ADSORPTION OF POLYMERS ONTO POLYMETHYLMETHACRYLATE

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ABSTRACT

The equilibrium adsorption and rate of adsorption of poly-

vinyl alcohol, methylcellulose, and hydroxypropylmethylcellulose

from aqueous solutions onto polymethylmethacrylate powder were

studied. Langmuir type adsorption isotherms were observed in

all three cases. The maximum amount of polymer adsorbed per

gram of polymethylmethacrylate followed the order methylcellu-

lose > polyvinyl alcohol > hydroxypropylmethylcellulose. The

rate of adsorption, however, followed the order polyvinyl

alcohol $\geq$ hydroxypropylmethylcellulose > methylcellulose. The

apparent difference in the order of the extent and rate of

adsorption was related to the proposed configuration of the

adsorbed polymer molecules on the polymethylmethacrylate and
the flexibility of the adsorbed molecules.

INTRODUCTION

Currently, wetting solutions are used to coat the rigid
contact lens in order to reduce the foreign body sensation in
the eye upon the insertion of the rigid lens. As wetting
phenomena is related to surface tension lowering, usual discus-
sions of the mechanism of wetting involve the role played by
surface active agents in reducing the interfacial tension
between the lens and the tear fluids. However, wetting solu-
tions usually contain one or more polymers whose function is not
related to surface tension lowering. These polymers, which are
hydrophilic in nature, tend to absorb onto the lens surface,
thereby altering the hydrophobic nature of the lens itself.
Consequently, polymers which possess the correct molecular size
and/or configuration can actually effect wetting through adsorp-
tion onto the rigid contact lens.

Wetting through adsorption is a phenomena which must be
considered in rigid lens care solution design. Utilization of
this type developmental technique for rigid lens wetting solu-
tion design seems only logical since wetting through adsorption
is a naturally occurring process in the formation of the human
precorneal tearfilm. **Studies regarding understanding of this**
tearfilm phenomena and its importance have been conducted[1] and

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applied to additive tear solution design by various workers[2-5].

Through further study and use, adsorption studies may assist in

the definition and solvation of observed clinical signs of

inadequate rigid lens wetting solution design. These signs

appear as noncontinuous films on the lens while in the eye,

blurring of vision during wear, and the contact lens induced

syndrome known as "3 and 9 o'clock" staining. The objective of

this study is to determine the extent and rate of adsorption of

several polymers commonly used in wetting solutions onto poly-

methylmethacrylate.

METHODS

Polymethylmethacrylate granules (Rohm and Haas) were

crushed and ground in a hammer mill in three stages. The

granules were first mixed with dry ice and liquid nitrogen and

fed slowly into the mill which had a size 2A screen. After the

milled powder was collected it was mixed with dry ice and liquid

nitrogen again. A size 2 screen was put on the mill and the

powders were fed into the mill again and milled. In the third

stage a screen of 50 mesh was used and the powders collected

from the second milling were milled again.

The fine powder resulting from the milling procedure was

washed with distilled water until the last four washings showed

a constant low absorbance reading (0.02) in the ultraviolet

spectrum (Cary Model 17). The last washing was retained for use

as the solvent in the preparation of polymer solutions. Follow-

ing the final washing, the polymethylmethacrylate powder was
dried in a vacuum oven at $30^{o}C$ and 28 mmHg for 36 hours.   The
dry powder was stored in a vacuum desiccator prior to use.   The
surface area of the powder was determined to be 0.8 meter^{2}/gram.

Preparation of Polymer Solutions

Solutions of methylcellulose 1500 cps (Fisher), hydroxy-
propylmethylcellulose (Methocel 65 HG, 1500 cps), and poly-
vinyl alcohol (Gelvatol 20-90 BP) were prepared using the final
washing as the solvent.   The solution concentrations were 0.1,
0.2, 0.4, 0.6, 0.8, 1.0, 1.5, and 2.0 grams/liter for each
polymer.

