prior to use. The columns were calibrated by measuring the retention time of the standards of known molecular weight. Construction of standard curves will be discussed at a later point. The chromatograms resulting from injection of HPC were analyzed manually by using the trapezoid rule to determine the area corresponding to a particular slice under the curve. Using these "area-slices" and the calibration curve data the various molecular weight averages which characterize the MWD were calculated with the help of a computer program described in Appendix 1.

7. Analysis of Polymer Concentration. Several techniques have been reported for measuring the concentration of cellulosic polymers in solution. Among these are viscosity (6), refractive index (52) and colorimetric methods (74-76). The colorimetric procedure described by Kanzaki and Berger (75) was chosen due to ease of adaptability to HPC and reliability; the precision is reported to be 2%.

Prior to each assay the reagent was prepared by dissolving 3.75 grams of colorless diphenylamine crystals (Aldrich Chemical Co., Milwaukee, WI) in 150 ml. of glacial acetic acid. Upon complete dissolution, 90 ml. of concentrated hydrochloric acid was

added and the solution was protected from light. Five (5) ml of this reagent was added to 200 µl of polymer solution in 13 X 100 mm. test tubes. Two hundred (200) µl of water and 5 ml of reagent served as a blank. The tubes were covered with marbles and heated for 45 minutes in boiling water. Immediately following heating, the tubes were cooled for 10 minutes in cold water. Prior to assay, the solutions were quantitativly transfered from the tubes to 10 ml volumetric flasks. The flasks were brought to volume with a mixture of the two acids in the above described proportions. The solutions exhibited a maximum absorbance at 610 nm and were read against the above described blank on a spectrophotometer. Adsorption experiments were analyzed by measuring the absorbance of the polymer solutions before and after being exposed to the solid. The initial solution concentrations were used to construct a calibration curve (Figure 10), which obeyed Beer's law in the concentration range studied. The amount of polymer adsorbed was calculated by subtracting the concentration in the supernatant from the initial polymer concentration.

8. Adsorption Isotherms. Adsorption isotherms for HPC on polystyrene latex and titanium dioxide were measured by mixing 20 ml of polymer solution with a preselected weight of solid in a 50 ml ground glass erhlenmeyer flask. The amount of solid used was chosen to maximize the change in solution concentration. Flasks were stoppered, sealed with Parafilm, and allowed to shake in a thermostated waterbath at 25^{o} C for 24 hours. Subsequent to equilibration, solutions were centrifuged at 20,000g in an ultracentrifuge for 30 minutes at 25^{o} C and the supernatant was

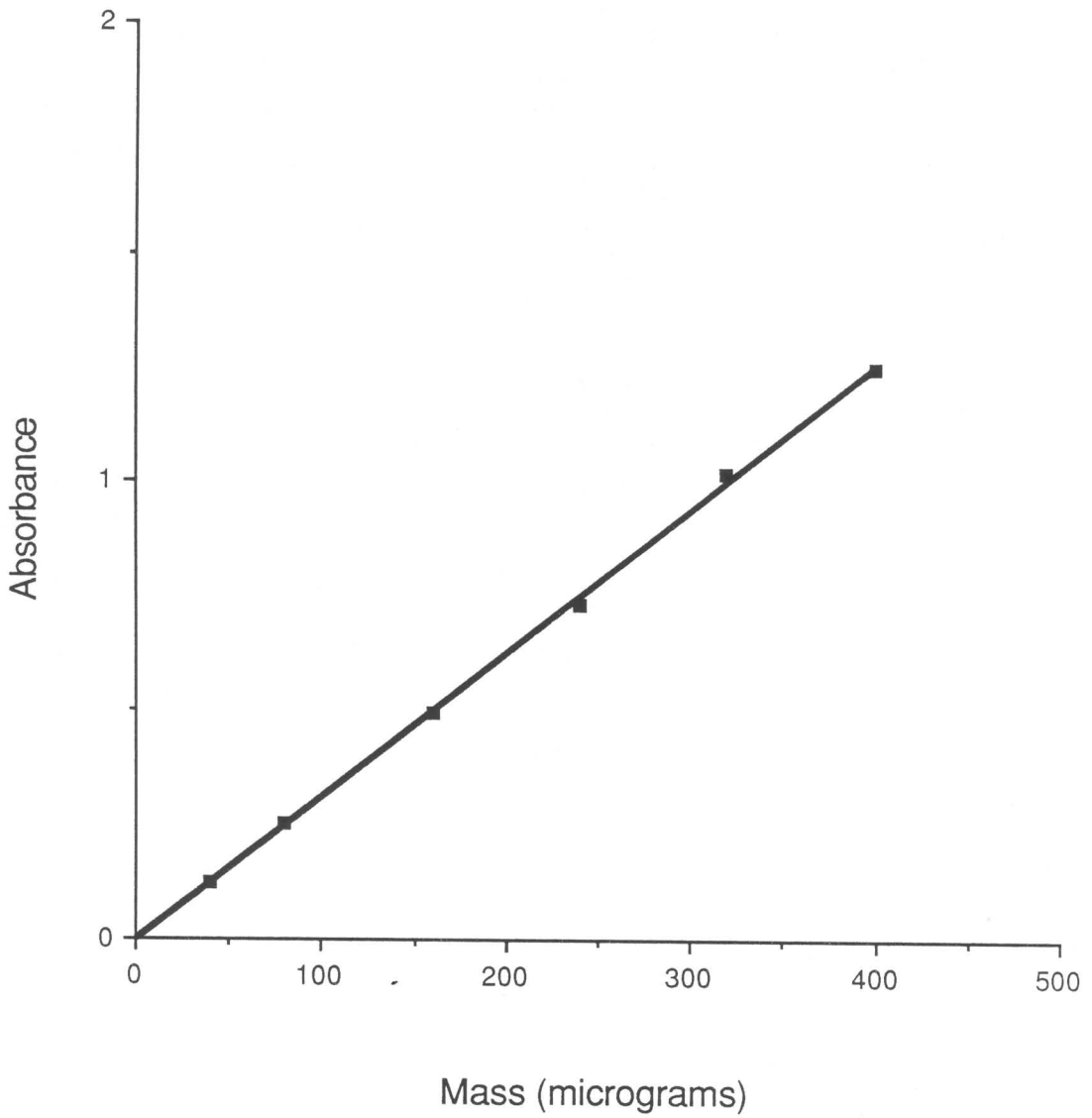


Figure 10. Typical standard curve for hydroxypropylcellulose. Absorbance versus mass of polymer.

subjected to analysis for solute concentration. Equilibrium time was established by measuring the amount of a fixed concentration of polymer solution adsorbed over a 72 hour period. It was found to be within two hours for HPC-H.

IV. Results and Discussion

A. Specific Surface Area

1. Titanium dioxide. The specific surface area of titanium dioxide in the dry state was obtained by measuring nitrogen and krypton gas adsorption and applying the B.E.T. equation. All B.E.T. plots were linear over the relative pressures used. Table 3 lists the specific surface area of the various samples. It can be seen that the surface area obtained using krypton and nitrogen are essentially the same, i.e. about 8 m^2/g. These values seem unaffected by the size of the aggregates used, indicating that the surface area of the primary particles has been measured.

Particle size measurements of titanium dioxide in the wet and dry state, estimated from light scattering and SEM techniques, were converted to specific surface areas using equation 8. The density of titanium dioxide, obtained from liquid pycnometry, was 3.680 $g./cm.^3$ at 25 ^{o} C. A shortcoming of this method of surface area estimation is the assumption that the solid particles are perfect spheres and monodisperse. For the latex beads this is a good assumption as the particles in the micrograph (Figure 8) appear very spherical and quite monodisperse. However, although titanium dioxide appears quite monodisperse the primary particles are clearly not spheres (Figure 7). Because of the non-spherical nature of these particles such surface areas, therefore, are at best only approximate.

Specific surface area measurements were also carried out using liquid phase adsorption of stearic acid, methylene blue and orange-II. The intent of adsorption

Table 3. Surface area of solids determined by various methods.

Technique		Surface Area ($m^2/g.$)	
		Titanium dioxide	PS-Latex
Nitrogen	#170	7.1	-
	Total	7.9	-
Krypton	#170	8.0	-
	Total	7.9	-
S.E.M.*		5.7	8.9
Light Scattering*		4.9	-
Stearic Acid		7.4	-
Methylene blue		5.5	NA
Orange-II		NA	-

* Assumption of spherical particles

NA No adsorption detected

from solution is the same as gas adsorption; i.e. estimation of monolayer capacity of the solid. In adsorption from solution monolayer capacity is determined by studying the relationship between the amount of solute adsorbed and the equilibrium solute concentration. Unlike vapor phase techniques, adsorption from solution requires a few extra considerations (14). First one must consider the possibility of solvent adsorption and competition between solute and solvent for the surface. Another difficulty often encountered when dyes are used is assigning an accurate value to the area occupied by the adsorbed molecule. This area depends on the orientation of the molecule at the surface, which is most often not precisely known for flexible molecules. In addition, highly surface active solutes in solution, and possibly at the surface, may self associate, which serves to further complicate data interpretation. The characteristics of an ideal solute for this purpose have been outlined in the literature (14).

Figure 11 shows the adsorption isotherm from methylene chloride of stearic acid on titanium dioxide. Previous studies (77) give evidence to support the conclusion that stearic acid forms a unimolecular layer upon exposure to a solid such as titanium dioxide. One molecule of a fatty acid is believed to occupy 20.5 $Å^2$ (65) upon adsorption regardless of its chain length, which is consistent with an "on-end" conformation. Thus the plateau of the isotherm in Figure 11 should correspond to monolayer coverage of titanium dioxide with stearic acid. The plateau represents a coverage of about 15 mg. of stearic acid per gram of titanium dioxide, which, when using equations 10 and 11, gives a surface area of 7.4 m^2/g. Depending on where the

