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PHYSICO-CHEMICAL STUDIES ON THE ADSORPTION OF POLYSILOXANE POLYMERS ONTO HYDROXYAPATITE

by
Abdulla Mahmoud Molokhia

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
(Pharmaceutical Chemistry)
in The University of Michigan
1973

Doctoral Committee:

Professor William I. Higuchi, Chairman
Professor Robert G. Craig
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T O

M Y W I F E

F A T M A

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CHAPTER I. INTRODUCTION, LITERATURE REVIEW AND STATEMENT OF THE PROBLEM

1.1 Introduction

Dental caries is one of the most prevalent diseases of man. The disease is initiated by masses of bacteria which accumulate on the tooth surface in what is known as dental plaque. These bacteria, in the presence of fermentable carbohydrates, produce acids essential for demineralization and caries development.

While bacteria in many natural environments have a tendency for growing on surfaces, this adhesive tendency seems to be a critical ecological determinant for the initiation of caries.

Despite its importance, relatively few studies have focused on how bacteria attach to teeth and epithelial surfaces and how they subsequently accumulate to form dental plaque. On a theoretical basis, plaque formation must, in the first step, entail an adhesive interaction between the bacteria and the tooth surface or the acquired pellicle.

Therefore, an approach to controlling dental plaque and, thus, dental disease may simply involve the interference with the bacterial attachment to and accumulation on the surfaces of teeth. This might be achieved in the following way. Since hydroxyapatite has marked adsorptive characteristics, it is possible that a surface film could be deposited to which bacteria could not readily adhere. This film would be analogous to the natural acquired pellicle, but would be composed of constituents which prevent attachment of those oral

organisms with pathogenic potential. A hydrophobic nonwetting film which resists protein adsorption might prevent plaque adhesion to teeth surfaces. The concept has been recently supported by an experiment in which Streptococcus mutans failed to colonize a siliconized glass surface (1).

The purpose of this investigation was to investigate: (1) the mechanism of adsorption of polydimethylsiloxane polymers onto hydroxyapatite and human dental enamel; (2) the properties of the resulting hydrophobic films; and (3) the potential effectiveness of such treatment in inhibiting bacterial plaque formation.

1.2 Literature Review

Dental plaque is composed almost entirely of various micro-organisms in an organic matrix which is derived from both salivary glycoproteins and extracellular microbial products (2). Clinical experiments have repeatedly shown that accumulation of plaque on the healthy gingivae may produce gingivitis and that the interplay between dietary carbohydrates and the microorganisms of the plaque may produce caries (3-6).

Although a detailed understanding of the specific action of the various microorganisms and the subtle mechanisms of the disease processes themselves may still be lacking, the present level of knowledge seems to justify the working hypothesis that without bacterial plaque, there can be no caries.

Plaque prevention and control based upon mechanical cleansing have been recommended by dentists. These, if carried out diligently are considered to be the most reliable means of controlling plaque (7,8). However, the technical skill, time, effort, and the cleaasing frequency required to continually maintain a high standard of oral cleanliness exceed motivation and capability of the average person.

The chemical methods of plaque control are divided into:

(a) Enzymatic methods: A series of crude pancreatic enzyme preparations containing trypsin, chymstrypsin, amylase, lipase, elastases and esterases, have been administered topically or in chewing gum (9,10). These enzymes are expected to dissolve the organic adhesive substances which may be essential to the adhesion of plaque to the tooth surfaces and the cohesion of the plaque components. Dextranase was recently

considered as a potential antiplaque agent. Although animal experiments had been quite encouraging (11), the dextranase preparations were found to possess limited effects in removing plaque in humans (12,13). This is probably because bacterial dextrans do not appear to be the only adhesive constituents in plaque.

(b) Fluoride treatment: Epidemiological observations have suggested that teeth exposed to natural fluoridation are cleaner than those from areas with low fluoride content (14). It was also found that fluoride treatment reduces caries incidence and increases the enamel resistance to decalcification (15). Other investigations (16,17) have shown that fluoridation may reduce the surface energy of the teeth and reduce the tendency of the enamel surface to adsorb proteins.

(c) Antibiotics and antibacterial agents: Several antibiotics have been tested for their plaque-inhibiting capacity. Penicillin, tetracycline (18, 19, 20), spiramycin (21) and vancomycin (22) were reported to be potent plaque inhibitors. However, the success with antibiotics has been limited as much criticism has been directed at the prolonged or unregulated use of antibiotics for the treatment of human diseases. A major problem with the use of an antibiotic for prolonged periods is the development of drug-resistant microorganisms.

Numerous antibacterial agents, other than antibiotics, have been marketed in mouthwashes and toothpastes, and applied topically in the treatment of gingival and periodontal diseases. With reference to his chemotherapeutic theory, Miller (1889) suggested that caries prevention could be achieved through the administration of antibacterial

substances. Recently, chlorhexidine has received much attention (23-26) in preventing experimental gingivitis and caries. Administered at intervals, it suppresses the oral flora and thereby inhibits bacterial colonization of the teeth and gingiva.

Despite the many antibacterial agents tested, a mouthwash or a toothpaste additive which would effectively solve the problem of clinical plaque is still unavailable.

Adsorption onto Hydroxyapatite

Several studies have been carried out on the adsorption onto hydroxyapatite and human dental enamel. Most of these studies (27-46) were concerned with the effect of the adsorbed materials on hydroxyapatite dissolution or on enamel demineralization. In few cases (47,48) the adsorption of gases on hydroxyapatite powder was investigated in order to elucidate the apatite surface energy and heat of wetting.

Manly and Bibby (27) compared the effect of 147 substances on the dissolution of enamel to that of 0.1 percent sodium fluoride solution. Enamel coated by Dow-Corning 200 and Eastman 910 adhesive were found by Caldwell (28) to decrease the dissolution rate. Similar coating effects were reported with oleic acid (29). Later studies on film-forming substances (30-33) have indicated that alkylamines are active inhibitors of enamel dissolution. Koulourides and Buonocore (32) have postulated that blocking of the diffusional pathways by an ionic shell is the cause of the demineralization inhibition by some ions.

A number of dyes have been found to bind to the apatite surface (34). Speirs (35,36) endeavored to study the mechanisms involved in the adsorption of a group of dyes onto hydroxyapatite. He was interested in the type of bonding possibly involved, the area of the surface covered by each molecule and the orientation of the dye molecules on the surface. While the author succeeded in demonstrating the structural dependence of the uptake of the dyes by the hydroxyapatite, he could not obtain sufficient evidence for a mechanism of adsorption. Among the difficulties he encountered was the imperfect understanding of the nature of the hydroxyapatite crystal surface.

Several qualitative and quantitative studies (37-46) on fluoride inhibition of tooth demineralization have been carried out. Buttner and Muhler (37) found that the teeth treated with stannic, sodium or zirconium fluorides resisted demineralization in a weak acid medium. Dean et al. (38) have reported that fluoridation of public water supplies reduced the incidence of dental caries. Hodge (39) showed that the decrease in dental caries was a linear function of the logarithm of the fluoride concentration. Other investigators (40-43) have also shown that fluoride has the ability to inhibit the demineralization process. Several physical models were proposed (44-46) to study the mechanisms by which the fluoride treatment was effective. A calcium fluoride layer was found to form on the apatite surface. Valvani (45) used the equilibrium chemical reaction occurring at the apatite-calcium fluoride moving boundary to determine the mechanism of the reaction.

Recently, more studies were carried out on the adsorption of compounds that adsorb on hydroxyapatite and possess antibacterial activity. The plaque-inhibiting capacity of 11 antibacterial compounds was studied by Gjermo et al. (24). The antibacterial activity of the compounds, which were chosen from different groups of disinfectants, was tested in vivo and in vitro. The authors found no correlation between the two systems and concluded that factors other than the antibacterial properties are important in plaque inhibition in vivo. Chlorhexidine, which was a potent plaque inhibitor in vitro and in vivo, was later found to adsorb on tooth surfaces and the salivary mucins. The adsorbed chlorhexidine was then released when its concentration in the ambient fluids of the oral environment was low. The authors pointed out that the possible formation of reservoirs of chlorhexidine on teeth surfaces in vivo from which chlorhexidine is slowly released could prevent bacterial colonization and the development of dental plaque. Further studies on chlorhexidine (23, 25 and 49) have supported this mechanism of action of the drug.

Turesky et al. (50) developed an in vitro procedure for testing the plaque inhibition ability of a variety of chemicals. Some were adhesive, some antibacterial, and some were both adhesive and antibacterial. The authors, however, were not able to differentiate between plaque growth on the tested tooth surfaces and growth in the medium. Their findings indicated that only adhesive antibacterial chemicals inhibited plaque formation; adhesive chemicals without antibacterial action and nonadhesive antibacterial chemicals were ineffective. It is

believed that the failure of the method to distinguish the surface and the bulk growth of bacteria may have resulted in underestimating the ability of some adsorbed films to inhibit plaque development on the surface but not in the bulk.

1.3 Statement of the Problem

The preceding introduction and review of the literature has shown that bacterial adhesion to teeth may be the most critical determinant in the microbial attack of the enamel surface. The relatively high surface energy of enamel and the presence of the adhesive polysaccharides synthesized from sucrose, together with the salivary mucin-like polymers, are the primary factors involved in the adhesion. Although numerous attempts have been made to prevent or treat dental plaque, a systematic study of agents that interfere with the bacterial adhesion is lacking.

It was the aim of this work to study the adsorption onto hydroxyapatite of siloxane polymers containing polar anchoring groups and to study such factors as the influence of the nature of the solvent, the effects of the chemical structure and molecular weight of the adsorbing agents, and the effects of the surface pretreatment of the adsorbing surfaces. Specifically, it was planned to investigate the following aspects:

(a) The extent of adsorption at maximum surface coverage.

(b) The degree of film hydrophobicity.

(c) Film strength and permanence.

(d) Molecular configuration at the solid-liquid interface.