Calibration Curves of the Polymer Solutions

The relative refractive index of five different solutions
of each polymer was determined in an interferometer (Hilger &
Watts) using the last washing as reference.   The interferometer
readings of these solutions were plotted against the solution
concentration.   A straight line,   which passed through the
origin, was obtained for each polymer solution.

The Equilibrium Adsorption Study

Five grams of the dry polymethylmethacrylate powder was
weighed to the nearest 0.1 mg into each of nine 50 ml volumetric
flasks.   Twenty-five ml of a polymer solution of each concentra-
tion were added to eight of the above flasks with a volumetric
pipette.   Twenty-five ml of wash water were added to the ninth
flask.   All nine flasks were put in a constant temperature

water bath which was set at 37°C and allowed to equilibrate for
24 hours. The flasks were agitated vigorously at 30 minute
intervals during the first 4 hours and every hour or two
thereafter. After 24 hours, 10 ml of solution were taken from
each flask through a 0.45 micron millipore filter (Millipore
Type HAWP) while the flasks were still in the water bath. The
polymer concentrations in the filtered samples were determined
with the interferometer. The interferometer reading of the
polymer solution prior to addition of the polymethylmethacrylate
adsorption was also taken and the original concentration veri-
fied. The difference in concentration of polymer solution
before and after adsorption was calculated as the difference
between the two readings and converted into the amount of
polymer adsorbed per gram of polymethylmethacrylate.

Kinetics of Adsorption

Polymer solutions of polyvinyl alcohol, methylcellulose,
and hydroxypropylmethylcellulose containing 2.0 g/l were pre-
pared using the polymethylmethacrylate wash water as the solvent.
Approximately 5 grams of the dry polymethylmethacrylate powder
were weighed to the nearest 0.1 mg and placed into each of five
50 ml volumetric flasks. The five flasks containing the poly-
methylmethacrylate powder, along with 200 ml of the appropriate
polymer solution were placed in a constant temperature shaker
bath at 37 ± 0.5^{o}C. After temperature equilibrium was reached,
25 ml of the polymer solutions were transferred by a volumetric

pipette into the five flasks, followed by constant vigorous
shaking. A 10 ml sample was taken from the first flask, through
a millipore filter, at the end of 15 minutes. Flasks 2, 3, and
4 were sampled at 15 minute intervals using the same procedure.
The 5th flask was sampled after 4 hours. The concentration of
the filtered samples was determined by the interferometer.
The differences in concentration before and after adsorption
were converted into amount of polymer adsorbed per gram of
polymethylmethacrylate powder at the different time periods.

Measurement of Dielectric Constant of Polymer Solutions

The dielectric constants of one percent solutions of methyl-
cellulose, polyvinyl alcohol, and hydroxypropylmethylcellulose
were measured by an oscillometer (Sargent Model V). The oscil-
lometer was calibrated with double distilled water. The oscil-
lometer readings for the three polymer solutions were essentially
equal and very close to that of the water indicating little, if
any, difference in the polarity of the three polymers in solution.

RESULTS AND DISCUSSION

Adsorption of Polymer from Solutions

The equilibrium adsorption studies were designed to deter-
mine the extent of polymer adsorption, or total amount of
polymer adsorbed onto polymethylmethacrylate powder. Type L-2
adsorption isotherms[6] were observed in all three cases studied,
i.e., for the adsorption of methylcellulose, polyvinyl alcohol,
and hydroxypropylmethylcellulose onto polymethylmethacrylate.

The adsorption isotherms are shown in Figure 1 and the pertinent
data given in Table 1. The observation of L-2 type adsorption
suggests that a monolayer of polymer is adsorbed onto poly-
methylmethacrylate. Monolayer formation has, in fact, been
observed in most polymer adsorption studies[7,8].

An analysis of the forces of adsorption requires a con-
sideration of the molecular interactions present in both the
polymer and the polymethylmethacrylate. The molecular structures
of the three polymers used in this study, along with the struc-
ture of polymethylmethacrylate, are shown in Figure 2. In addi-
tion to dispersion forces, the methylcellulose, polyvinyl
alcohol, and hydroxypropylmethylcellulose contain polar hydroxyl
and carbonyl groups. The same is essentially true for polymethyl-
methacrylate which contains polar methyl ester groups.