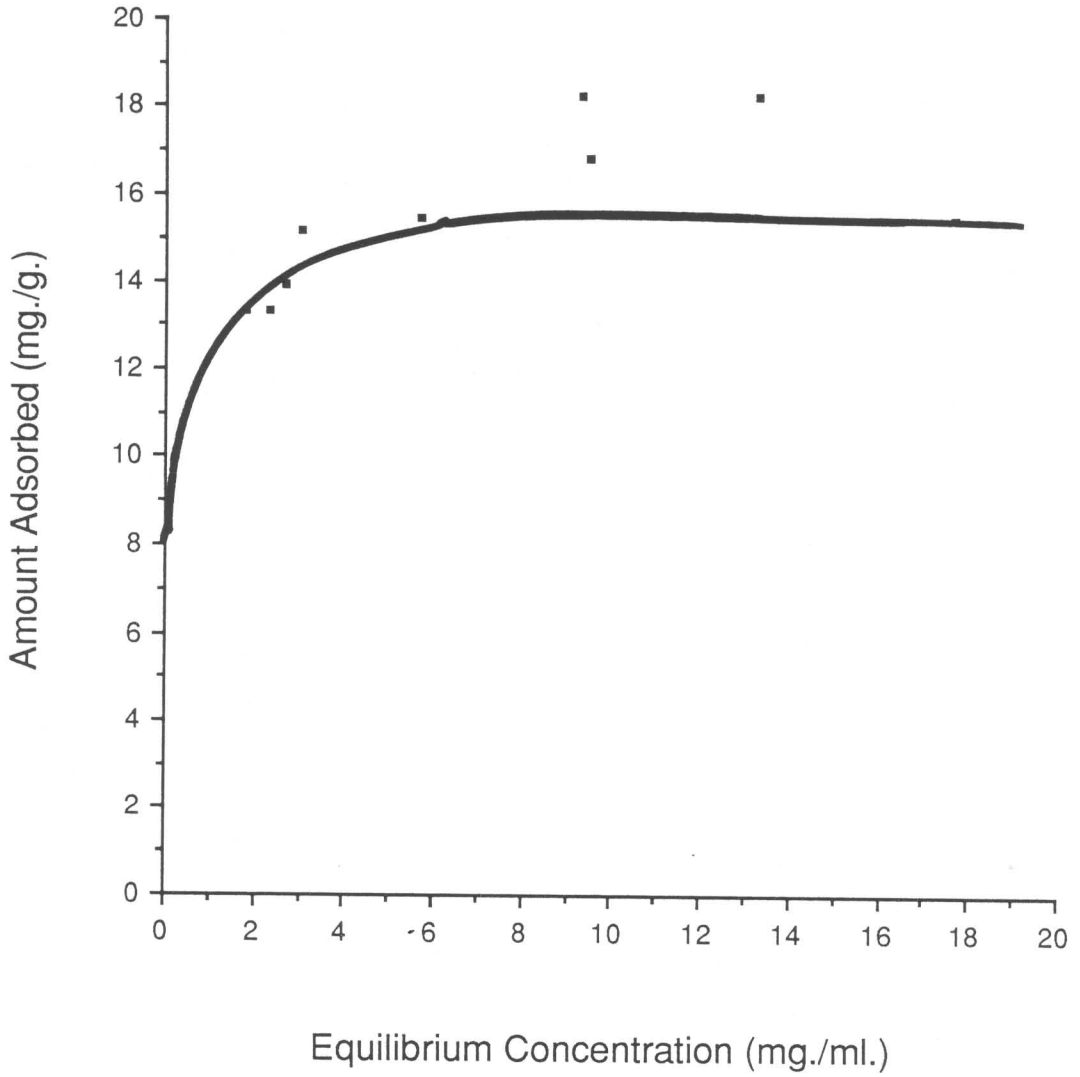


Figure 11. Adsorption isotherm for stearic acid on titanium dioxide from methylene chloride at 25 ^{o} C.

plateau is drawn (15 -18 mg/g) the surface area will range from (6.5 - 7.8 m^2/g).

Methylene blue has been reported earlier to adsorb as an aggregate of molecules (66) necessitating the alteration of equation10 such that

$$S_t = X_m N A_e / n M \qquad (17)$$

where n is a coverage factor representing the average number of aggregated methylene blue molecules (n = 2.0 for m.b.). Several values for A_e, the area occupied by a single molecule adsorbed on the surface, have been reported for methylene blue: 120 $Å^2$ (66), 130 $Å^2$ (78) and 135 $Å^2$ (79). In this work we used the intermediate value of 130 $Å^2$, and as depicted in Figure 12, the plateau shows a coverage of 14 mmol./kg. of solid. This translates into a surface area of 5.5 m^2/g.

Contrary to the work of Ewing and Liu (67), no adsorption of orange-II on titanium dioxide was detected. Instead, adsorption experiments showed a slight increase in concentration, most likely attributable to solvent (water) adsorption. This is not surprising as many solid surfaces acquire a negative charge in water (66), which would not favor the adsorption of a negatively charged dye such as orange-II. Indeed, measurement of electrophoretic mobilities (PenKem 3000, Electrokinetics analyzer) for titanium dioxide in water indicated a net negative charge on the particles. The high surface energy of titanium dioxide certainly would favor the adsorption of polar molecules such as water.

All of the surface area techniques yielded numbers in the range of 4.9 - 8.0 m^2/g. Which of these numbers is most indicative of the surface area available for

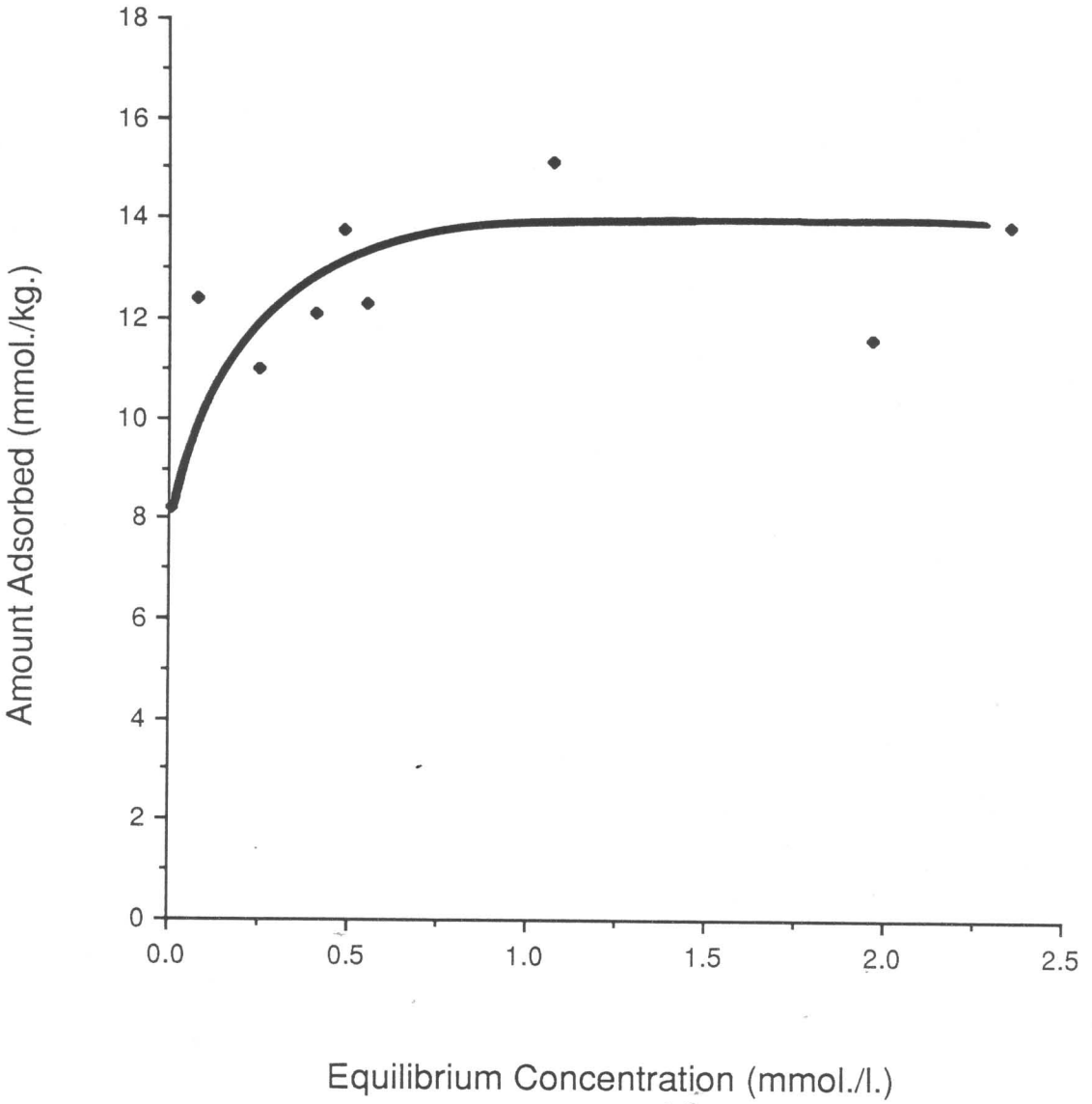


Figure 12. Adsorption isotherm for methylene blue on titanium dioxide from water at 25 ^{o} C.

adsorption? Considering the nonporous nature of titanium dioxide all of the techniques should be equally good in reflecting the true surface area barring uncertainty in the technique and experimental error. All three methods suffer uncertainty to varying degrees. Accuracy of surface area estimates from particle size measurements depend on how close the particles are to true spheres and the degree of monodispersity. The liquid phase methods suffer from the assumption of complete closest packing monolayer coverage at the plateau of the adsorption isotherm. This is not necessarily always true. In addition, problems in assigning a value to the area occupied by an adsorbed molecule serve to further add to uncertainty. For methylene blue the different cross-sectional areas can give surface areas that differ by as much as 7%. Problems, inherent with the use of the B.E.T. equation, in gas adsorption, can give errors on the order of 10-20% (80). With all of these considerations in mind it is the opinion of the author that the surface area of titanium dioxide is best represented by those values obtained using the B.E.T. and stearic acid techniques. In assigning a surface area to titanium dioxide, therefore, a value between 7.1 and 8.0 m^2/g would be most appropriate. The value of 7.6 m^2/g will be used in all subsequent work.

2. Polystyrene Latex. The surface area of the latex calculated from average particle diameters using equation 8 was found to be 8.9 m^2/g. This seems to be an appropriate value to use in view of the spherical and relatively monodisperse nature of these particles (Figure 8). Latex density was measured using a liquid pyconometry technique, described in the literature (81). It was found to be 1.004 $g/cm.^3$. The

latex was also subjected to surface area analysis using the methylene blue technique. However, no adsorption could be detected.

B. Gel Permeation Chromatography.

One of the major limitations of using GPC for molecular weight analysis is that the system must be calibrated with standards of known molecular weight. The most straightforward approach to calibration is to run a series of standards, (which hopefully resemble the characteristics of the sample), and generate a calibration curve over the fractionation range of the column. Ideal primary calibration standards should be monodisperse and available over a wide range of molecular weights. Unfortunately, HPC is a polymer for which standards of a narrow molecular weight distribution (MWD) are unavailable. For the analysis of HPC, chromatograms were run with two polymer standards, PEO and Pullulan, and the log of each molecular weight (as reported by the manufacture) was plotted against the retention time (Figure 13). Table 4 shows the molecular weight and polydispersity indices of the two primary standards used; both standards are of fairly monodisperse character. The use of such standards, however, leads to a major problem because the radius of gyration of the standards is most likely different from that of HPC. As a general rule the radius of gyration increases with increasing molecular weight, and is also dependent on the nature of the polymer species because of differences in steric factors as well as intramolecular interactions. Figure 14 shows a tracing of two chromatograms illustrating the retention time of HPC relative to one of the Pullulan standards. Ideally, standards should be chosen such that their molecular weights fall