CHAPTER II. CONTACT ANGLE STUDIES

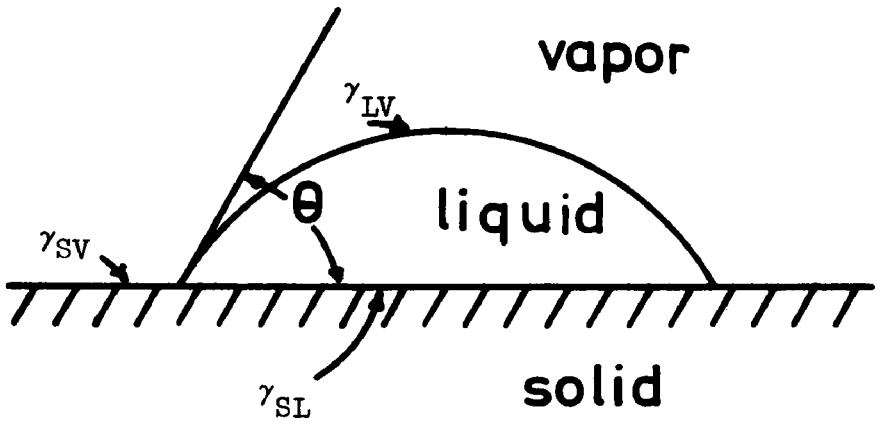
2.1 Introduction

In the oral cavity, the forces of adhesion and cohesion play an important role in the microbial attack of the enamel surface. Estimates of surface energy of solids can be obtained by various methods, such as by determination of heats of immersion (51), forces of adhesion (52,53,54), or by measuring the contact angles between clean, plane surfaces of the solids and pure liquids with known surface tensions (55). The contact angle experiments in this chapter were undertaken to shed light on the wettability of hydroxyapatite pellets and human teeth and its relationship to surface treatments.

The relationship between the free energies when a liquid drop is placed on a solid surface was developed by Young (56),

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \quad ,$$

where γ_{SV}, γ_{SL} and γ_{LV} represent the interfacial tensions at the solid-vapor, the solid-liquid, and the liquid-vapor interfaces, respectively, and θ is the contact angle as shown in Fig. 2.1. Obviously, since the tendency for the liquid to spread increases as θ decreases, the contact angle is a useful inverse measure of spreadability or wettability. Surface treatments of enamel that increase its aqueous angle of contact presumably would interfere with protein adsorption and might prevent bacterial colonization of such surfaces.



(γ_{SV}, γ_{LV} and γ_{SL} are the interfacial tensions at the solid-vapor, liquid-vapor and solid-liquid interfaces, respectively. θ is the angle of contact.)

FIG. 2.1 CONTACT ANGLE OF A SESSILE DROP.

2.2 Materials Used

2.2.1 Hydroxyapatite: $Ca_{10}(PO_4)_6(OH)_2$. A finely powdered material prepared by precipitation method was chosen for both contact angle and adsorption isotherm studies because of its chemical resemblance to human enamel and its high surface area, 70 m^2/gm* (determined by BET method).

2.2.2 Method of Synthesis. The above-mentioned precipitation procedure is essentially similar to that reported by Avnimelech (57). The apparatus used is shown in Fig. 2.2, where equivalent amounts of phosphoric acid and calcium oxide react together to produce hydroxyapatite. Analytical grade calcium carbonate was calcined at 1100°C for 24 hours, and the product was kept in a desiccator. The calcium oxide was then transferred into a 20-liter heavy-wall polypropylene flask containing 12 leters of preboiled double-distilled water. The flask was placed in an electric heating jacket thermostatically controlled to keep the contents boiling during the synthesis period. Approximately 1.8 liter of 2 molar phosphoric acid** solution (recrystallized pure grade) was pumped through a peristaltic pump at a rate of 1 ml per minute. It reached the contents of the flask after being diluted about fifteenfold by water coming down from the condenser. The reaction took place under a nitrogen atmosphere with stirring maintained throughout the procedure. All of the inlets and outlets were protected against carbon dioxide contamination.
The reaction proceeded for 30 hours and was allowed to digest

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* Kindly determined by Dr. Hiller Rootare, School of Dentistry, The University of Michigan.

** Mallinckrodt, New York.

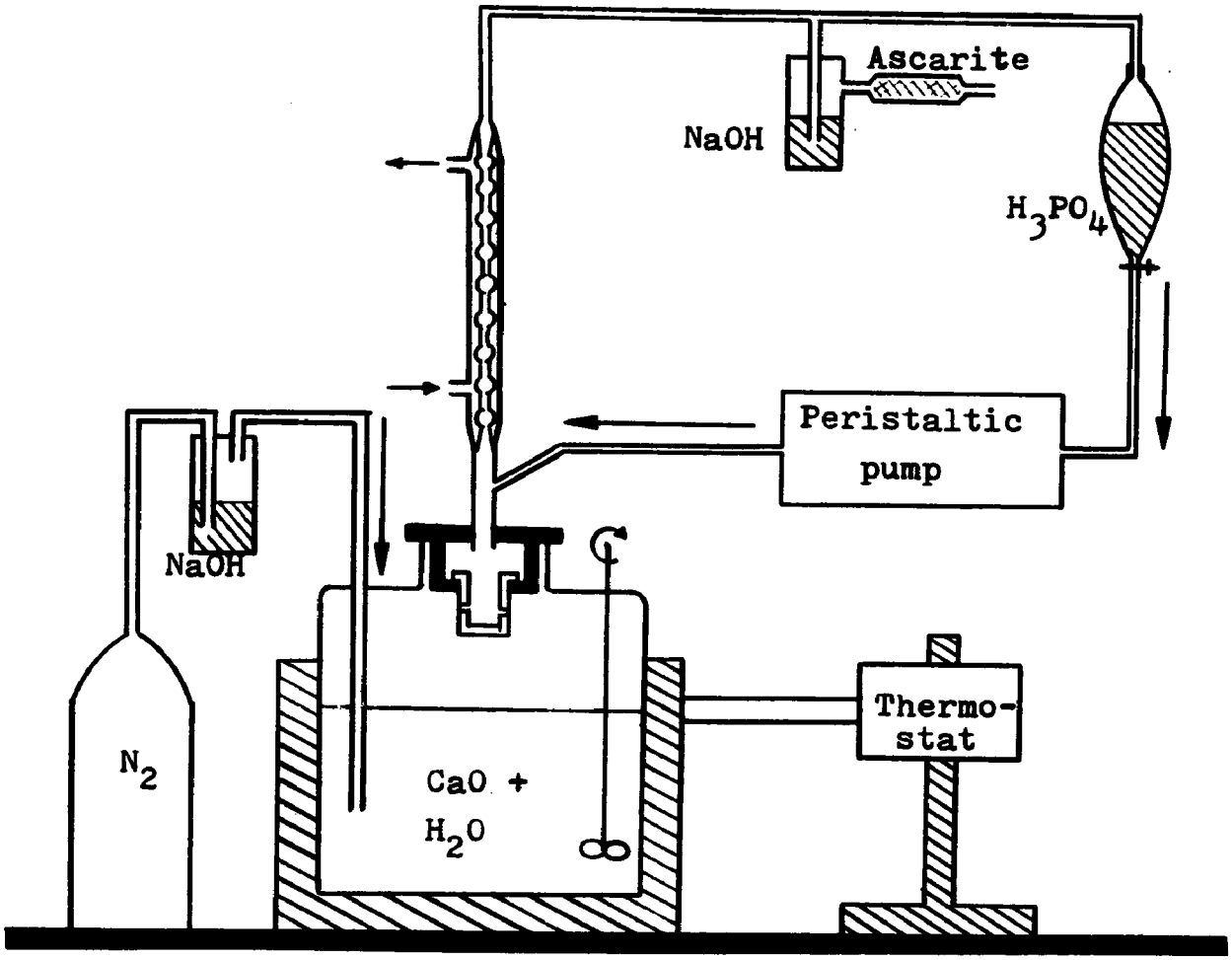


FIG. 2.2 APPARATUS USED FOR HYDROXYAPATITE SYNTHESIS.

for 48 hours more. The supernatant liquid was then removed and replaced by freshly boiled water and boiling was continued for 72 hours. The process of water rinsing was repeated again prior to washing the precipitate with acetone and drying it at 105°C for 24 hours.

Analytical methods to compare this sample with the commercially available high surface area Victor hydroxyapatite and the highly pure low-surface area Tennessee Valley Authority (TVA) hydroxyapatite were carried out. The compositions of the samples compared are listed in Table 2.1. Both the calcium and the phosphate contents were determined on solutions in 0.5 N hydrochloric acid after appropriate dilution with water. The x-ray diffraction and infrared absorption patterns of the precipitated sample (Figs. 2.3 and 2.4) are in close accord with the TVA hydroxyapatite sample prepared at the Tennessee Valley Authority laboratories.

Table 2.1

Composition of Hydroxyapatite Samples

HAP Sample	Calcium (%)	Phosphate (%)	Ca/PO_4 (Molar Ratio)
$Ca_{10}(PO_4)_6(OH)_2$	39.92	56.76	1.667
TVA I*	39.90	56.90	1.662
TVA II*	39.76	56.14	1.678
Victor	38.67	57.91	1.582
Precipitated	38.84	55.98	1.644

* TVA I and TVA II are two different batches prepared according to TVA procedure [58].