In considering adsorption forces, it is the molecular
structure of polymethylmethacrylate at the surface which is the
important factor to consider. The backbone of polymethylmetha-
crylate is a long chain hydrocarbon. In polymethylmethacrylate
every other backbone carbon atom has a methyl group and a
methyl ester group attached to it. There are three possible
arrangements of those groups: (1) All methyl groups are
sticking outward on the surface of polymethylmethacrylate;
(2) All methyl ester groups are sticking outward on the surface;
or, (3) The hydrocarbon backbone lies parallel to the surface
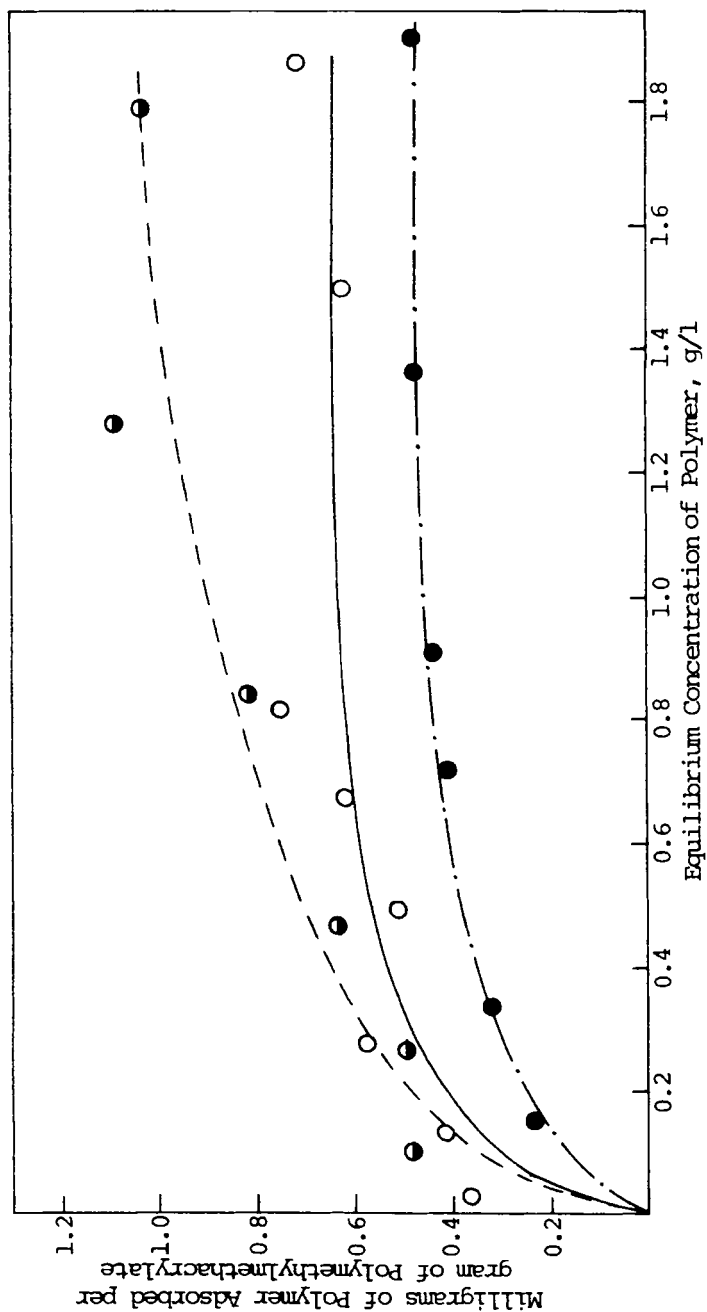and the surface contains an equal number of methyl-and methyl

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FIGURE 1.