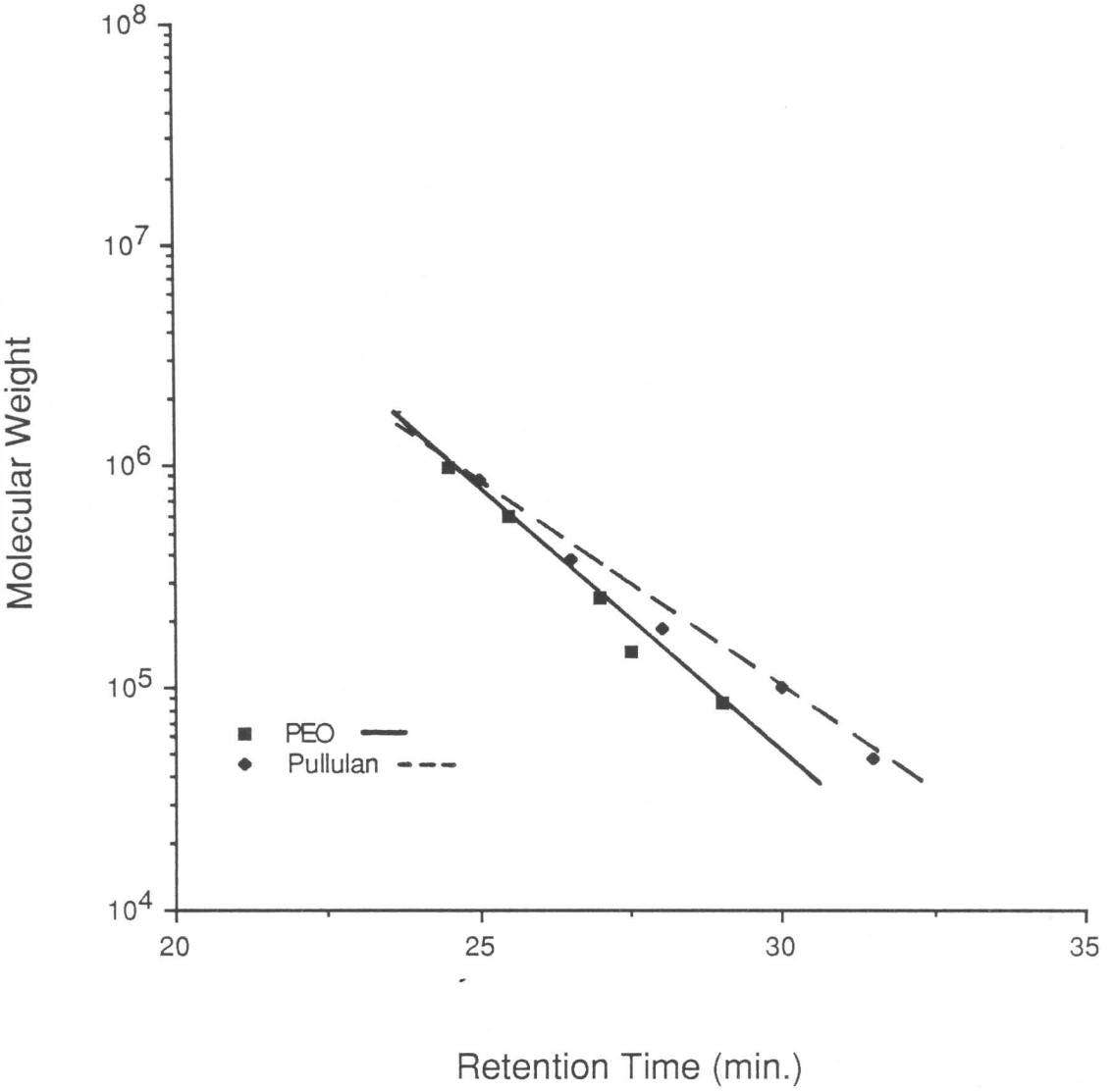


Figure 13. GPC primary calibration curve. Log molecular weight of GPC standards versus retention time.

Table 4. Molecular weights and polydispersity indices (M_w/M_n) for primary standards used in this study.

PEO

Mw*	Mw/Mn
86,000	1.02
145,000	1.03
252,000	1.04
594,000	1.04
996,000	1.05

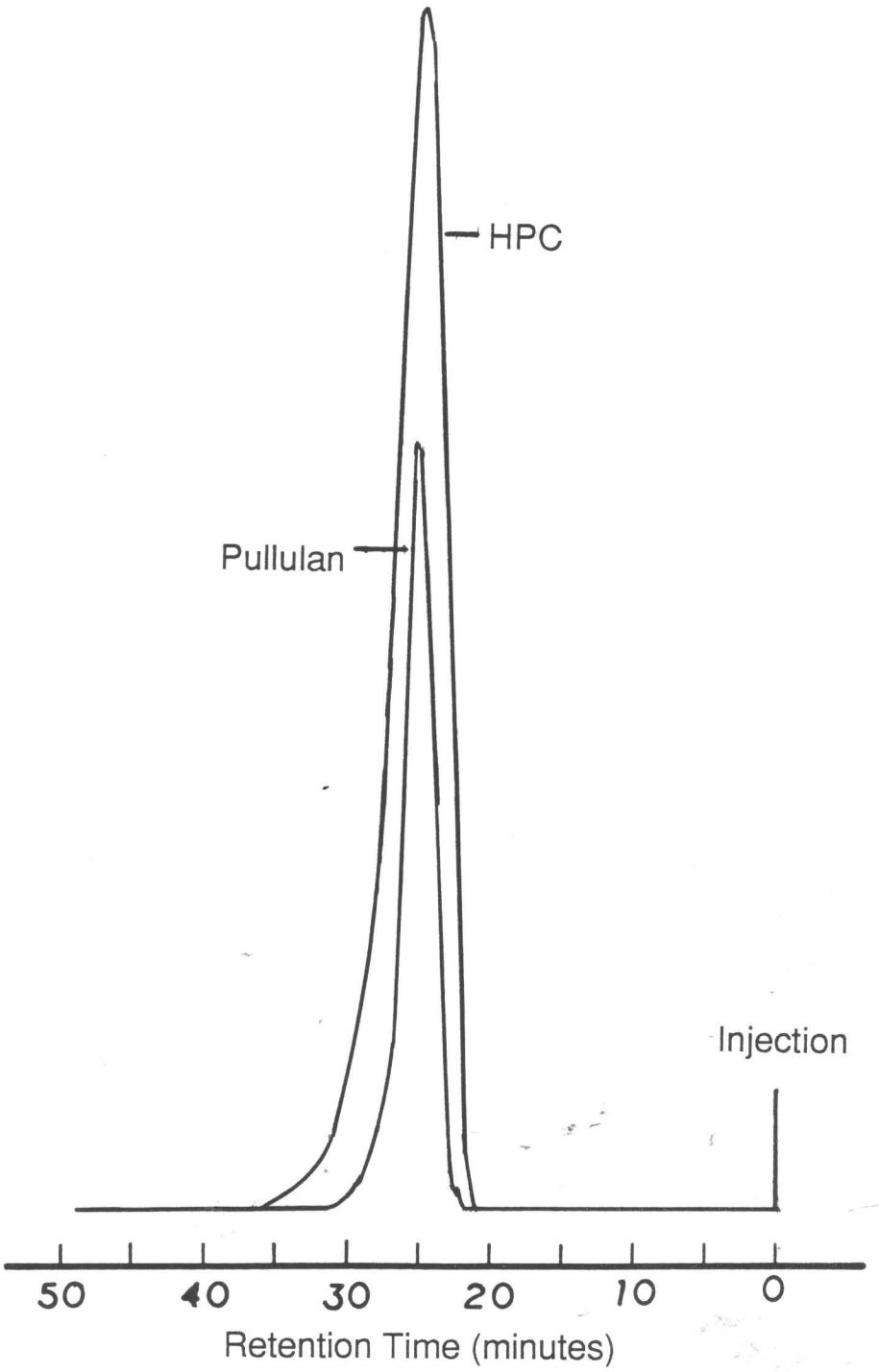
Pullulan

Mw**	Mw/Mn
48,000	1.09
100,000	1.10
186,000	1.13
380,000	1.12
853,000	1.14

* Light Scattering

** Ultracentrifugal Sedimentation

Figure 14. GPC chromatograms for HPC-H (fraction 6) and Pullulan (Mw-853,000).



above and below the anticipated molecular weight of the polymer being analyzed. In the case of HPC-H it would have been better to have a few standards with molecular weights in excess of 1 X 10^6, the nominal molecular weight reported by the manufacturer, however these were unavailable. It is important to realize that the magnitudes of the weight and number average molecular weights, obtained from the calibration curve using such standards, are not necessarily absolute because to some extent they depend on the chemical characteristics of the standard used. The polydispersity ratios, however, can serve as a good indication of the effectiveness of the fractionation procedure. The various molecular weight averages were calculated relative to each of the two standards and are shown in Table 5. Both sets of data show that the unfractionated polymer basically contains two major molecular weight components: (1) fractions 3, 4, 5, and 6; and (2) fraction 1, which seems to be of a much lower molecular weight than the others. This is not surprising as it is a standard practice of manufacturers to add together several molecular weight grades of a polymer to obtain a desired viscosity often used as a product specification.

Comparison of the data in Table 5, generated by subjecting the same chromatograms to calibration curves for PEO and Pullulan, shows that both sets of standards yield similar weight average molecular weights. However, there is a significant difference between the number average molecular weights which is manifested in the polydispersity indices. The reason for this inconsistency is not clear to the author. Overall, the fractionation procedure has served to remove the lower molecular weight component but otherwise has not significantly altered the

Table 5. Weight average and number average molecular weights and polydispersity indicies for HPC-H fractions using polyethylene oxide and pullulan as primary standards.

PEO

Fraction	M_w	M_n	M_w/M_n
1	382,409	24,663	15.5
2	1,309,679	101,015	13.0
3	1,278,949	257,482	5.0
4	1,063,336	224,267	4.7
5	1,338,410	224,114	6.0
6	1,172,165	208,444	5.6
Whole	1,368,129	171,456	8.0

Pullulan

1	399,164	77,514	5.1
2	1,063,535	246,145	4.3
3	1,070,175	439,815	2.4
4	929,687	397,898	2.3
5	1,098,565	419,799	2.6
6	1,000,796	384,481	2.6
Whole	1,114,257	347,005	3.2

MWD of the polymer. More efficient separation of the higher molecular weight components might be accomplished by the use of a different solvent/nonsolvent extraction scheme.