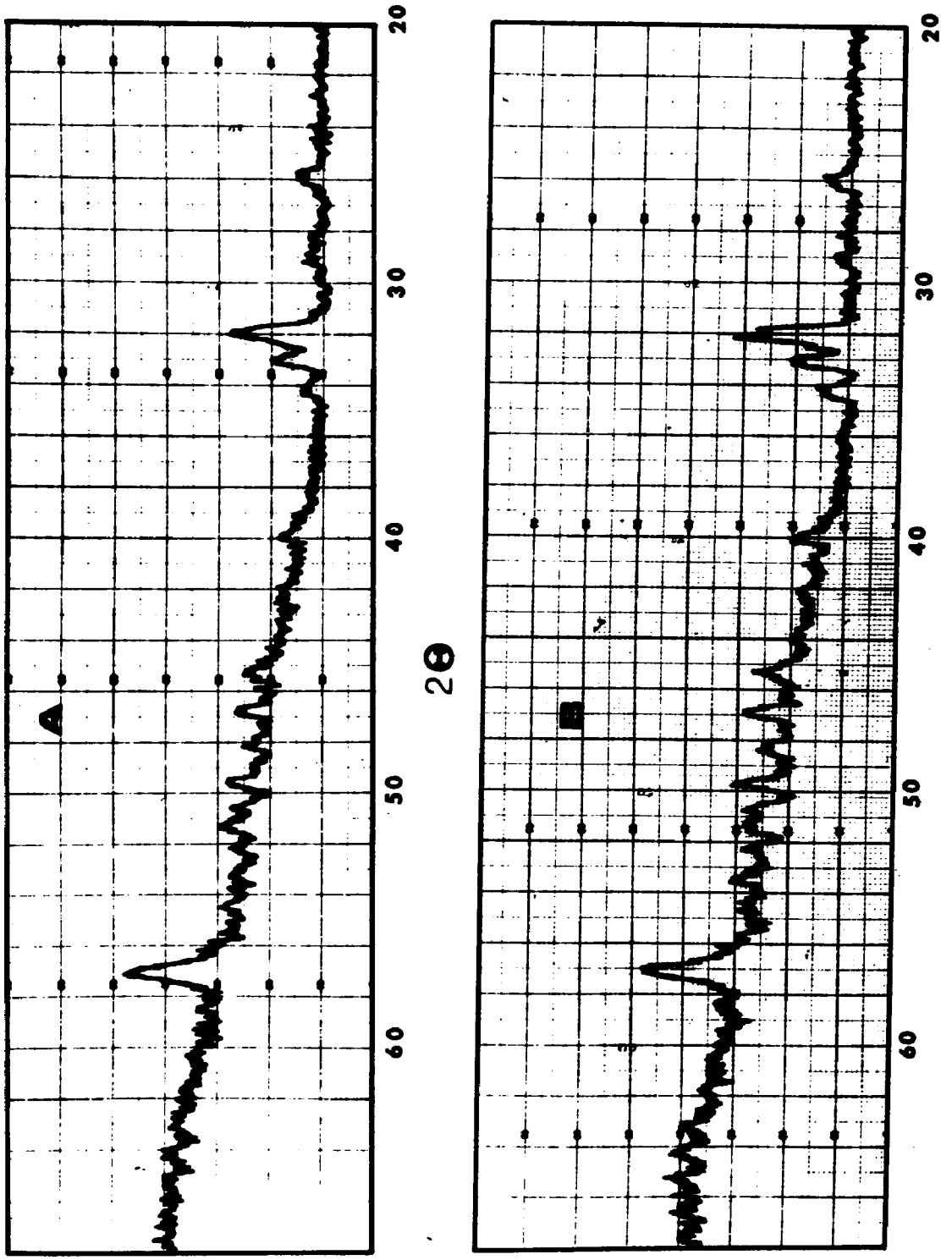
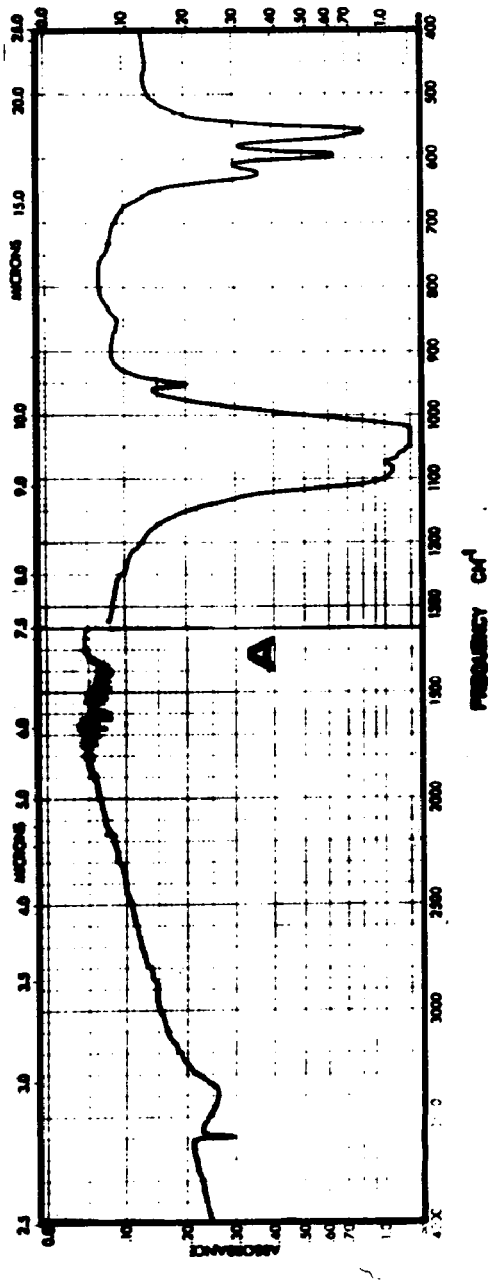


FIG. 2.3 X-RAY DIFFRACTION OF HYDROXYAPATITE. (A) THE SYNTHESIZED SAMPLE. (B) TVA SAMPLE.



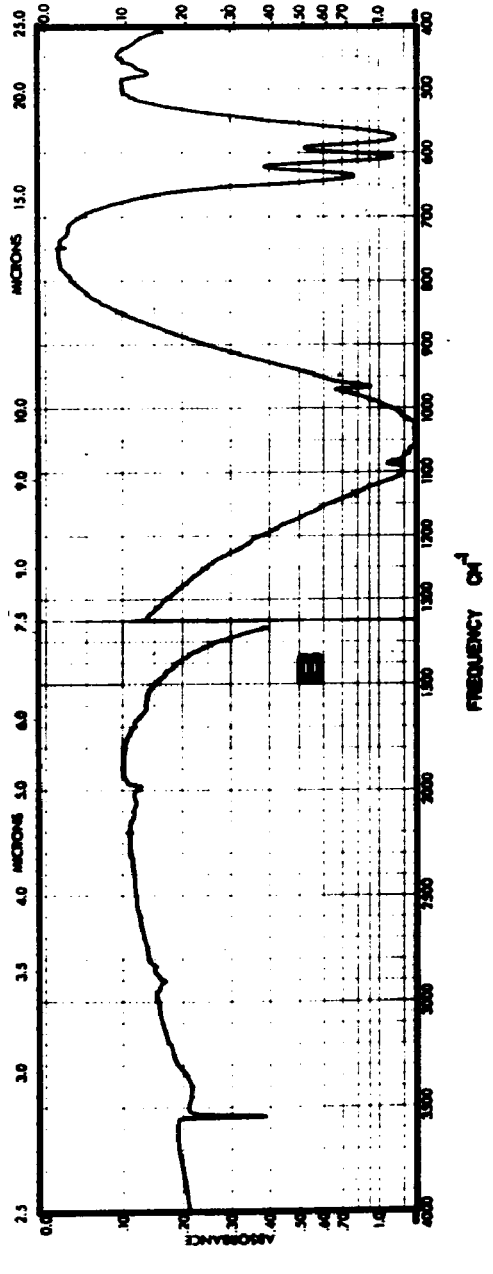


FIG. 2.4 INFRARED SPECTRA OF HYDROXYAPATITE. (A) THE SYNTHESIZED SAMPLE. (B) TVA SAMPLE.

The pure powdered sample was used for adsorption isotherm studies and 200 mg of the powder was compressed into discs under pressure of 7,000 lb (8,900 lb/inch^2) in a Carver Laboratory Press, Model B* for contact angle determination.

2.2.3 Silicone Polymers. A group of organo (polysiloxane) polymers (Tables 2.2 and 2.3) were selected for this study in an attempt to establish methods for "siliconizing" the tooth surface. The dimethylsiloxane chain was chosen because of the comparatively high degree of flexibility it possesses. The polar amine groups are known to strongly link to the hydroxyapatite surface, and studies on enamel dissolution retardation by adsorbing alkyl amine films (32,33) showed marked inhibition.

In general two types of the siloxane polymers were tested: (1) The straight chain type with polar anchoring groups at both ends of the chain (P-1 and P-2), and (2) the side branch type with polymers differing in the molecular weight, the ratio of the polar to the nonpolar units and the type of the amine group.

These polymers (Tables 2.2 and 2.3) were synthesized and purified by Dr. E. P. Pleuddemann.** The purity was partially confirmed by the determination of the "neutralization equivalent" by a nonaqueous titration procedure. The number average molecular weights were calculated on the basis of the respective amine content.

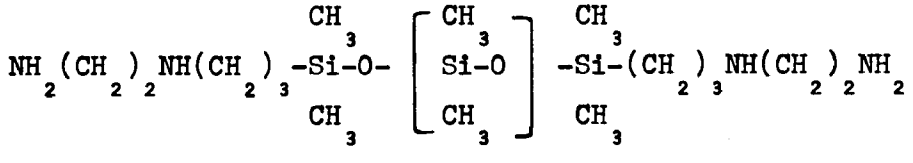
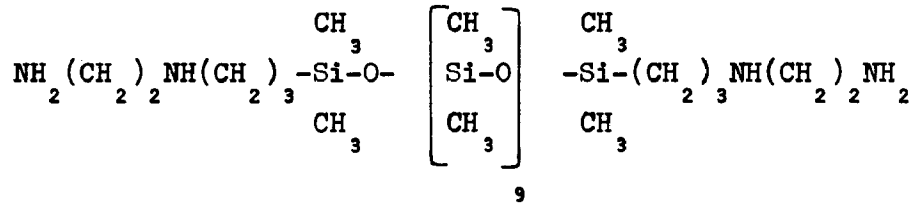
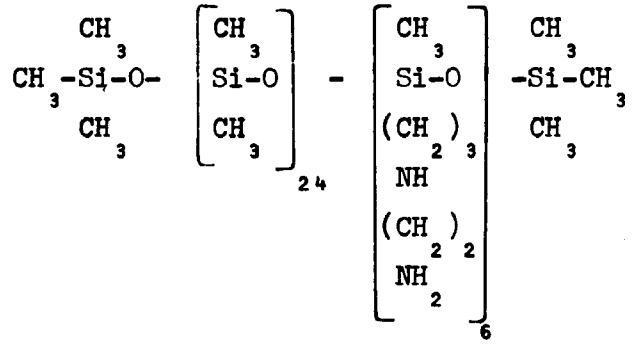
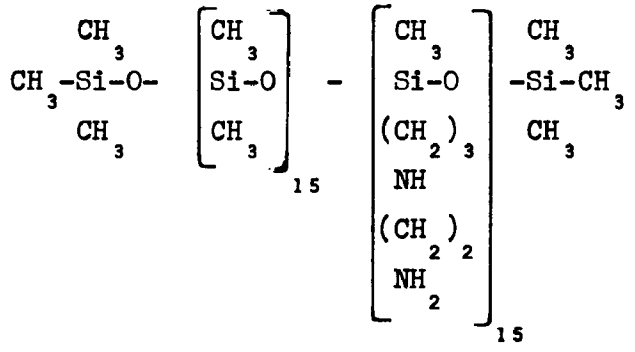
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* Carver Laboratory, Summit, N. J.