Adsorption isotherms of methylcellulose (⊝ and ----), polyvinyl
alcohol (○ and ——), and hydroxypropylmethylcellulose (● and
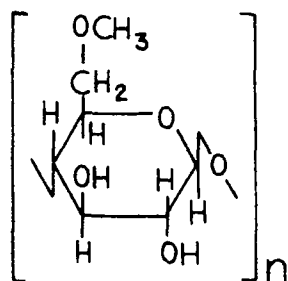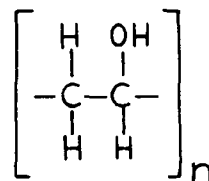—·—) on polymethylmethacrylate.

TABLE 1

Amount of Polymer Adsorbed onto Polymethylmethacrylate
as Related to Equilibrium Polymer Concentration

| Polymer	Equilibrium Concentration (gm/l)	Milligram Adsorbed per Gram Polymethylmethacrylate
Hydroxypropylmethyl-cellulose	1.91	0.469
	1.36	0.483
	0.912	0.445
	0.720	0.402
	0.336	0.321
	0.154	0.230
Polyvinyl Alcohol	1.86	0.70
	1.38	0.61
	0.850	0.75
	0.678	0.61
	0.502	0.49
	0.284	0.58
	0.122	0.39
	0.028	0.36
Methylcellulose	1.79	1.03
	1.28	1.09
	0.840	0.80
	0.476	0.62
	0.304	0.48
	0.082	0.48

ester groups. Since the first arrangement would give polymethyl-
methacrylate a hydrocarbon surface similar to that of polyethy-
lene with -CH groups on the surface, the critical surface
tension of polymethylmethacrylate should be close to that of
polyethylene. However, the critical surface tension of poly-

Methylcellulose

Polyvinyl Alcohol
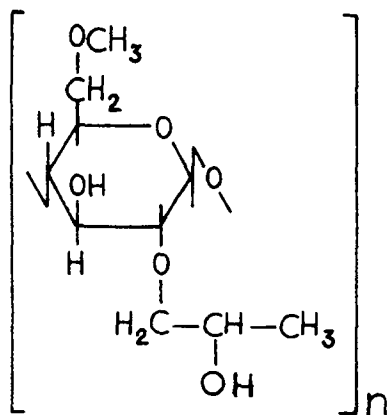
Hydroxypropyl
Methylcellulose
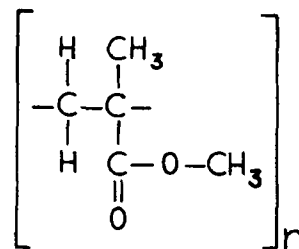
Polymethylmethacrylate

FIGURE 2.
Molecular Structure of Polymers.

ethylene is 22-24 dynes/cm which is much smaller than the 39

dynes/cm critical surface tension determined for polymethyl-

methacrylate[9]. This rules out the possibility of a pure hydro-

carbon surface arrangement in polymethylmethacrylate.

The third arrangement, that of 50 percent methyl groups in

the surface may also be discounted on the same basis. Any

surface that is rich in hydrocarbon groups would most certainly
have a critical surface tension closely approaching 30 dynes/cm.

It is apparent, then, that the surface of polymethyl-
methacrylate must be rich in methyl ester groups. A comparison
of the critical surface tension of polymethylmethacrylate with
that of other solids substantiates this conclusion. Table 2
lists the critical surface tension, along with the proposed sur-
face groups, of two polymers in addition to polymethylmetha-
crylate. The similarity of their structures and critical surface
tensions leaves little doubt that the polymethylmethacrylate
surface is composed of methyl ester groups.