Reporting molecular weights of a polymer relative to a standard of different chemical identity makes comparisons between laboratories virtually impossible. To overcome this problem much work has been devoted to the development of a universal calibration technique (71,82-84), which would be applicable to any given polymer sample. The originators of these various calibration procedures realized that a plot of log molecular weight vs. elution volume (or retention time) was insufficient. What was needed was a calibration plot in which the ordinate reflected the factors controlling separation. Since separation is felt to take place on the basis of differences in hydrodynamic volume, a plot of log([n] M) vs. elution volume should be universal for a given column, temperature and solvent regardless of the standard used. In addition to hydrodynamic volume, other parameters thought to influence separation, such as the polymer's unperturbed dimension, have been used in attempts at universal calibration. The relationship between hydrodynamic volume (V), molecular weight (M), and intrinsic viscosity ([n]) is given by Einstein's equation for spheres.

$$[n] = K\ (V/M) \qquad (18)$$

Although polymers are not generally spherical in shape, this equation does indicate that the product of intrinsic viscosity and molecular weight will give some measure of molecular hydrodynamic volume (82). By plotting the log ([n]M) vs. elution volume

it has been shown that this procedure does indeed provide a linear plot for different types of polymers. This has been done for Pullulan and PEO as shown in Figure 15. Thus for a particular polymer sample, one can assign values of $[\eta]M$ at various points in the chromatogram. It is therefore necessary to know the dependence of intrinsic viscosity on the molecular weight of a sample. This relationship has been described by Mark and Houwink (discussed earlier in equation 16). Using the two Mark-Houwink equations for the standard (1) and the polymer (2) being analyzed

$$[\eta]_1 = K_1 M_1^{a1} \qquad (19)$$

$$[\eta]_2 = K_2 M_2^{a2} \qquad (20)$$

the universal calibration curve for the polymer can be calculated point by point. At a specified elution volume (and thus at a given hydrodynamic volume) the log of the product $[\eta]M$ is the same for any given polymer, thus we can write

$$[\eta]_1 M_1 = [\eta]_2 M_2 \qquad (21)$$

Substituting equations 19 and 20 into 21 it can be shown that

$$\log M_2 = (1/(a_2 + 1)) \log(k_1/k_2) + [(a_1 + 1)/(a_2 + 1)] \log M_1 \qquad (22)$$

Knowledge of the Mark-Houwink constants for the polymer and standard (in the same solvent and at the same temperature as the GPC analysis) allows generation of a secondary calibration curve from the primary calibration curve (Figure 13). Constants for the standards are listed in Table 6 and were used to generate a universal calibration plot for HPC secondary to the PEO and Pullulan standards (Figure 16). The data from both standards were pooled and used to generate the various molecular

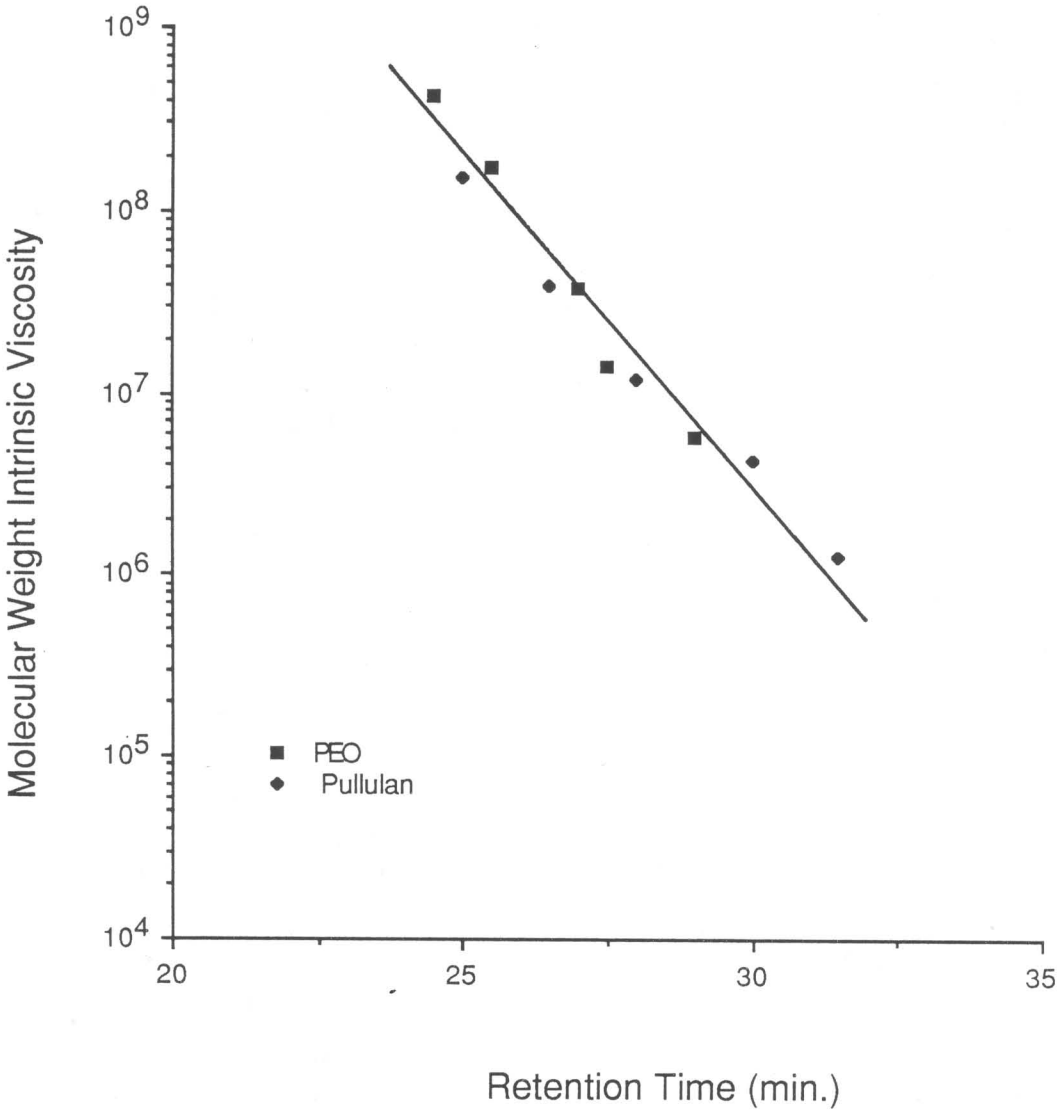


Figure 15. GPC universal calibration curve. Log hydrodynamic volume (molecular weight times intrinsic viscosity) versus retention time for PEO and pullulan.

Table 6. Mark-Houwink constants* for hydroxypropylcellulose, polyethylene oxide and pullulan.

Polymer	K	a	Ref.
HPC	2.6×10^{-5}	0.915	60
Peo	1.19×10^{-2}	0.76	11
Pullulan	1.56×10^{-1}	0.50	86

* Obtained from light scattering measurements

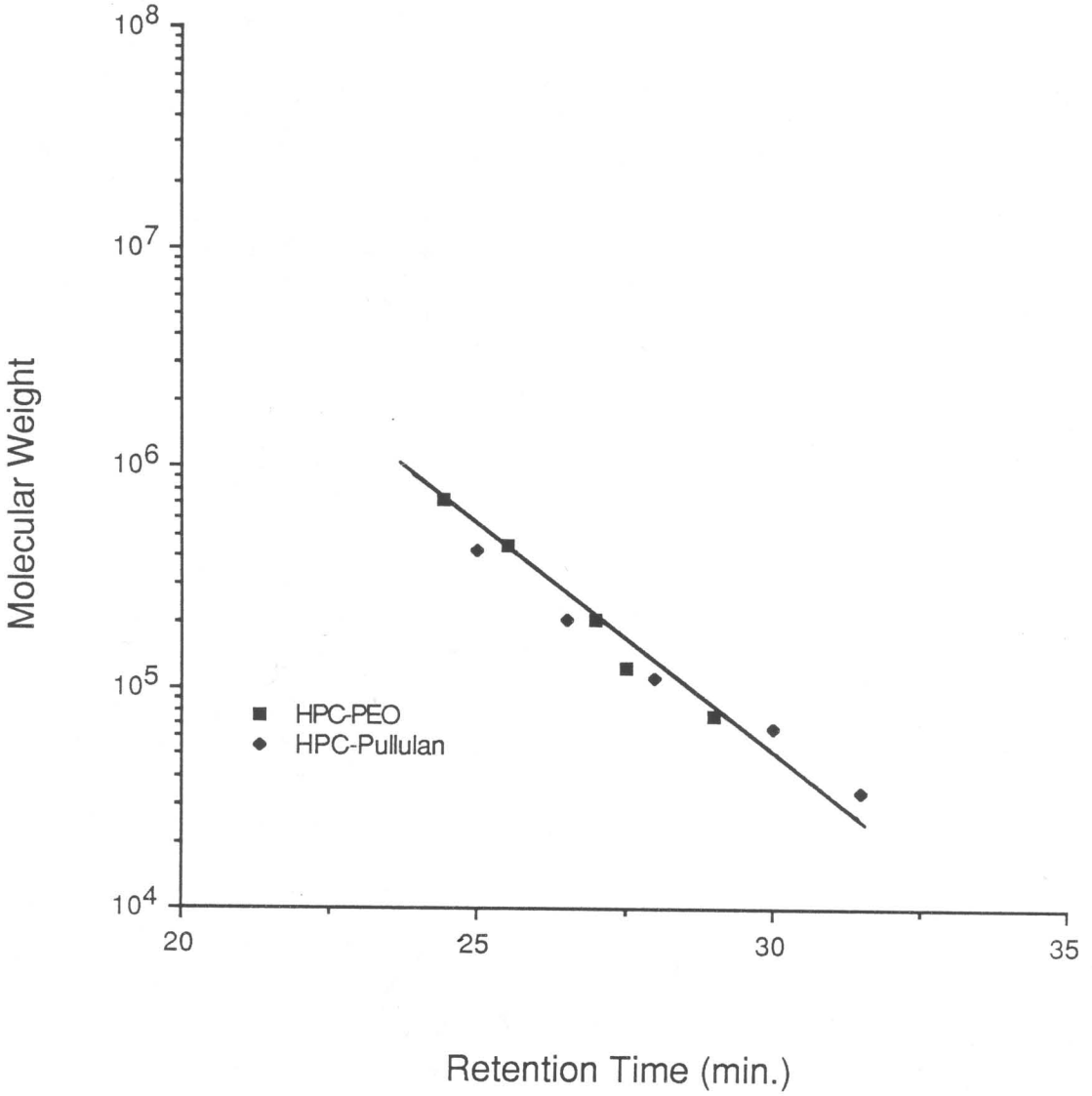


Figure 16. GPC secondary calibration curve. Log molecular weight of HPC (calculated from equation 22 in text) versus retention time.

weight averages listed in Table 7. Comparison of the data in Tables 5 and 7 shows that the universal calibration procedure yields a different molecular distribution for HPC than that reported directly from either standard. The molecular weight distribution as given in Table 7 should be most representative of the true distribution since the data are no longer dependent on the standards used to calibrate the GPC columns.

C. Intrinsic Viscosity Measurements.

Results of intrinsic viscosity measurements on unfractionated and fractionated samples of HPC-H, obtained through application of Martin's equation (60) (Figure 17), are listed in Table 8. Intrinsic viscosities of only a few fractions were measured due to limited sample size. Also listed in Table 8 are the viscosity average molecular weights, M_V calculated from the Mark-Houwink equation (69). The Mark-Houwink constants for HPC are listed in Table 6.

D. Solution Surface Tension

Measurements of the surface tension of unfractionated and fractionated HPC-H (0.2%w/v) gave values of 42.4 dynes/cm, which are in accordance with the literature value of 42.2 dynes/cm reported earlier (28).

E. Cloud Point Determinations

A phase diagram of HPC in water is shown in Figure 18. Both unfractionated and fractionated systems showed a lower critical solution temperature between 42.5 - 45.5^{o} C. The phase diagram confirms the dependence of the lower critical solution temperature (LCST) on polymer concentration and molecular weight. It is interesting to note that the surface tension of HPC solutions is not affected by molecular weight,

Table 7. Weight average and number average molecular weights and polydispersity indices for HPC-H fractions using the universal calibration technique.