** Dow Corning Chemical Co., Midland, Michigan.

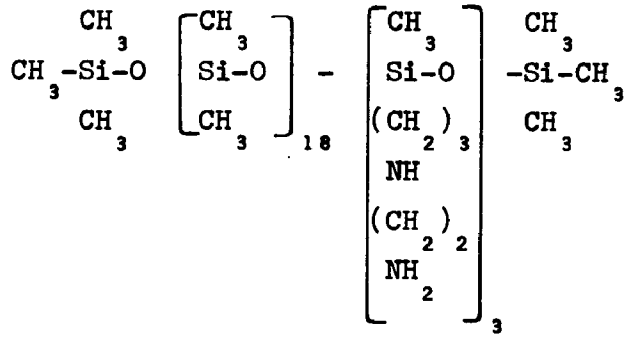
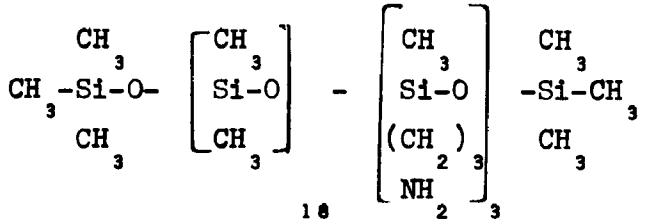
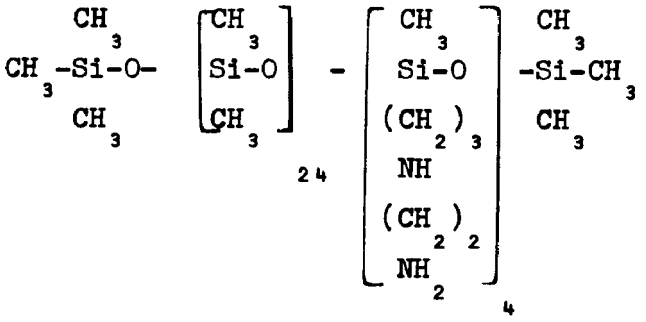
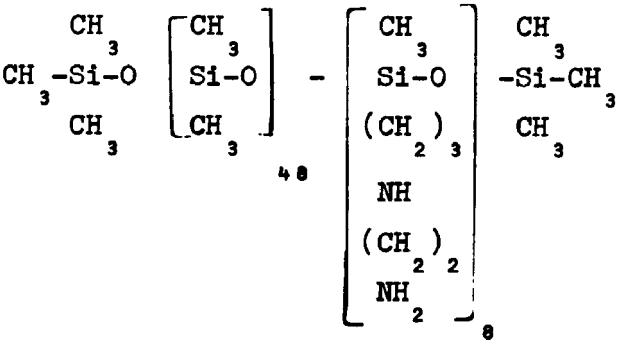
Table 2.2

Polysiloxane Polymers

Polymer Type	Formula
P-1	
P-2	
P-3	
P-4	

(cont.)

Table 2.2 (cont.)

Polymer Type	Formula
M-1	
S-1	
M-3	
WM-3	

(cont.)

Table 2.2 (cont.)

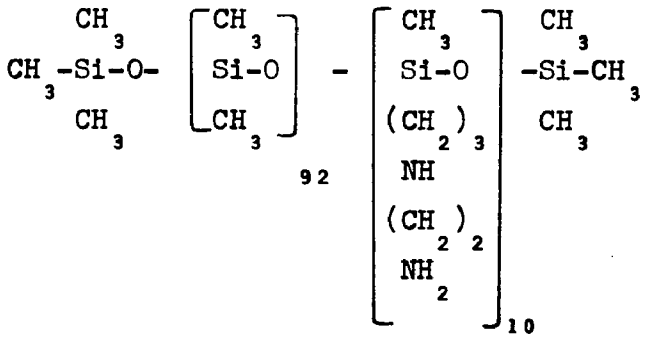
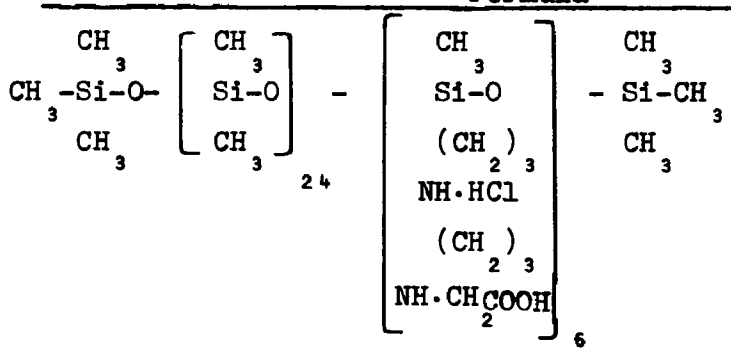
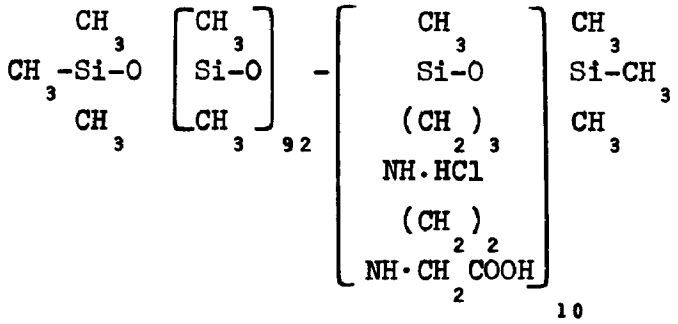
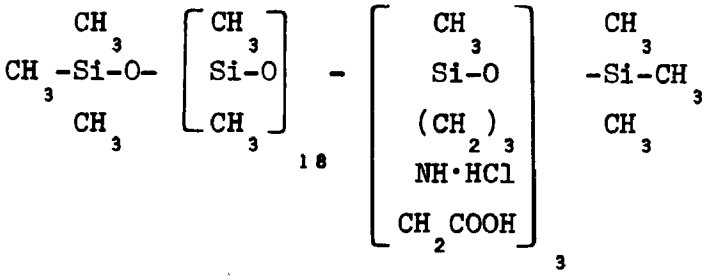
Polymer Type	Formula
S-4	

Table 2.3

Polysiloxane Polymers with Sarcosine-Type Polar Groups

Polymer Type	Formula
S-3	
S-5	
S-6	

2.3 Experimental Procedure

2.3.1 Polymer Adsorption on Hydroxyapatite Discs. The apatite discs were shaken for 24 hours at 30°C with the polymer solution, rinsed with the solvent used, dried under vacuum at 55°C for one hour, and then placed in a desiccator. The hydro-alcoholic solvent used was a mixture of 20 percent absolute ethanol and 80 percent of 0.05 M acetate buffer (pH 4.6). The final pH of the mixture was 4.85.

In the case of metal-ion pretreatment, the apatite tablets were shaken with the metal salt solution at 30°C for the indicated time period, rinsed with water, dried at 55°C for one hour and then kept in the desiccator for polymer treatment.

2.3.2 Polymer Adsorption on Teeth. Freshly extracted teeth (mostly molars) were cleaned and polished. The surface was then etched either in acetate buffer (pH = 4.6) for 30 seconds, or in 0.1 N hydrochloric acid solution for 10 seconds to remove the residues from the surface. The teeth were then rinsed with water and stored in water until used. When the polymer treatment was carried out using organic solvents, the teeth were dried before polymer contact; otherwise, they were used while wet. Polymer adsorption with and without metal-ion pretreatment was carried out in the same manner as with the compressed apatite discs.

2.3.3 Contact Angle Measurements. The water angle of contact was carefully measured on the treated and dried solid surfaces by means of a Gaertner Scientific cathetometer.* A drop of double-distilled water approximately 15 μl in size was dropped from a syringe placed directly above the surface and the sessile angle of contact was measured within 30 seconds.

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* Gaertner Scientific, Chicago.

Two readings were taken on each apatite disc and two discs were used for each treatment. The readings on a given surface were averaged.

On the tooth surface, the contact angle was measured after placing the tooth on a microscopic glass slide with its flattened surface in an upward position. In most cases, the tooth was fixed from its root to the glass slide by a small piece of Scotch tape to adjust the flat surface horizontally.

A preliminary contact angle measurement was conducted on ten samples of apatite discs treated with a 1000 γ/ml P-3 polymer solution in acetaone. The data from this experiment were statistically treated to determine the standard deviation and the coefficient of variation of the sample. The results are listed in Table 2.4.

2.3.4 Permanence Test. The apatite discs or the teeth, after measuring the contact angle, were shaken with acetate buffer (pH = 5.8), presaturated with hydroxyapatite for 24 hours at 30°C. The discs were then rinsed with double-distilled water and dried, and the contact angle was measured again. This second measurement gives some insight about the film resistance toward desorption at pH 5.8.

2.4 Results

From the analysis of the variance of the set of contact angles measured on hydroxyapatite discs (Table 2.4), it appears that the scatter around the mean is low. Since most of the contact angles measured are as high as those in Table 2.4, subsequent estimates were made on only four measurements on each sample.

Table 2.4

Contact Angle Measured on Hydroxyapatite Discs

Treated with 10^3 γ P-3/Acetone

Sample No.	Contact Angle (x) (degrees)	$x-\bar{x}$	$(x - \bar{x})^2$
1	132	1	1
2	135	4	16
3	134	3	9
4	128	-3	9
5	126	-5	25
6	130	-1	1
7	130	-1	1
8	129	-2	4
9	136	5	25
10	130	-1	1
			92

The mean value of contact angle $(\bar{x}) = \frac{\Sigma x}{n}$ (where n is the total number of samples) = 131

Variance $s^2 = \Sigma(x - \bar{x})^2/n = 92/10 = 9.2$

Standard deviation: $s = \pm 3.033$

Coefficient of variation of the sample: $s/\bar{x} = \pm 0.0231 = \pm 2.31$ percent

A zero angle of contact was obtained when a water droplet was placed on a hydroxyapatite disc that received no treatment. The cleaned and polished human teeth gave contact angles that ranged from 68 to 77 degrees. After etching in the acetate buffer, the contact angle dropped to the range of 53 to 59 degrees, while etching in hydrochloric acid brought it down to zero.

2.4.1 Contact Angle Results on P-1 to P-4 Polymers. Figures 2.5 and 2.6 show the effect of polymer concentration upon the contact angle. These data show that polymers P-3 and P-4 gave the highest contact angles (Fig. 2.5) when acetone is used as the solvent. This is probably because, in this case, the apatite sites and the diamine anchors are efficiently utilized which results in a surface that is rich in dimethylsiloxane and relatively condensed.