TABLE 2

Polymer	Surface Group	Critical Surface Tension ergs/cm^2
Polyhexamethylene Adipamide	$-\overset{\text{O}}{\underset{\text{}}{C}}-NH-$	46 [11]
Polymethylmethacrylate	$-\overset{\text{O}}{\underset{\text{}}{C}}-O-CH_3$	39 [9]
Polyvinyl Alcohol	$-OH$	37 [12]

As such, the surface of polymethylmethacrylate is fairly polar in nature; it is certainly not as polar as polyhydroxyethylmethacrylate, which contains the additional hydroxyl group, but is definitely much more polar than pure hydrocarbon materials such as polyethylene. It is not surprising, therefore, that polar polymers such as methylcellulose, polyvinyl alcohol, and hydroxypropylmethylcellulose should be adsorbed onto the surface of polymethylmethacrylate through polar interactions. The magnitude of the interaction is, however, surprising with methylcellulose > polyvinyl alcohol > hydroxypropylmethylcellulose (Table 1).

As stated in the Experimental Section, measurement of the dielectric constants of one percent solutions of the polymers indicated little, if any, difference in the polarity of the three polymers in solution. Since the polarity of the polymers in solution cannot account for the order of adsorption, it is necessary to consider the configuration of the adsorbed polymers on the surface of polymethylmethacrylate.

Jenkel and Rumbach[10] have suggested that instead of lying parallel to the surface of the adsorbent, the adsorbed polymers are generally lined up perpendicular to the surface. Each adsorbed polymer may then be anchored on the surface of the adsorbent, in this case polymethylmethacrylate, at one or more sites. The number of sites occupied by a polymer will depend,

to a large extent, upon the flexibility of the polymer. This is
illustrated in Figure 3. Obviously, the greater the number of
sites occupied by a single polymer molecule, the fewer the
number of molecules which can be adsorbed. For example, a
flexible polymer, such as polyvinyl alcohol, may occupy more
than one adsorption site on polymethylmethacrylate while methyl-
cellulose, which lacks flexibility due to the six member ring
and the ether linkage, may be restricted to one site per
molecule. This concept of polymer adsorption would explain the
fact that the adsorption of methylcellulose on polymethylmetha-
crylate is greater than that of polyvinyl alcohol. In the case
of hydroxypropylmethylcellulose, it is likely that the presence
of the hydroxyl group side chain provides more than one anchor
for each adsorbed polymer molecule, even though the backbone of
hydroxypropylmethylcellulose is the same as methylcellulose.
As a result, the extent of hydroxypropylmethylcellulose adsorp-
tion is less than that observed for methylcellulose. It is
important to note, however, that the multiple attachment should
result in a slower rate of desorption of the polymer from the
polymethylmethacrylate. In a practical sense, a slow rate of
polymer desorption is desirable to provide a long lasting polymer
coating when the polymethylmethacrylate is used as a contact
lens in the eye. Based on the above analyses, polyvinyl alcohol
and hydroxypropylmethylcellulose would function better in contact
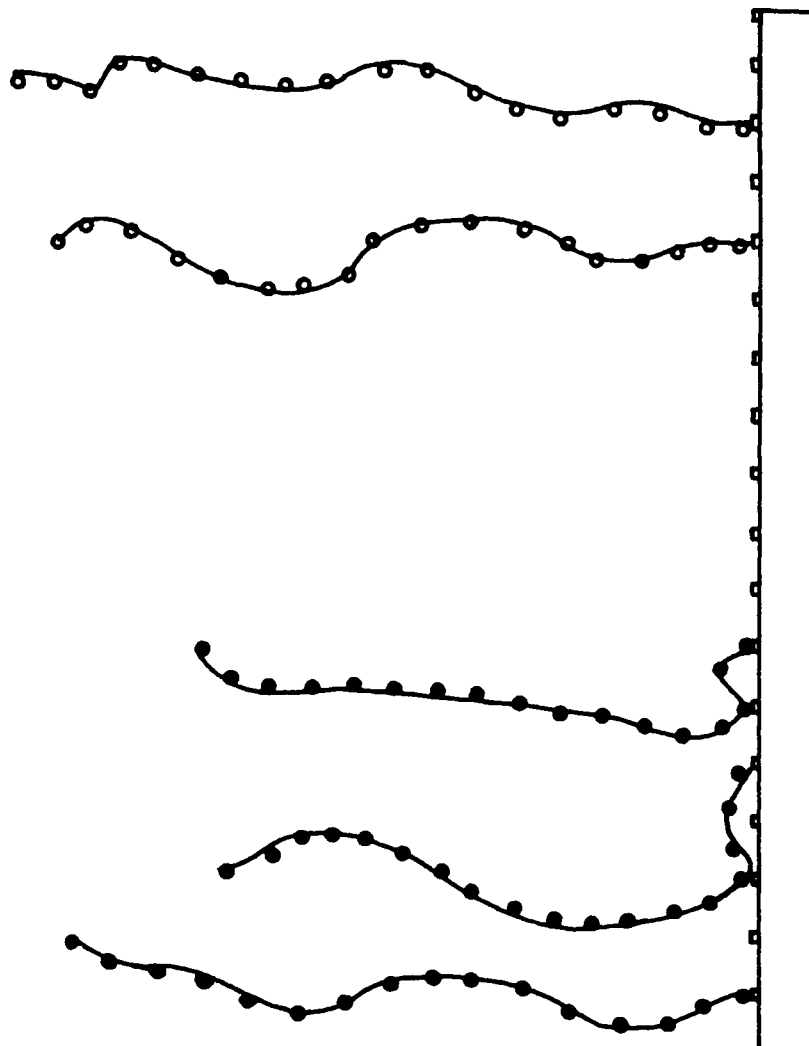lens solution than would methylcellulose.