Fraction	M_w	M_n	M_w/M_n
1	238,469	48,020	5.0
2	628,855	146,082	4.3
3	633,806	266,269	2.4
4	551,134	236,535	2.3
5	649,824	248,747	2.6
6	593,161	233,368	2.5
Whole	658,670	203,952	3.2

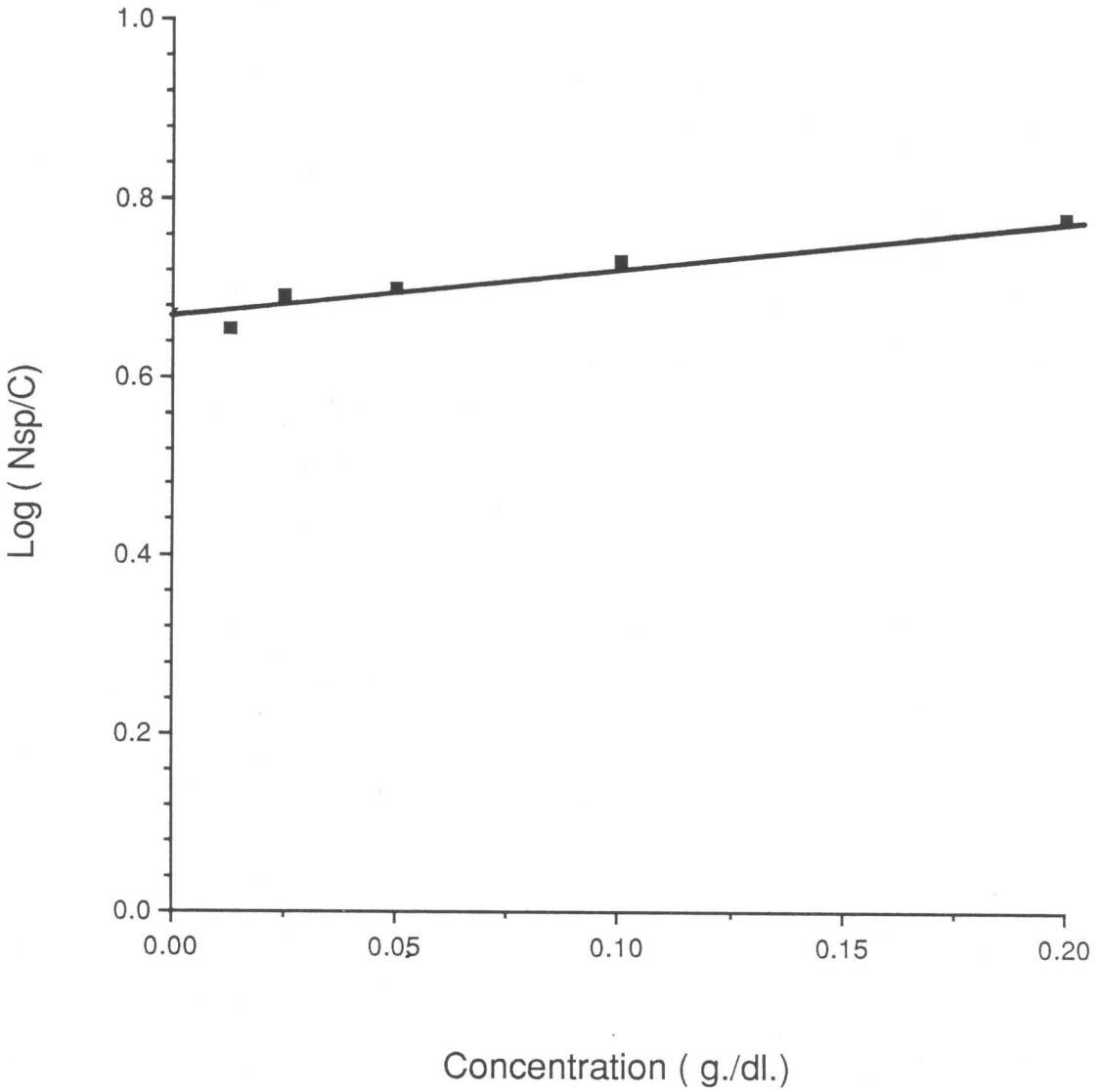


Figure 17. Plot of Martin's equation (equation 15 in text) for unfractionated HPC-H.

Table 8. Intrinsic viscosity and molecular weight for various samples of HPC-H.

Fraction	[η] (dl./g.)	M_V X 10^{-5} *
H-3	7.086	8.7
H-4	7.224	8.9
H-5	7.447	9.2
Unfractionated	4.743	5.6

* calculated from equation 16 in text

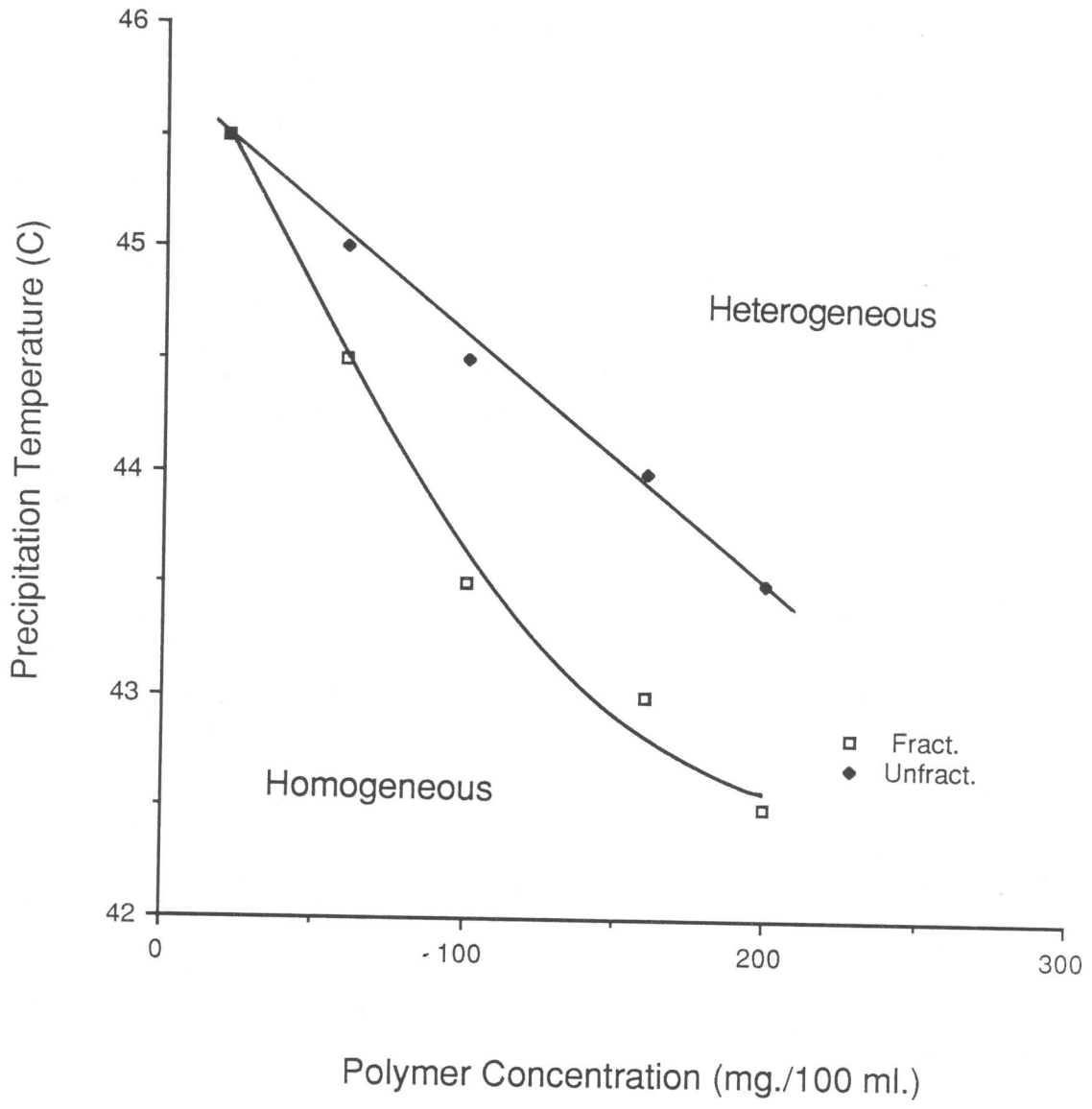


Figure 18. Phase diagram for hydroxypropylcellulose. Precipitation temperature (cloud point) versus solution concentration for unfractionated and fractionated samples.

indicating a somewhat flat conformation for the molecules at the interface. This is consistent with the molecule, which is hydrophobic and tends to minimize its contact with water. Cloud point, however, is apparently sensitive to the presence of the lower molecular weight fractions, as seen by comparing GPC results for the unfractionated and fractionated samples.

F. Adsorption Isotherms with Polystyrene Latexes

Adsorption isotherms for unfractionated and Fraction 3 samples of HPC-H at 25^{o} C., using various weights of polystyrene latex are given in Figures 19 and 20 (data in Tables 9 and 10). Note that the curves are hyperbolic in shape; approaching an apparent plateau with increasing concentration. The mass of unfractionated polymer adsorbed per cm^2 of polystyrene latex is greatest for the 0.5 g. sample, less for the 1.0 g. sample and then less and constant for the 2, 5 and 10 g samples. Likewise, for fraction 3, adsorption on the 2, 5, and 10 g. samples are constant while the 1 g sample shows a higher uptake. Comparing adsorption of unfractionated vs. fractionated samples at the same slurry density reveals that the amount of polymer adsorbed is similar, with that of the fractionated sample being a little higher. For example, at a mass of 1 g. of solid, the unfractionated isotherm appears to be approaching a plateau of 40 - 45 X 10^{-9} g/cm^2 while the fractionated sample reaches a plateau in excess of 50 X 10^{-9} g/cm^2. The same trend, however is not seen at higher slurry densities. For masses of 2, 5, and 10 g. the maximum amount of polymer adsorbed for both samples is constant, at about 25 X 10^{-9} g/cm^2.