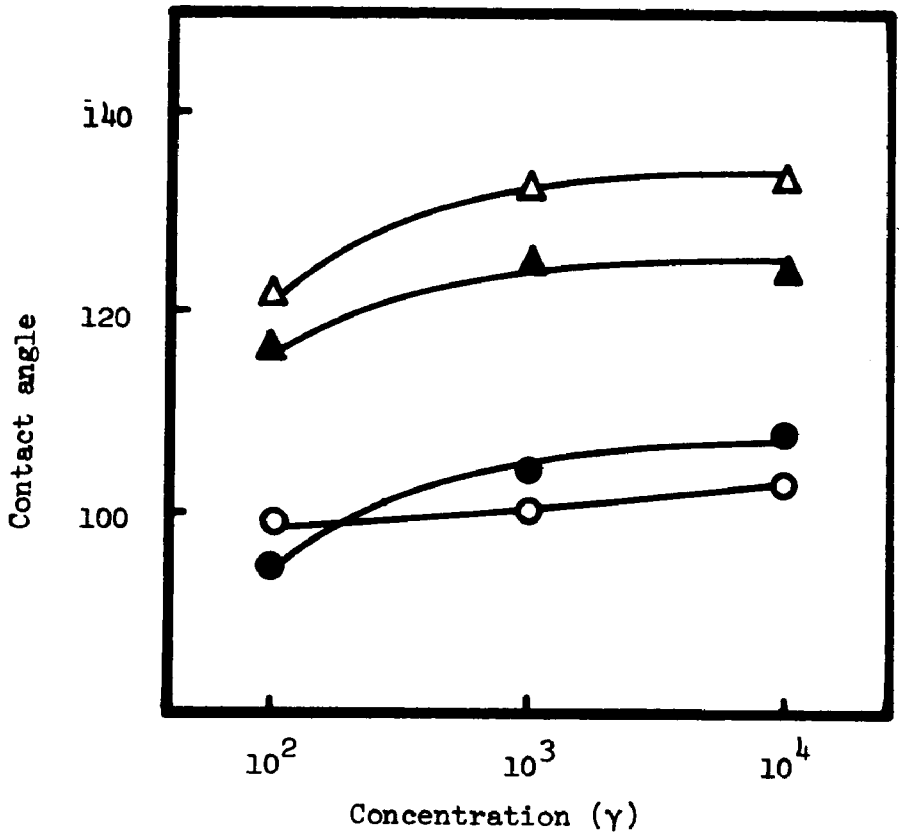
For polymers P-1 and P-2 the lower contact angles with acetone as the solvent might be explained perhaps by either of two interpretations. These polymers may be "loosely" adsorbed when acetone is the solvent so that both diamine groups are not always acting as anchors and some may be found on the "outside" of the adsorbed film. The other interpretation, which may be the more likely one in view of the results with calcium fluoride*, is that only a fraction of the sites may be occupied by polymer molecules due to solvent competition involving some of the sites.

The slightly higher contact angles found with P-3 than with P-4 (Fig. 2.5) may be due to the fact that there are too many diamine groups in P-4 to be shielded by the dimethylsiloxane segments.

The contact angle data for P-3 and P-4 with hexane (Figs. 2.6) suggests that the "poorness" of hexane as a solvent is responsible for the behavior.

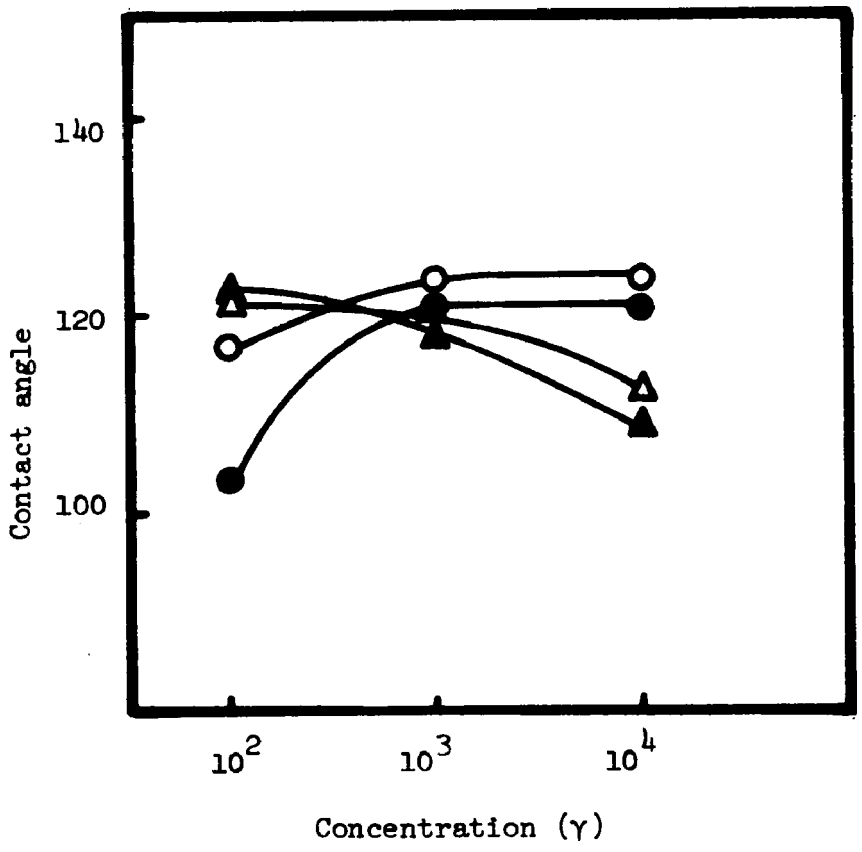
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* See Chapter IV.



⊙ (P-1) , ●(P-2) , Δ (P-3) , ▲ (P-4)

FIG. 2.5 RELATION BETWEEN CONTACT ANGLES AND INITIAL CONCENTRATIONS (ACETONE SOLUTION).



○ (P-1) , ● (P-2) , Δ (P-3) , ▲ (P-4)

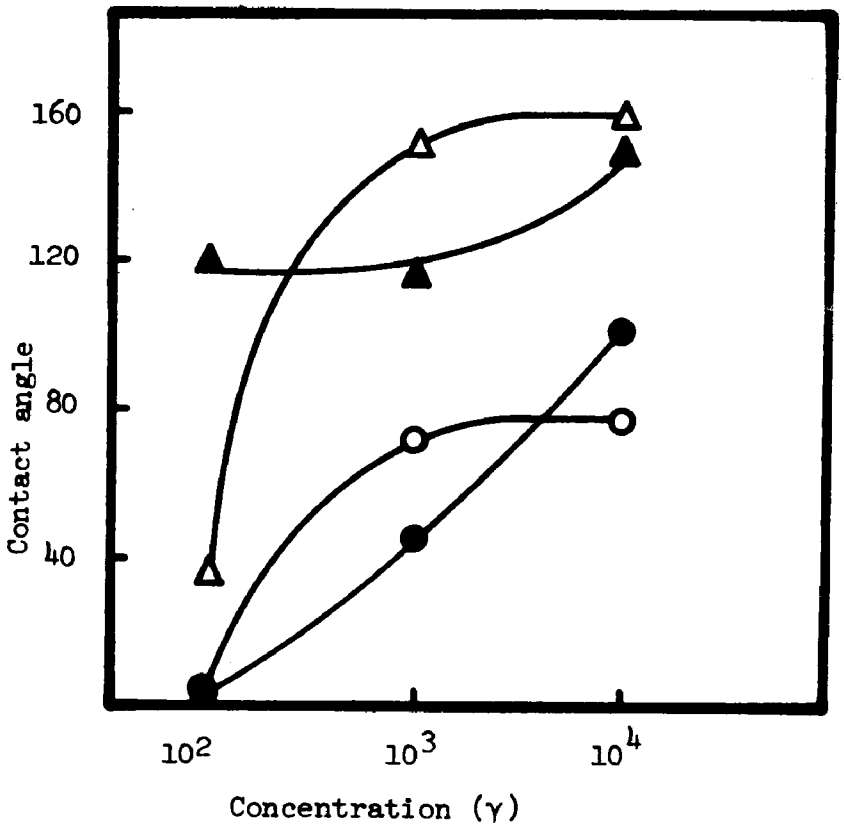
FIG. 2.6 RELATION BETWEEN CONTACT ANGLES AND INITIAL CONCENTRATIONS. (n-HEXANE SOLUTIONS).

Both P-3 and P-4 polymers give decreasing contact angles with increasing concentration. Probably many of the diamine groups are finding themselves "caught" on the outside, and, because the solvent is poor, these groups cannot "relax" onto the sites that become less available with increasing polymer concentration. The hexane data for P-1 and P-2 show that, in this solvent, these polymers give better (higher) contact angles. It is believed this is mainly due to the absence of solvent competition for adsorbing sites (in contrast to acetone). Again the data with calcium fluoride* support this viewpoint. This is probably because of the greater condensed nature of the adsorbed polymer in this case (in contrast to acetone) rather than the better burying of the diamines.

Figure 2.7 shows the contact angle data measured on hydroxyapatite discs treated with polymer solutions in aqueous mediums. The solvent used was the 20 percent ethanol, 80 percent acetate buffer mixture (pH = 4.85). The data show that except for P-4 polymers, very low contact angles were obtained at the 10^2 γ concentration level and the contact angles were generally increasing by increasing the polymer concentration to a limiting value at the 10^4 γ level. While P-1 and P-2 polymers showed comparatively low and unstable contact angles, P-3 and P-4 at higher concentration levels gave very high contact angles. For both P-3 and P-4 the higher than acetone values for the contact angle is probably due to very efficient utilization of the sites on the adsorbent and the polar groups in the polymer. This might be explained on the basis that, adsorption occurs onto sites that are solvated by water and the water molecules may act as bridges through hydrogen bonding to

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*See Chapter IV.



○ (P-1) , ● (P-2) , △ (P-3) , ▲ (P-4)

FIG. 2.7 RELATIONSHIP BETWEEN THE CONTACT ANGLE AND THE POLYMER CONCENTRATION IN THE AQUEOUS SOLVENT.

the diamine groups. It is also possible that ionization of the diamine groups plays a role here.

When these polymer-treated discs were subjected to the permanence test, contact angles dropped sharply, especially at 10^2 γ and 10^3 γ levels where the wettability became very high. Only P-3 and P-4 polymers at 10^4 γ levels showed signs of permanence on the apatite surface.