FIGURE 3.

Suggested Configuration of Adsorbed Polymer Molecules (From
Reference 10)

Kinetic Adsorption Study

The rate of adsorption of methylcellulose, polyvinyl alcohol, and hydroxypropylmethylcellulose onto the surface of polymethylmethacrylate was determined by following the amount of polymer adsorbed as a function of time over a four hour time period. The results are shown in Figure 4. From Figure 4 it can be seen that the rate of polymer adsorption, as determined by the amount of polymer adsorbed per unit time, follows the
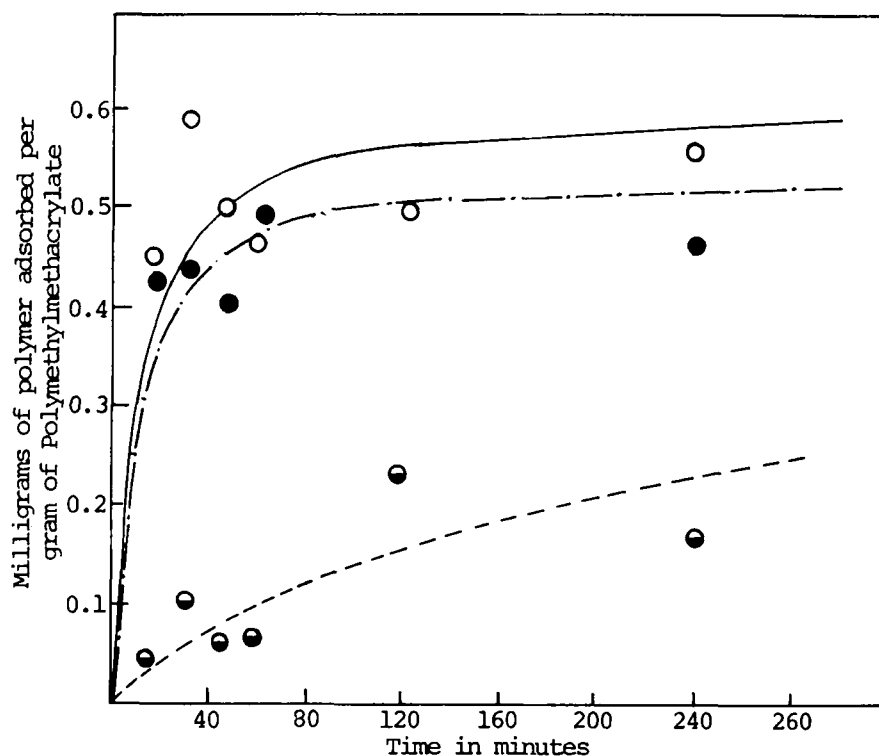