Central to the discussion of the adsorption results two issues need to be addressed:

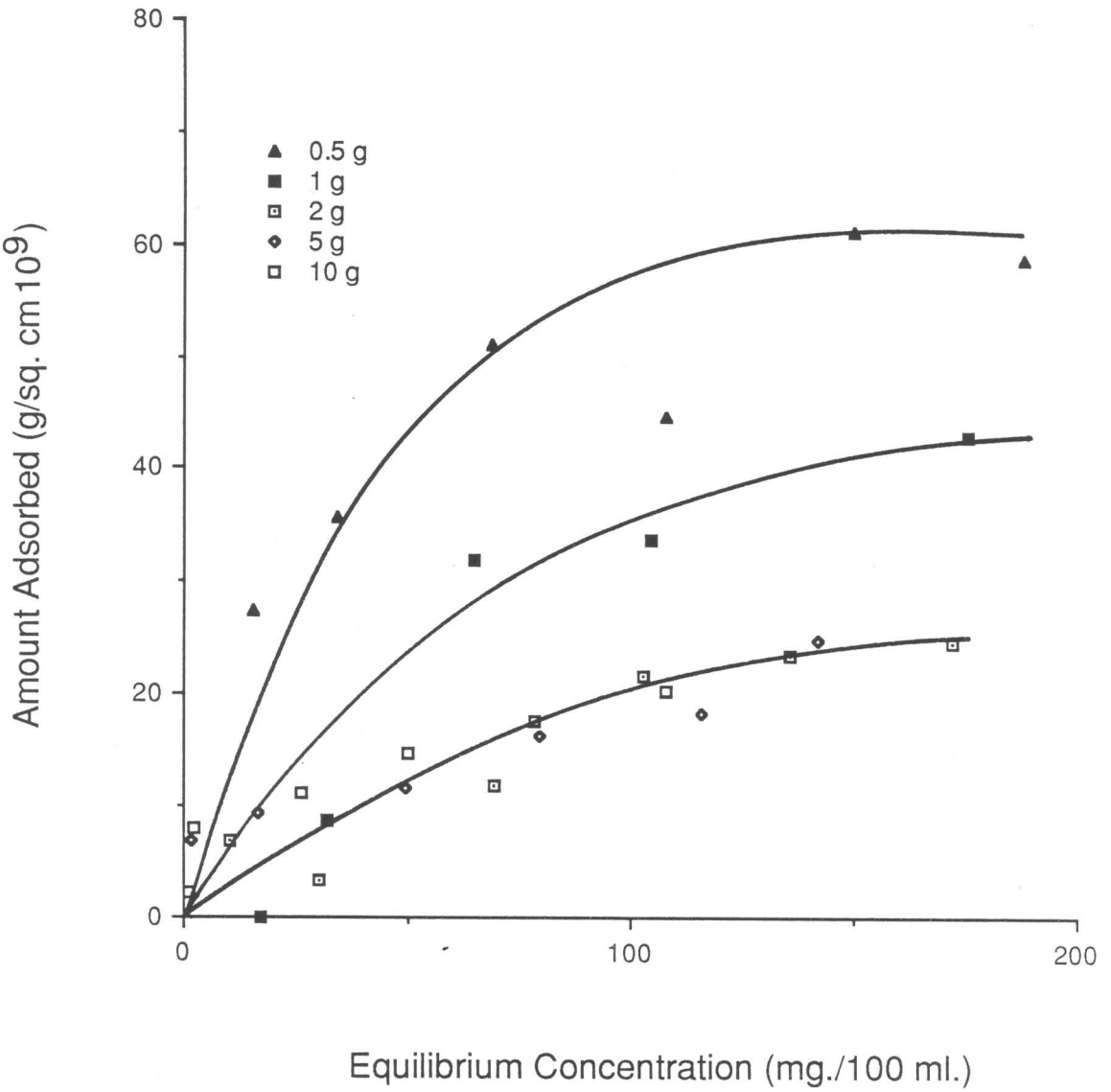


Figure 19. Adsorption isotherms for unfractionated and fractionated HPC-H on polystyrene latex particles for a variety of slurry densities.

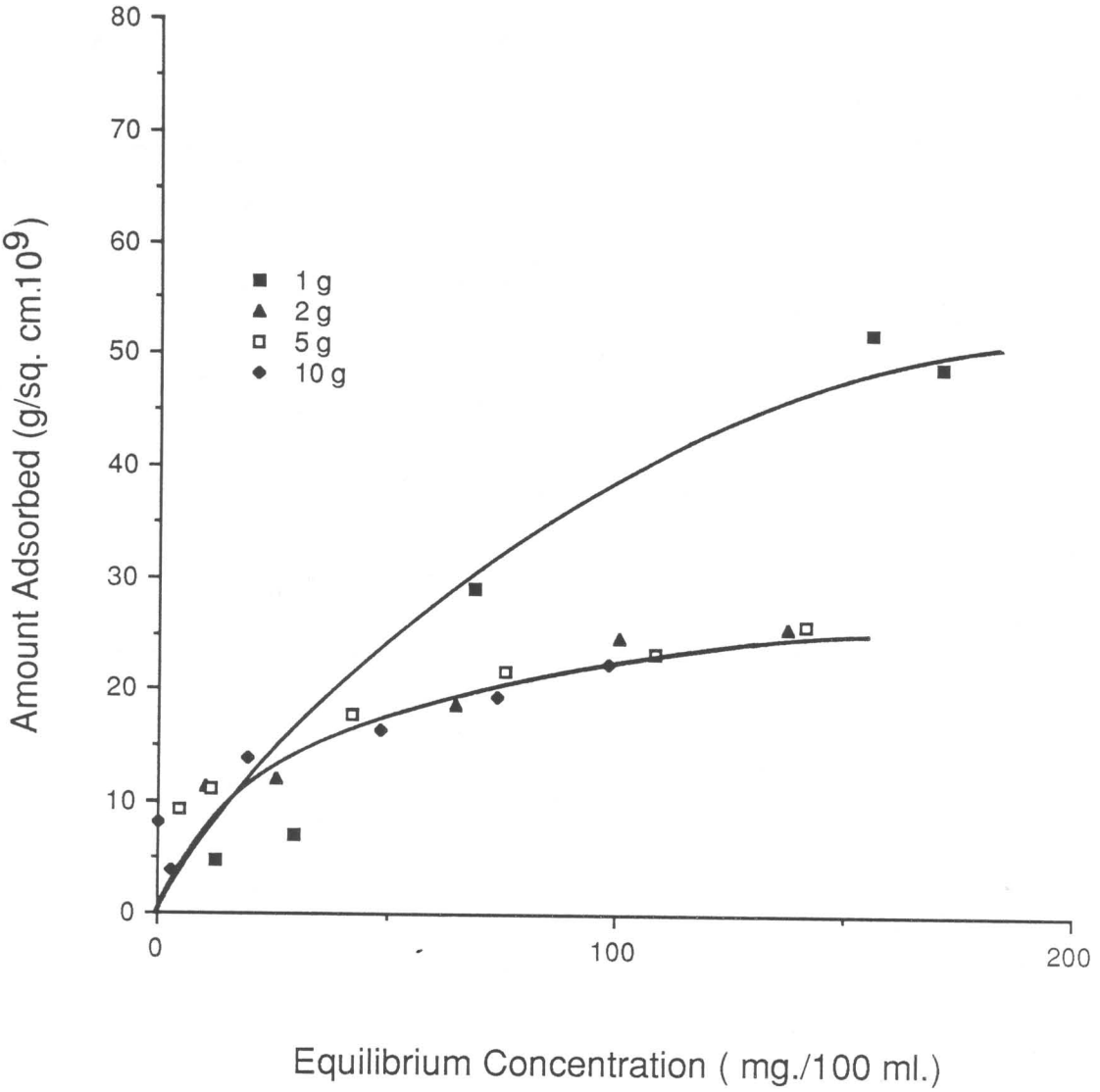


Figure 20. Adsorption isotherms for fractionated HPC-H (fraction 3) on polystyrene latex particles for a variety of slurry densities.

Table 9. Adsorption of unfractionated HPC on polystryene latex for varying amounts of solid.

Amount of Solid (g.)	Equilibrium Concentration (mg/100 ml.)	Amount Adsorbed, A ($g/cm^2 \times 10^9$)
0.5	15.4	27.3
	33.9	35.7
	68.9	51.1
	108.2	44.5
	149.8	61.1
	187.8	58.7
1.0	17.3	0
	31.8	8.6
	64.9	31.9
	104.3	33.6
	175.4	42.7
2.0	10.2	7.0
	30.2	3.4
	69.3	11.9
	103.0	21.6
	136.1	23.5
	172.2	24.5

Table 9. (Continued)

Amount of Solid (g.)	Equilibrium Concentration (mg/100 ml.)	Amount Adsorbed, A ($g/cm^2 \times 10^9$)
5.0	1.8	6.9
	16.3	9.4
	49.7	11.6
	79.4	16.2
	116.3	18.3
	142.6	24.8
10.0	1.1	2.3
	2.0	8.1
	26.4	11.2
	50.1	14.7
	78.4	17.5
	107.8	20.3

Table 10. Adsorption of fractionated HPC (fraction 3) on polystryene latex for varying amounts of solid.

Amount of Solid (g.)	Equilibrium Concentration (mg/100 ml.)	Amount Adsorbed, A ($g/cm^2 \times 10^9$)
1.0	17.3	0
	31.8	8.6
	64.9	31.9
	104.3	33.6
	175.4	42.7
2.0	10.0	11.5
	25.6	12.1
	65.0	18.8
	100.8	24.6
	137.6	25.7
5.0	4.6	9.4
	11.6	11.1
	42.3	17.9
	75.3	21.6
	108.6	23.4
	141.2	25.8
10.0	2.9	3.9
	0	8.3
	19.5	14.0
	48.4	16.5
	73.8	19.5
	98.3	22.4

1. Why is a greater amount of adsorption observed in the presence of a smaller amount of solid, followed by independence with larger latex samples?

2. Several theories of polymer adsorption for **monodisperse polymers** predict a very sharp initial rise, followed by an abrupt change to a constant plateau (26). Why do Figures19 and 20 show isotherms that are more rounded (Langmuir-like) with a more gradual rise to a plateau?

Two factors could possibly give rise to an effect on adsorption per unit area when changing the amount of solid. 1.) Changes in the area available for adsorption and 2.) polymer polydispersity.

It is possible that the adsorption of HPC induces flocculation of the PS -latex, reducing the effective surface area available for adsorption of the polymer. This effect would be greater as the volume fraction of latex present increases. However, several problems exist with such an explanation as the sole reason for these observations. First, no evidence for the occurrence of flocculation was observed with increasing polymer concentrations; e.g. no particles were observed to rise or settle out and no apparent viscosity increase was observed. Second, if flocculation was important, a difference in the amount of adsorption between 2, 5 and 10 g. of solid would be expected because of the increasing volume fraction of latex. Last, the occurrence of flocculation cannot explain the rounded shape of the isotherms.

The rounded isotherms observed in Figures19 and 20, as well as the greater mass of polymer adsorbed for smaller slurry densities, might be explained by polymer polydispersity, known to give rise to surface to volume (S/V) ratio dependence, as

described in the introduction. Since both the unfractionated and fractionated HPC samples used in this study were quite polydisperse such behavior might be expected for both samples. Recalling our earlier discussion, polydispersity effects on adsorption isotherms are attributable to the preferential adsorption of long chain polymers over shorter ones. For small amounts of available solid surface only the larger molecular weight molecules can adsorb, leaving smaller molecular weights in solution. As the surface to volume ratio is increased a greater number of smaller molecules are then able to be accommodated on the surface. This is manifested by a lower total mass of polymer adsorbed per unit area because of the smaller mass associated with each small molecule. As shown by Cohen Stuart, et.al. (26), adsorption data for polydisperse polymers can be normalized with respect to the surface to volume ratio (S/V) used by defining a term A^*, where

$$A^* = C_p\,(V/S) \qquad (23)$$

In essence A^*, with units of mg./m^2, represents the mass of nonadsorbed polymer per unit area and, therefore

$$A_{Total} = A + A^* \qquad (24)$$

where A is the mass of polymer adsorbed per unit area. For a given equilibrium concentration of polymer, therefore, we can estimate the fraction, F, of polymer adsorbed since

$$F = A/A_{Total} \qquad (25)$$

Table 11 lists the fraction of the unfractionated polymer adsorbed at an equilibrium

Table 11. Fraction of Unfractionated HPC adsorbed at various amounts of solid.