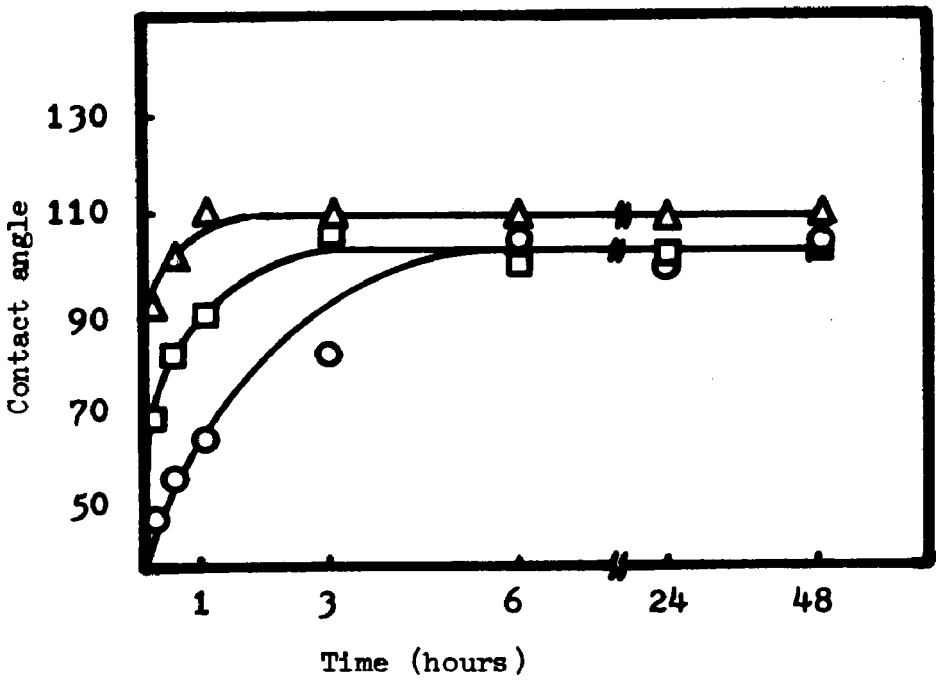
Figures 2.8 and 2.9 show the effect of adsorption times on contact angles for P-1 and P-3 polymer solutions in acetone. The figures show that an equilibrium value for the contact angle was reached after a period that varied from two to six hours.

2.4.2 Effect of Metal-Ion Pretreatment. Figures 2.10 through 2.16 summarize experiments aimed at elucidating the effect of metal-ion pretreatment upon the water contact angle. Acetone solutions of polymer P-3 was chosen for this comparative study as it gave high contact angles in the previous studies.

Figure 2.10 shows that an aqueous Sn^{2+} pretreatment gives extremely high contact angles that are independent of the applied acetone polymer solution concentration. Ca^{2+} and Mg^{2+} appear to show little improvement over the control.

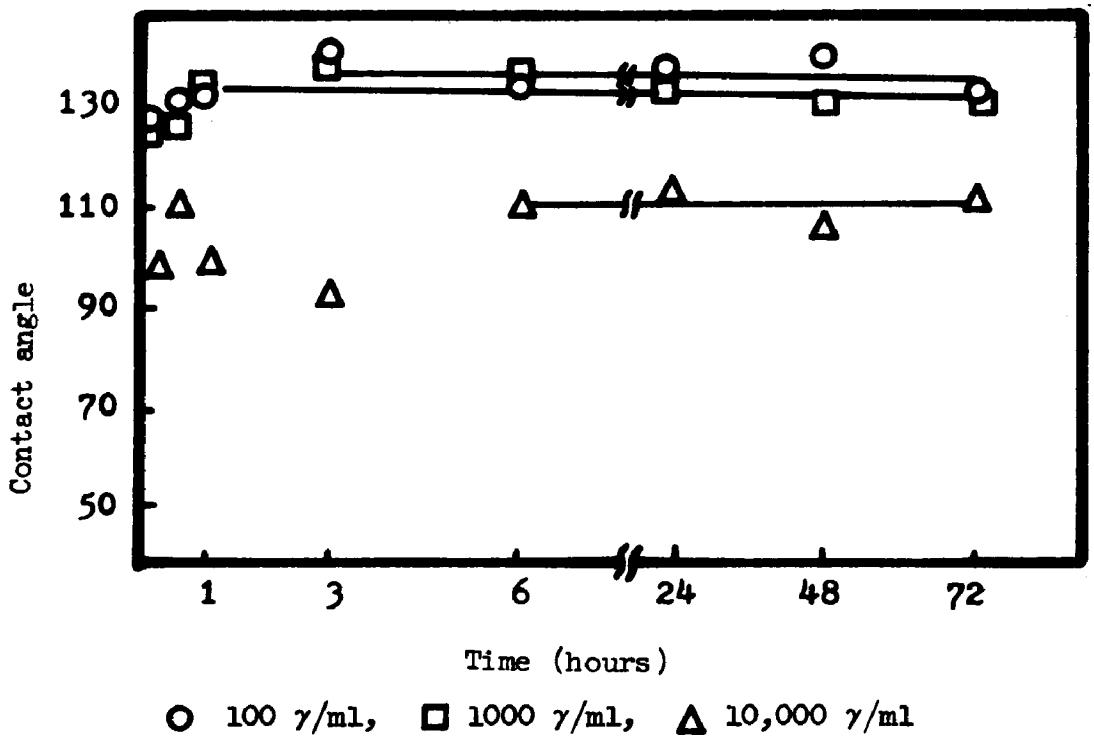
Figure 2.11 presents the concentration and time of pretreatment effects for Sn^{2+}. The data show that adequate incorporation of Sn^{2+} on the apatite surface takes place within ten minutes from the 0.10 M aqueous solution of $SnCl_2$ to give maximum contact angles.

Figure 2.12 shows that the aqueous Sn^{2+} pretreatment (for 24 hours) followed by P-3 adsorption from an aqueous solvent can give the same high contact angle on hydroxyapatite as with adsorption from acetone.



○ 100 γ/ml, □ 1000 γ/ml, △ 10,000 γ/ml

FIG. 2.8 RELATIONSHIP BETWEEN CONTACT ANGLES AND SHAKING TIMES OF (P-1) ACETONE SOLUTIONS.



○ 100 γ/ml, □ 1000 γ/ml, △ 10,000 γ/ml

FIG.2.9 RELATIONSHIP BETWEEN CONTACT ANGLES AND SHAKING TIMES OF (P-3) ACETONE SOLUTIONS.

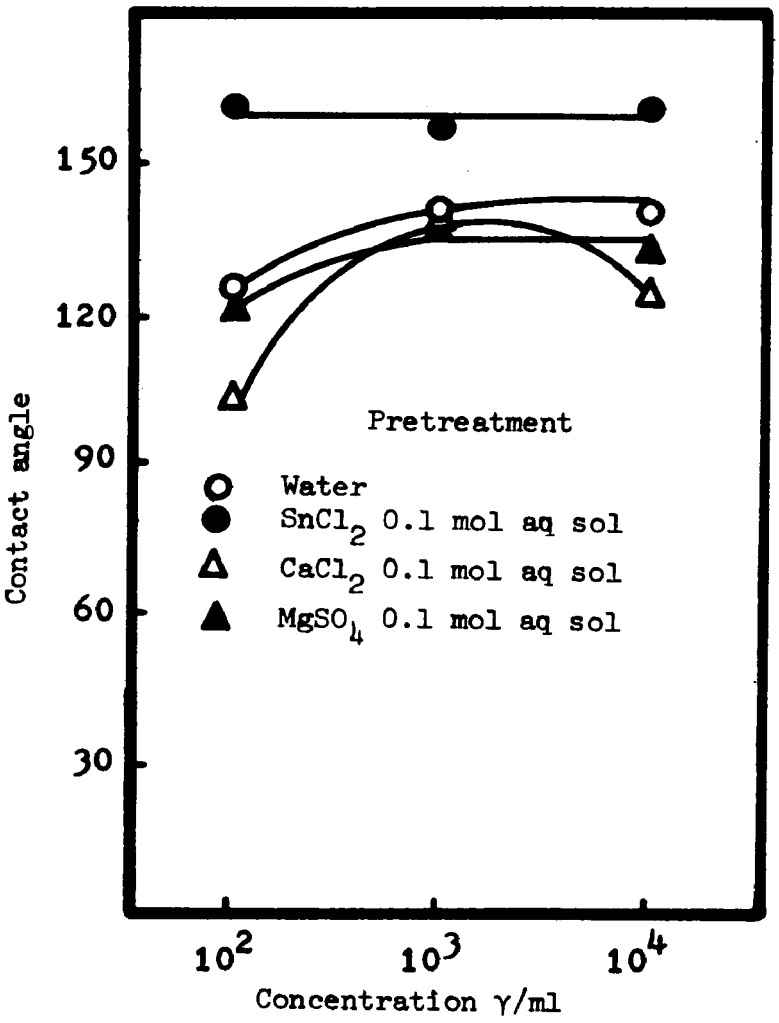


FIG. 2.10 EFFECT OF METAL ION PRETREATMENT ON VICTOR APATITE CONTACT ANGLES AFTER P-3 ADSORPTION FROM ACETONE SOLUTIONS.

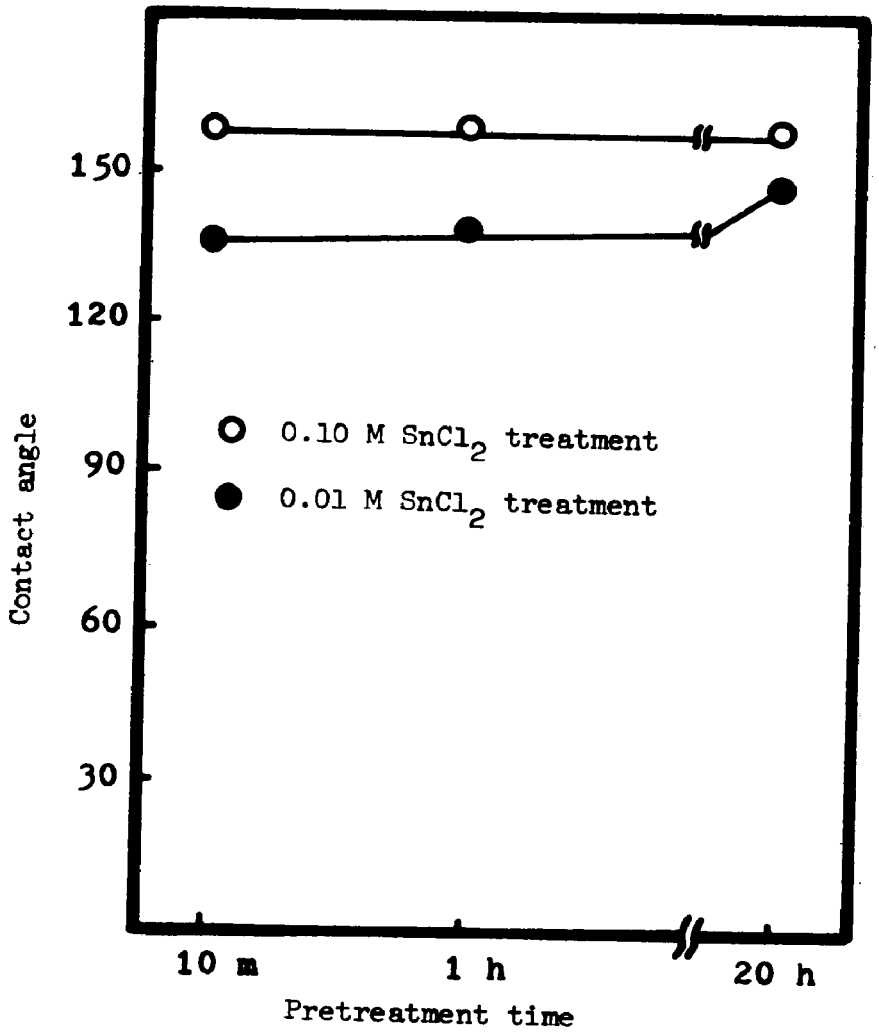


FIG. 2.11 RELATIONSHIP BETWEEN CONDITIONS OF PRETREATMENT AND CONTACT ANGLE IN THE CASE OF P-3 ADSORPTION FROM ACETONE SOLUTIONS (100 γ/ml).