FIGURE 4.
Adsorption of polymers from solution onto polymethylmethacrylate as a function of time. Key: 0 and ——, polyvinyl alcohol; ● and —— . ——, hydroxypropylmethylcellulose; ◐ and ----, methylcellulose.

order polyvinyl alcohol $\geq$ hydroxypropylmethylcellulose >
methylcellulose. This order is not the same as that obtained
in the equilibrium studies where the total amount adsorbed at
equilibrium followed the order methylcellulose > polyvinyl
alcohol > hydroxypropylmethycellulose. From the comparison
between the results of the equilibrium and kinetic adsorption
studies, it can be seen that, as in many chemical reactions,
the extent and the rate of adsorption must be considered
separately. The discussion in the previous section on the polar
and polymethylmethacrylate are still valid in considering
kinetics of adsorption; however, further consideration must be
given to the configuration of adsorbed polymer.

It should be noted at this time that relatively few studies
on the rate of polymer adsorption have been previously reported
in the literature. Therefore, while some theoretical considera-
tion has been given to equilibrium polymer adsorption, the
corresponding treatment of kinetic data has not been initiated.
The kinetic data does not follow the straightforward Langmuir
approach to the treatment of adsorption data. In the Langmuir
approach, the rate of adsorption is considered in developing
the equation for equilibrium adsorption. The rate of adsorption
is given by the equation:

$$R = K C (1 - \theta) \qquad\qquad \text{Eq. 1}$$

where K is the adsorption rate constant, C is the concentration

of the solution, and θ is the fraction of sites occupied. The

adsorption rate is then directly proportional to the number of

free adsorption sites.

Unfortunately, it is not possible to rationalize the poly-

mer kinetic data on the basis of this simple theory. The concept

of multiple and single point adsorption discussed for equilibrium

polymer adsorption would suggest that the number of free adsorp-

tion sites would decrease faster per molecule with the multiple

point adsorption of polyvinyl alcohol and hydroxypropylmethyl-

cellulose than for the single point adsorption of methylcellulose.

From Figure 4, it is apparent that the opposite is true. It is

most likely that in considering the adsorption of long molecular

chains, the accessibility of the solid surface must be taken

into account. For example, the initial adsorption of a few

molecules of nonflexible polymer perpendicular to the solid

surface may occlude the surface and make it extremely difficult

for subsequent molecules to approach the adsorption sites. The

ability of methylcellulose to approach the surface could cer-

tainly be the rate limiting step in methylcellulose adsorption.

This is not likely to be a problem for a flexible polymer such

as polyvinyl alcohol which, as a result of its flexibility, has

a faster adsorption rate. The hydroxypropylmethylcellulose,

however, has a structure similar to methylcellulose and has an

adsorption rate similar to polyvinyl alcohol. There is

presently no satisfactory explanation for this phenomena.   It
is possible that the repulsive forces between hydroxypropyl
groups extending from the molecular chains may prevent extensive
intertwining of the hydroxypropylmethylcellulose molecules,
thus leaving holes which are easily penetrated by the adsorbing
hydroxypropylmethylcellulose molecules. This is, of course,
speculation and will require extensive research to determine
the mechanism which is responsible for the large difference
between the adsorption rates of methylcellulose and hydroxy-
propylmethylcellulose. It should be clear, that in a rigid
contact lens solution containing two or more polymers, the poly-
mer adsorbing at the faster rate will most likely determine
the resulting surface characteristics of the lens. This is
particularly true if the adsorption rates are significantly
different; in fact, the usefulness of the slow adsorbing poly-
mer must be questioned. Such is the case for solution contain-
ing polyvinyl alcohol and methylcellulose.

In cases where the rates of adsorption are of the same
magnitude, both polymers will contribute to the resulting sur-
face characteristics of the rigid contact lens. Of the solu-
tions studied, solutions containing both polyvinyl alcohol and
hydroxypropylmethylcellulose are an example of this case where
both polymers most likely function to produce a hydrophilic
rigid lens surface.

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