Amount of Latex (g)	Amount Adsorbed, $A \times 10^3$	Amount Nonadsorbed, $A^* \times 10^2$	Fraction Adsorbed, F
0.5	2.0	2.2	.08
1.0	3.0	2.1	.13
2.0	4.0	2.1	.16
5.0	8.2	2.3	.26
10.0	18	2.2	.45

concentration of 100 mg./100 ml. with various amounts of solid. We see that as the amount of solid is decreased the fraction of polymer adsorbed decreases. However, the amount of polymer adsorbed on a per unit area basis increases. Figure 21 shows a plot of A (mg/cm^2) versus the term A^* and, indeed as might be expected, the data collapse into one plot which appears to be approaching one plateau value while becoming less rounded relative to Figures 18 and 19. A sharp isotherm would only be expected for adsorption of a monodisperse species. If it were possible to use a smaller S/V ratio, we would expect to see points at even higher A^* fall out on the plateau region. Indeed, it can be argued theoretically that a point can be reached where the amount of solid present is small enough to preclude all molecular weights except the largest molecular component and that this would be the plateau value for Figure 21. Using less solid or more liquid volume, however, proved to exceed the ability of our analytical assay to accurately determine changes in solution concentration due to adsorption.

We have empirically fitted the data in Figure 21 to a hyperbolic equation like the Langmuir equation:

$$A = B(1)\, A^* / (1 + B(2)\, A^*) \qquad (26)$$

to obtain an apparent plateau where B(1) and B(2) are constants related, respectively, to the maximum amount of polymer adsorbed A_m, and an adsorption constant K, such that

$$B(1) = (A_m)\, K \qquad B(2) = K \qquad (27)$$

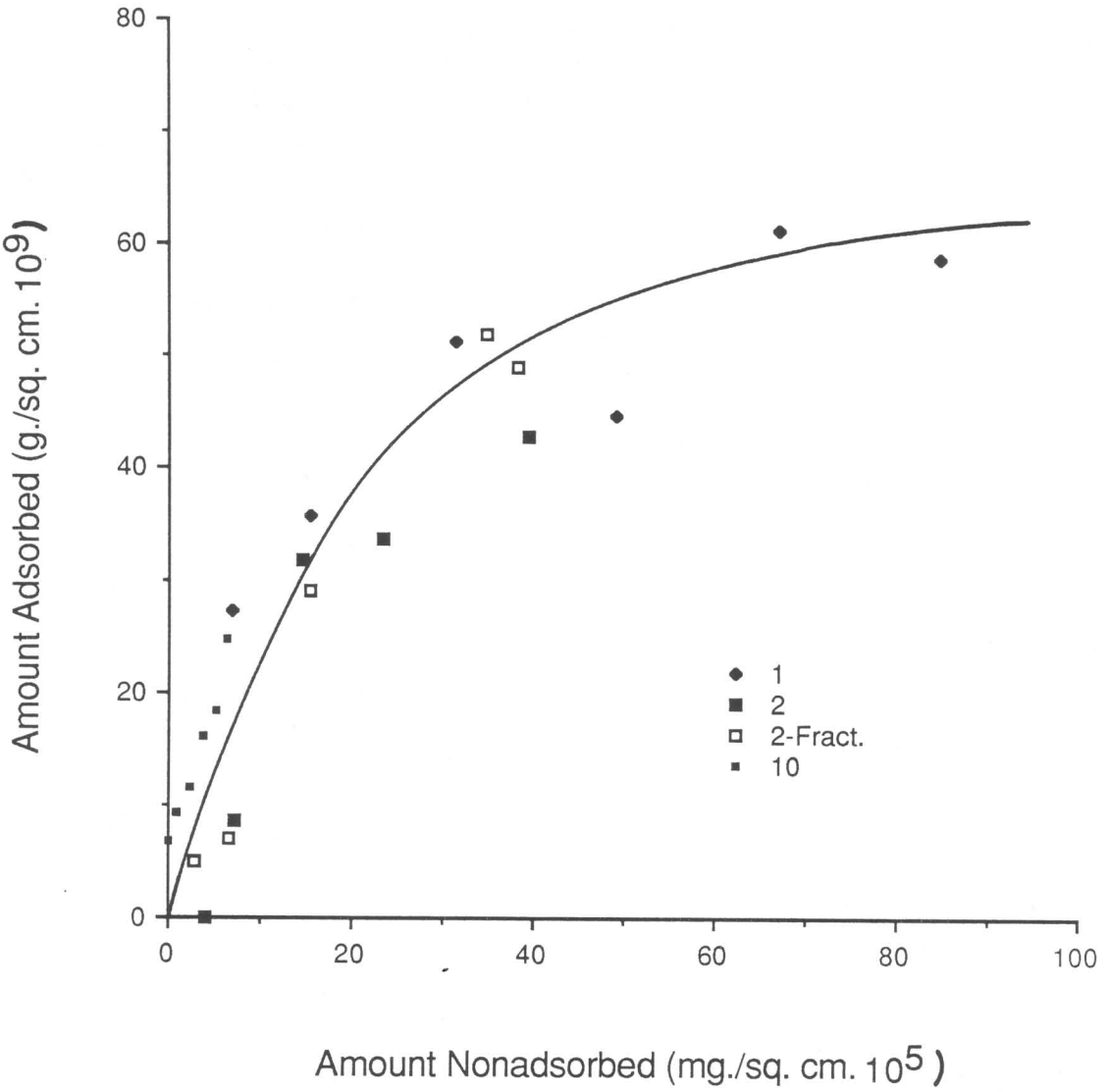


Figure 21. Adsorption isotherms for HPC-H (unfractionated and fraction 3) on polystyrene latex particles corrected for surface to volume (S/V) effects. Line through points was calculated from non-linear regression analysis.

The experimental data were fit to this equation with a nonlinear regression computer program (87). Initial estimates of the two parameters B(1) and B(2) were obtained by a reciprocal plot of equation 26 where 1/A was plotted against $1/A^{*}$ (Figure 22). Nonlinear regression analysis yielded an estimate of 6.5×10^{-8} g/m^2 for monolayer coverage of the surface while the linear plot gave a value of 6.3×10^{-8} g/cm.^{2}. This plateau value is reflective of the theoretical plateau for a monodisperse species spoken of earlier. This tells us, however, that it is impossible to interpret adsorption isotherms for any polymers exhibiting polydispersity of molecular weight on a molecular basis unless one takes the slurry density into account. Such considerations have been addressed in the literature (26) and have been used by Koopal (85) for determining the molecular weight dependence of PVA adsorption on silica, but have been ignored in previous adsorption studies with HPC and other cellulosic polymers (25,52,54).

Given some estimate of a maximum mass of polymer which would be adsorbed in this sample of HPC, it was of further interest to see if the amount adsorbing corresponds to more than monolayer coverage, as suggested by Law and Kayes (54). To see if monolayer coverage was occurring, the amount of HPC necessary to completely cover one square centimeter of surface with a tightly packed monolayer was calculated, using molecular models. Two extreme conformations were considered: 1) the molecule lying flat with maximum points of attachment to the solid surface and 2) an "on-end" conformation consistent with a minimum number of attachment points. The cross-sectional areas for each of these conformations was estimated from

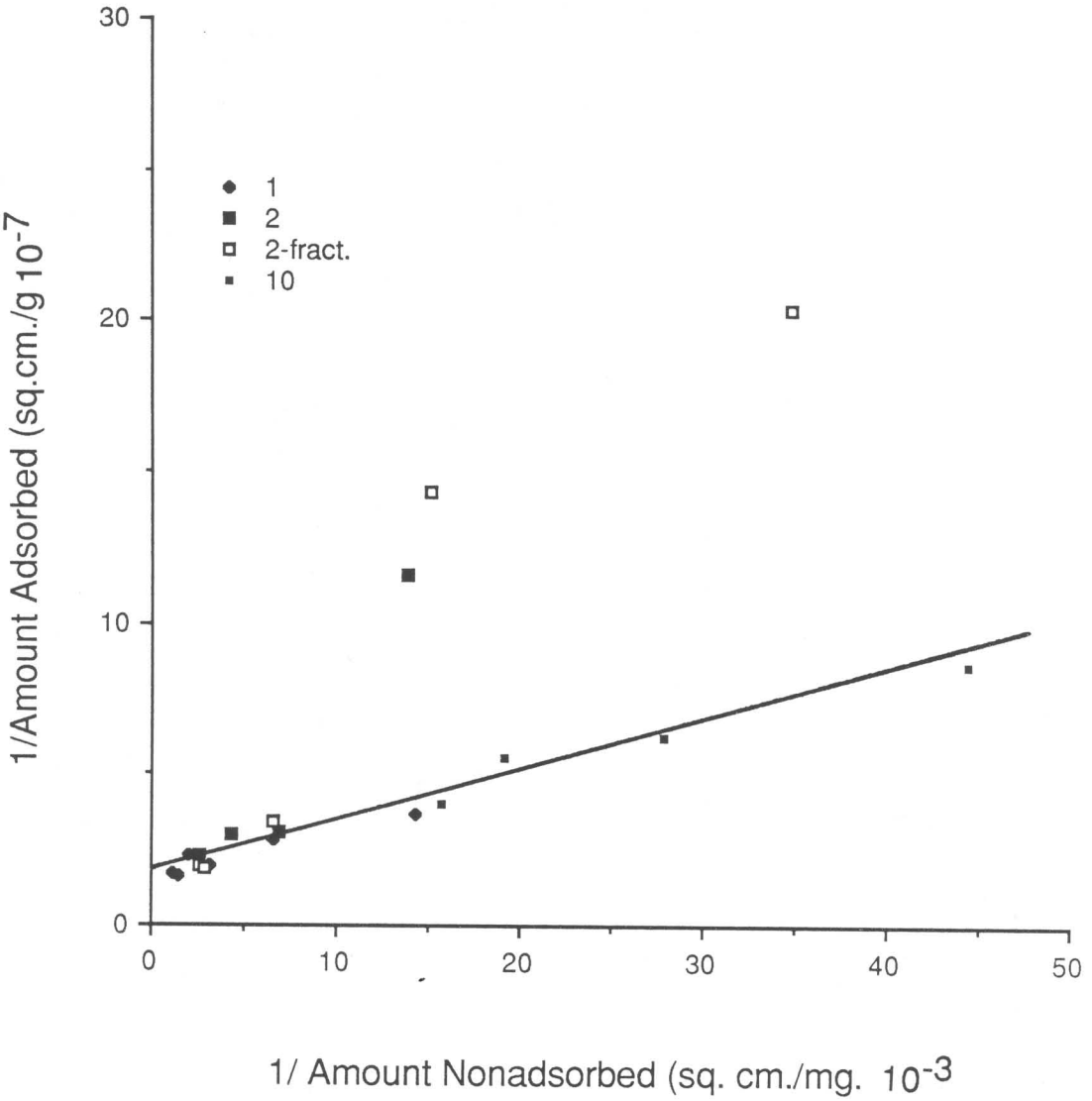


Figure 22. Reciprocal plot of equation 26 in text, used for obtaining preliminary estimates of the non-linear regression parameters.