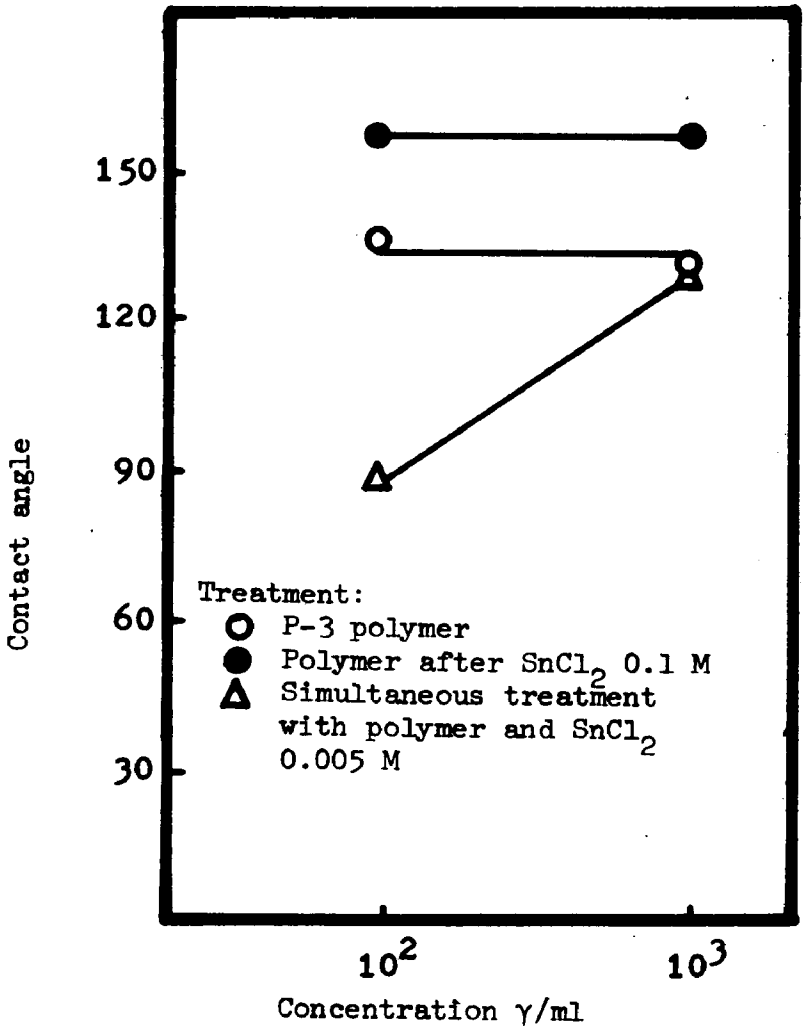
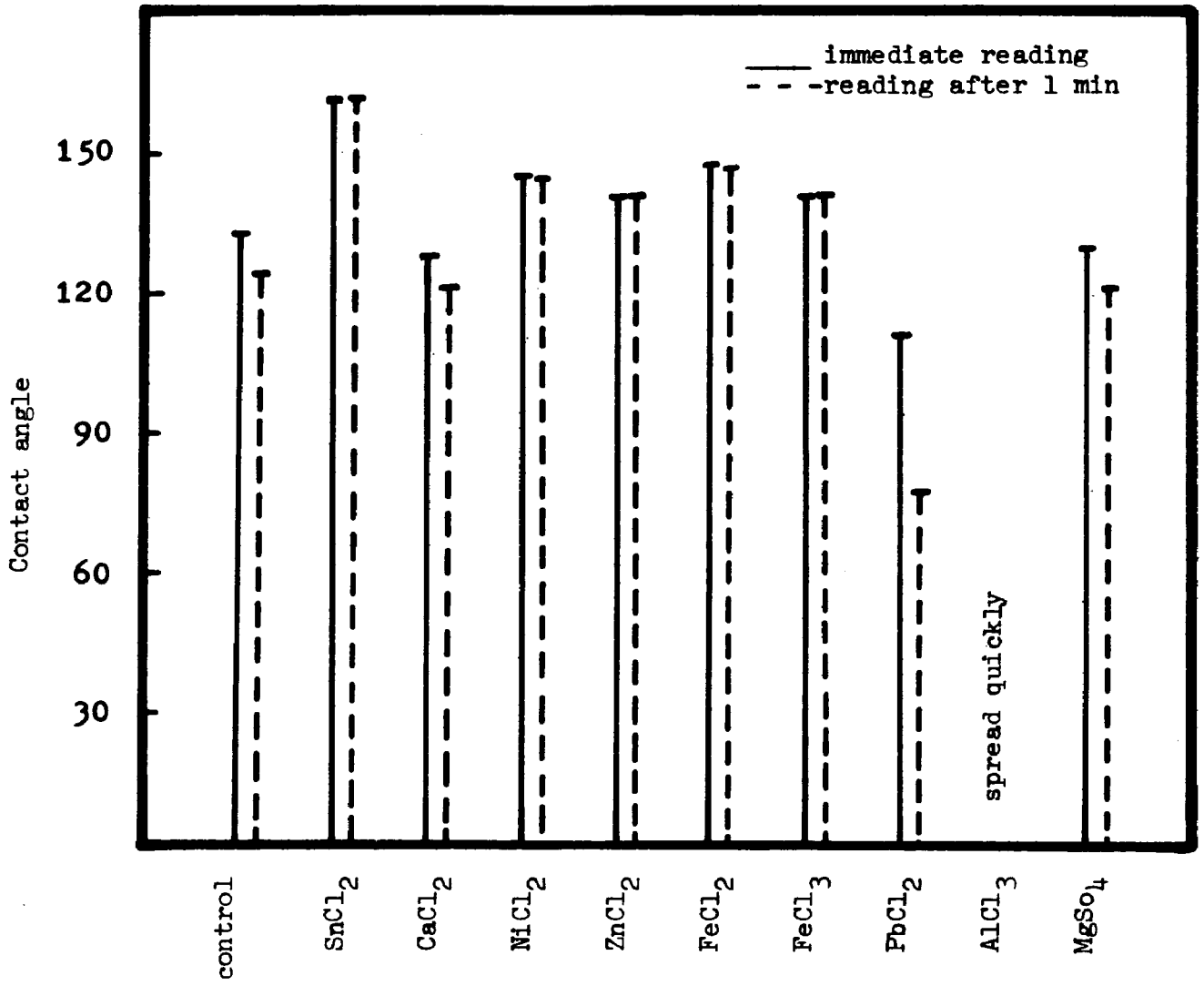
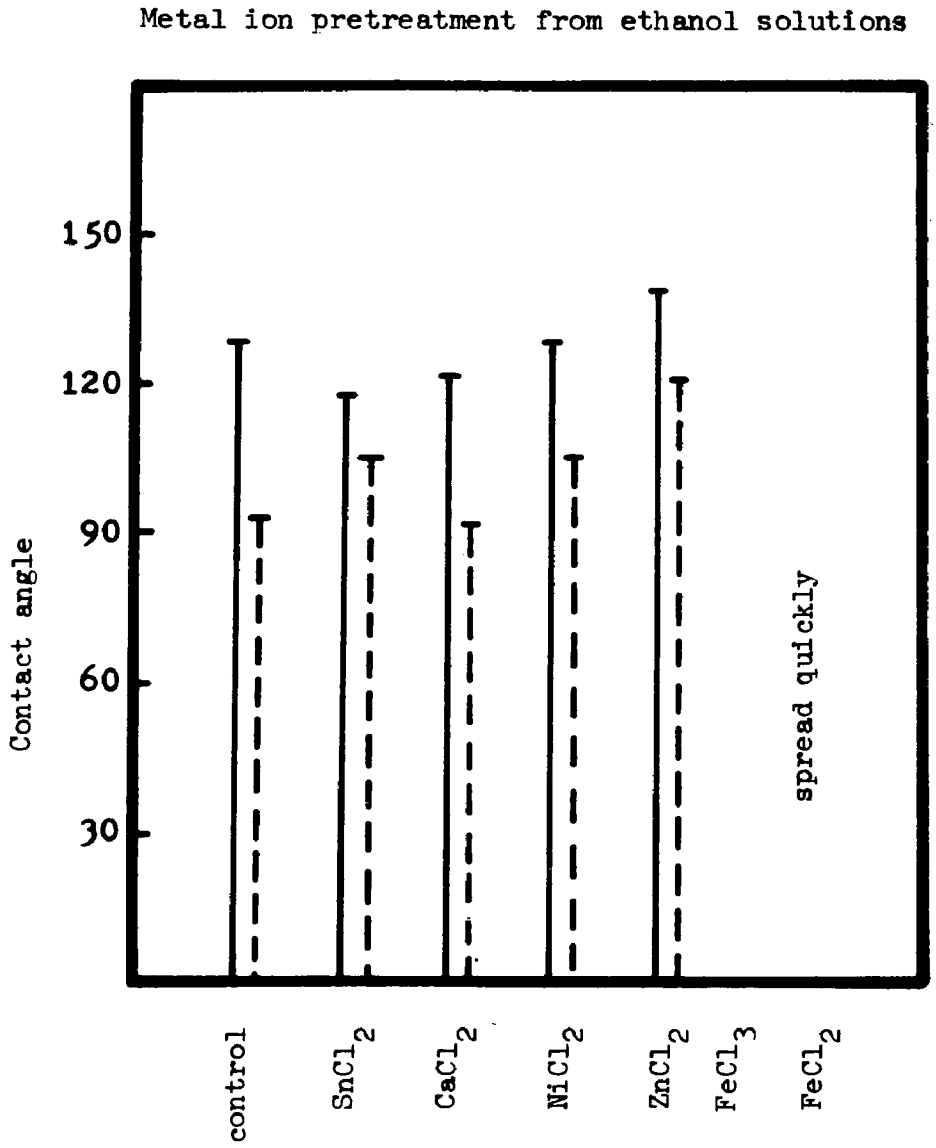


FIG. 2.12 CONTACT ANGLES ON VICTOR APATITE SHOWING EFFECTS OF $SnCl_2$ TREATMENT AND POLYMER ADSORPTION FROM ACETATE BUFFER (pH = 4.85).