projections of molecular CPK models (12). Such estimates gave the area per HPC monomer in contact with the surface to be 250 $Å^2$ for the molecule lying flat and 138 $Å^2$ for the "on-end" conformation. Taking the monomer molecular weight as 395 and using the viscosity average molecular weight of the unfractionated HPC-H sample (560,000) values for the maximum amount of polymer adsorbed at a closest packing monolayer were determined. These were found to be 2.6 X 10^{-8} g/cm^2 and 6.7 X 10^{-5} g/cm^2 in the lying down and "on-end" conformations respectively. The experimental value of 6.5 X 10^{-8} $g./cm.^2$ obtained from the data in Figure 21 is well within an order of magnitude of the calculated value of 2.6 X 10^{-8} g/cm^2 for HPC in a flat conformation on the solid surface. Such a relatively flat conformation might be understood by recognizing that the hydrophobic polymer most likely prefers to minimize its contact with the polar solvent water. While the experimental and calculated values are in reasonably good agreement, it would be unlikely that HPC actually forms a true close packed monolayer. Instead a certain degree of looping and tailing would be anticipated such that the surface would not be completely covered. Considering the nonpolar latex surface one might expect that the molecules in the polymer chains would align themselves with the hydrophobic propyl groups at the surface leaving the anhydroglucose portion of the monomer unit directed out into the bulk solution. Unfortunately adsorption data alone and the calculation performed above can provide no information about the orientation of the polymer molecule or the number of segments attached to the surface. Information independently determined on the fraction of segments in contact with the solid and the thickness of the adsorbed

layer could lead to a better understanding of the conformation of the adsorbed molecule.

G. Adsorption of HPC on Titanium Dioxide

Adsorption experiments were performed on titanium dioxide using surface to volume ratios of 1 and 10. **No adsorption** was detected in any of the experiments. Instead, a slight increase in the polymer concentration after exposure to the solid was observed, evidence of possible preferential solvent adsorption. The lack of adsorption for titanium dioxide relative to significant adsorption on the polystyrene latex can be easily understood by considering the factors which would be expected to control adsorption. The first is related to the polar nature of the chemical groups exposed on the surface of the solid. Solids such as titanium dioxide possess highly polar groups exposed at the surface which contribute to high bond energies. Such polarity would favor strong adsorption in an attempt to satisfy the unbalanced forces at the interface. The polar nature of the solid, however, can also be a deterrent to adsorption as it apparently is in the case of titanium dioxide. Solids of high polarity will have a strong affinity for polar solvents. The interaction between these two polar species (solid and solvent) would be expected to far outweigh the second effect favoring adsorption, namely the hydrophobic effect. Considering the high surface energy of titanium dioxide it is easy to understand the preferential adsorption of water over the hydrophobic HPC polymer.

V. Summary and Conclusions

1. An attempt was made to measure the surface area of titanium dioxide by a variety of means presented in the literature. Good agreement was seen between krypton and nitrogen gas adsorption with application of the B.E.T. equation and adsorption of stearic acid from methylene chloride. Adsorption of methylene blue from aqueous solution and particle size analysis produced significantly lower values.

2. Attempts to fractionate one sample of HPC were successful in eliminating a significant small molecular weight fraction, possibly blended in by the manufacturer to meet viscosity specifications. However, the procedure used was unable to significantly affect the average molecular weight, nor reduce the extent of polydispersity for each fraction.

3. In general the adsorption of unfractionated and fractionated samples of HPC-H are similar, both being highly sensitive to the total surface area available for adsorption. The strong dependence of the amount adsorbed on surface to volume ratio appears to be due to polydispersity of the polymer samples. Such polydispersity also serves to explain the roundness of the adsorption isotherms. It was possible to obtain one set of data for adsorption independent of S/V ratio using the method of Cohen Stuart et. al. (26).

4. The polarity of the solid surface and extent of hydrophobicity of the polymer strongly dictates the degree of polymer adsorption. Titanium dioxide, apparently due

to its high surface polarity and strong hydration, shows no adsorption of HPC while the relatively nonpolar polystyrene latex shows adsorption on the order of that calculated for monolayer coverage.

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Appendix 1. Computer Program for Polymer Molecular Weight Distribution Analysis.

```
]LIST

5  REM  LINES 80-490 ARE FOR LINE
     AR CAL.
10  REM  LINES 500-595 ARE FOR ST
     ATS ON
15  REM  STD. CURVE
18  REM  LINES 600-1199 ARE FOR C
     ALC. MWD
20  PR# 1
40  PRINT "MWD 2 "
42  PRINT
45  PRINT "CREATED BY EUGENE MCNA
     LLY AUGUST 1986 "
47  PRINT
50  PRINT "THIS PROGRAM WILL CALC
     ULATE THE MOL. WT. DISTRIBUT
     ION OF POLYMERS FROM GPC DAT
     A"
51  PRINT
52  PRINT "AREA IS ESTIMATED USIN
     G THE TRAPEZOID RULE "
55  PRINT
58  PR# 0
59  INPUT "ENTER DATE ";D$
60  PRINT "ENTER DATA FOR GPC CAL
     IBRATION"
65  PRINT
80  PR# 0
81  INPUT "NAME OF STANDARD USED
     ? ";P$
85  INPUT "NO. OF POINTS ON CALIB
     RATION CURVE? ";N
90  DIM A(N),E(N),B(N)
100  FOR X = 1 TO N
110  INPUT "ENTER RT,MW OF STDS "
     ;A(X),E(X)
120  NEXT X
```

```
130  PR# 0
135  PRINT "CHECK DATA FOR MISTAK
     ES"
140  PRINT "LINE"; SPC( 3);"RT"; SPC(
     3);"MW"
150  PRINT
160  FOR X = 1 TO N
170  PRINT X; SPC( 6);A(X); SPC(
     3);E(X)
180  NEXT X
210  INPUT "ANY CORRECTIONS TO DA
     TA? Y/N ";Z$
220  IF Z$ = "N" THEN 350
230  INPUT "LINE # FOR CORRECTION
     ";X
240  INPUT "NEW RT,NEW MW ";A(X),
     E(X)
250  GOTO 210
350  PR# 1
351  PRINT "DATE ";D$
355  PRINT "LINEAR CALIBRATION CU
     RVE DATA "
356  PRINT "STANDARD USED WAS "P$

360  PRINT "RT"; TAB( 9);"MW"
400  FOR X = 1 TO N
410 B(X) =  LOG (E(X))
420 A1 = A1 + A(X)
430 B1 = B1 + B(X)
440 A2 = A2 + (A(X) * A(X))
450 B2 = B2 + (B(X) * B(X))
460 C = C + (A(X) * B(X))
470  PRINT A(X); TAB( 9);E(X)
490  NEXT X
500 U1 = C - (A1 * B1 / N)
510 U2 = A2 - ((A1 ^ 2) / N)
520 S = U1 / U2
530 U3 = B2 - ((B1 ^ 2) / N)
535  PRINT "----------------"
540  PRINT "SLOPE=",S
550 I = (B1 - (S * A1)) / N
560  PRINT "INTERCEPT=",I
```

```
570 U4 = (U2 * U3) ^ 0.5
580 U5 = U1 / U4
582 U6 = (S ^ 2) * U2
584 U7 = U3 - U6
586 U8 = U7 / (N - 2)
588  PRINT "S YX ^2=";U8
590  PRINT "CC=",U5
591  PRINT "S(X-X)^2=";U2
592  PRINT "AVERAGE X= ";A1 / N
595  PRINT "N=";N
596  PR# 0
597  LET N = 100
599  DIM T(N + 1),Y(N + 1),R(N),D
     (N),Z(N),M(N)
600  INPUT "ENTER NAME OF POLYMER
      BEING ANALYZED ";H$
601  INPUT "ENTER # OF AREA SLICE
     S ";N
602  REM  D IS AREA, T IS RT, R I
     S RT AT MIDPOINT OF SLICE, M
      IS MOL. WT.
603  INPUT "ENTER WIDTH (CM.) OF
     AREA SLICE ";F
604  INPUT "ENTER RT (MIN.) OF AR
     EA SLICE WIDTH ";K
610  INPUT "ENTER RT (MIN.) CORRE
     SPONDING TO BEGINNING OF POL
     YMER PEAK ";G
615  FOR X = 1 TO N + 1
620  INPUT "ENTER HT (CM.) TO POL
     YMER CURVE ";Y(X)
630 T(X) = G + K * (X - 1)
635  NEXT X
640  PRINT "CHECK DATA FOR MISTAK
     ES"
645  SPEED= 10
650  PRINT "LINE"; TAB( 7);"RT"; TAB(
     11);"HT. TO PEAK"
660  PRINT
670  FOR X = 1 TO N + 1
680  PRINT X; TAB( 7);T(X); TAB(
     15);Y(X)
```

```
690  NEXT X
710  INPUT "ANY CORRECTIONS TO DA
     TA? Y/N ";A$
720  IF A$ = "N" THEN 746
730  INPUT "LINE # FOR CORRECTION
      ";X
740  INPUT "ENTER NEW PK. HT. (CM
     .) ";Y(X)
745  GOTO 710
746  FOR X = 1 TO N
747 R(X) = (T(X + 1) + T(X)) / 2
748 D(X) = 0.5 * (Y(X) + Y(X + 1)
     ) * F
750  NEXT X
755  SPEED= 255
760  PR# 1
761  PRINT
762  PRINT
763  PRINT H$
765  PRINT "RT"; TAB( 7);"AREA"
770  PRINT
775  FOR X = 1 TO N
780  PRINT R(X); TAB( 7);D(X)
785  NEXT X
800  FOR X = 1 TO N
810 Z(X) = R(X) * S + I
815 M(X) =  EXP (Z(X))
820  NEXT X
900  FOR X = 1 TO N
910 D2 = D2 + D(X)
920 W1 = D(X) * M(X)
930 W2 = W2 + W1
940 V1 = D(X) / M(X)
950 V2 = V2 + V1
960 W3 = D(X) * M(X) * M(X)
970 W4 = W4 + W3
980  NEXT X
985 H =  SQR ((W2 / V2) - ((D2 /
    V2) ^ 2))
```

```
990  PRINT
995  PRINT
1000  PRINT "WT.AVG MW = ";W2 / D
     2
1010  PRINT "NO.AVG MW = "D2 / V2

1015  PRINT "MW/MN = ";(W2 * V2) /
     (D2 * D2)
1020  PRINT "Z AVG. MW = ";W4 / W
     2
1022  PRINT "MOL. WT. STD.DEV. =
     ";H
1025  PRINT
1027  PRINT
1030  PRINT "RT"; TAB( 9);"MW/SLI
     CE"; TAB( 26);"%AREA"; TAB(
     45);"CUM.%AREA"
1040  FOR X = 1 TO N
1050  REM  D3= % OF TOTAL AREA
1060 D3 = (D(X) / D2) * 100
1070  REM  D4 = CUMULATIVE % AREA

1080 D4 = D4 + D3
1090  PRINT R(X); TAB( 9);M(X); TAB(
     26);D3; TAB( 45);D4
2000  END
```