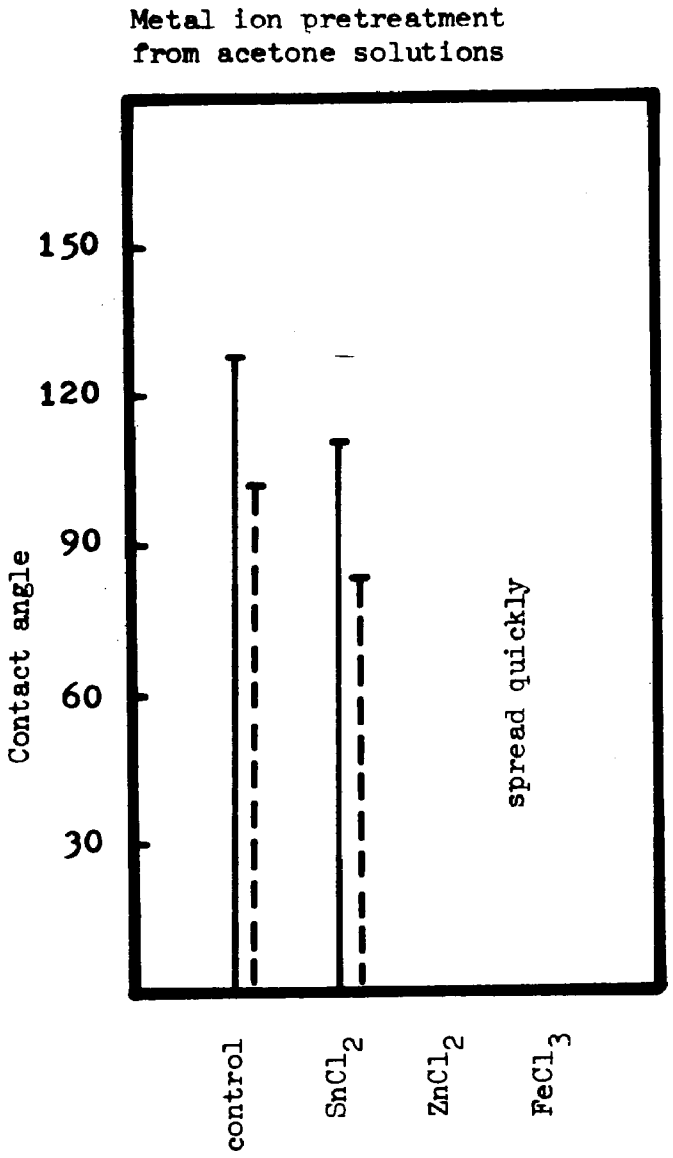
Control: Apatite discs treated directly with the polymer solution.

FIG. 2.13 CONTACT ANGLES ON VICTOR APATITE AFTER PRETREATMENT WITH VARIOUS METAL IONS (0.10 M AQUEOUS) AND ADSORPTION OF P-3 (1000 γ/ml ACETONE SOLUTION).



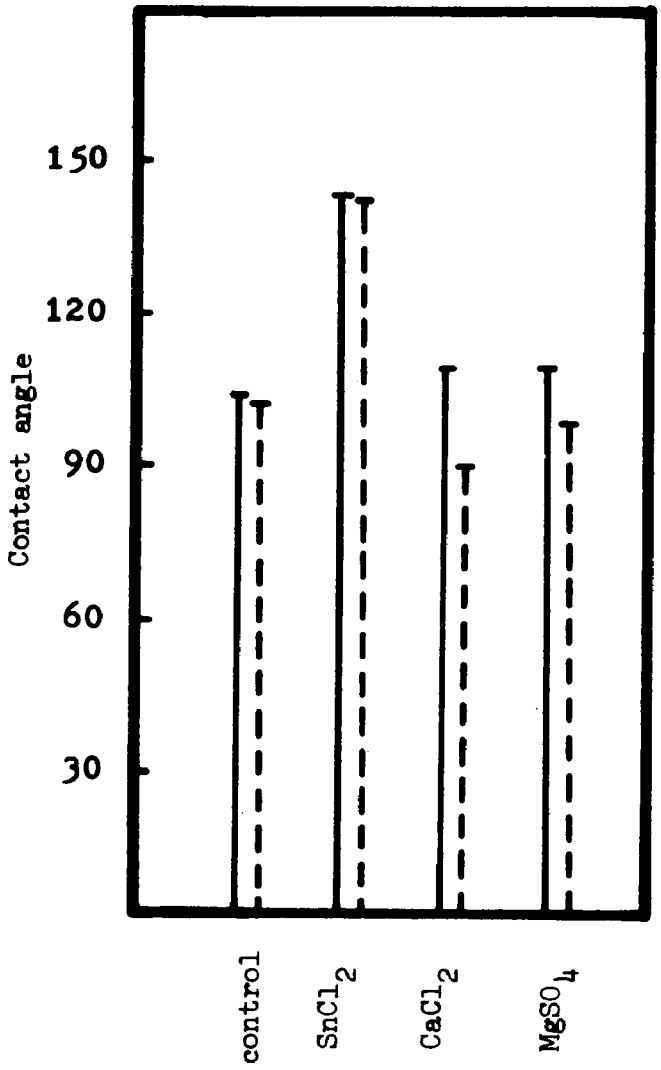
Control: Apatite discs treated directly with the polymer solution.

FIG. 2.14 METAL ION PRETREATMENT FROM ETHANOL SOLUTIONS.



Control: Apatite discs treated directly with the polymer solution.

FIG. 2.15 METAL ION PRETREATMENT FROM ACETONE SOLUTIONS.



Control: Apatite discs treated directly with the polymer solution.

FIG. 2.16 CONTACT ANGLES ON VICTOR APATITE. P-3 ADSORPTION FROM HEXANE SOLUTION (3500 γ/ml). AQUEOUS METAL ION PRETREATMENT (0.10 M).

Figure 2.13 compares the Sn^{2+} pretreatment with those of other metal ions all from aqueous solutions. The data show that Sn^{2+} is far superior to the others in this group. Ni^{2+}, Zn^{2+} and Fe^{2+} appear to be significantly better than the control.

Figures 2.14 and 2.15 show that metal-ion prepreatments from nonaqueous solvents generally gave much lower contact angles. The data suggest that the "activation" of the apatite surface by metal ion for optimal interaction with the diamine group is best achieved by direct adsorption of the metal ion.

Figure 2.16 shows that the metal ion effect is also present when the polymer, P-3, is adsorbed from hexane instead of acetone.

Tables 2.5 through 2.8 present the contact angle data for the aqueous-alcoholic solutions of P-1 to P-4 polymers at three different concentration levels and emphasize the effect of the presence of the metal ion on the solid surface. Table 2.5 shows the data where 0.10 M zinc chloride aqueous solution was the pretreating reagent applied for ten minutes. Table 2.6 shows the data when stannous chloride was used instead of zinc chloride. A significantly higher water angle of contact in both cases is observed than those in the absence of the metal ion (Fig. 2.7). Also a better permanence was obtained (Tables 2.5 and 2.6).

Tables 2.7 and 2.8 show the results of ten minutes and 24 hours of simultaneous treatment of polymer-$ZnCl_2$ and polymer-$SnCl_2$ mixtures. In both experiments 0.10 M concentration levels of the metal salt was used in the treating solutions. It is very significant that high contact angles and very good permanence was observed with the mixtures containing

Table 2.5

Contact Angles Measured on Apatite Surfaces After Zinc Chloride Pre-treatment Followed by Polymer Contact
Results Obtained after 24 Hours

Polymer Concentration	P-1 (degrees)	P-2 (degrees)	P-3 (degrees)	P-4 (degrees)
10^2 γ/ml	121	132, 134	151, 150	138, 141
10^3 γ/ml	138, 142	135, 147	146, 143	148, 150
10^4 γ/ml	140, 141	134, 137	149, 149	151, 147

Results of the Permanence Test

Polymer Concentration	P-1 (degrees)	P-2 (degrees)	P-3 (degrees)	P-4 (degrees)
10^2 γ/ml	zero	zero	67	136, 135
10^3 γ/ml	147, 146	155	128, 133	123, 125
10^4 γ/ml	129, 134	151, 150	142, 142	128, 122

The zinc chloride concentration was 0.1 M in aqueous solution and the pH of the polymer solution was 4.85.

Table 2.6

Contact Angles Measured on Apatite Surfaces After Stannous Chloride Pretreatment Followed by Polymer Contact

Results Obtained after 24 Hours

Polymer Concentration	P-1 (degrees)	P-2 (degrees)	P-3 (degrees)	P-4 (degrees)
10^2 γ/ml	136, 141	148, 143	147, 141	118, 123
10^3 γ/ml	126, 137	163, 161	148, 148	150, 146
10^4 γ/ml	161, 160	153, 159	163, 154	127, 123

Results of the Permanence Test

Polymer Concentration	P-1 (degrees)	P-2 (degrees)	P-3 (degrees)	P-4 (degrees)
10^2 γ/ml	zero	zero	81, 76	42, 39
10^3 γ/ml	142, 137	148, 146	141, 146	127, 137
10^4 γ/ml	146, 148	161, 164	150, 157	141, 143

The stannous chloride concentration was 0.1 M in aqueous solution, and the pH of the polymer solution was 4.85.

Table 2.7

Contact Angles Measured on Apatite Surfaces After Simultaneous Treatment with Zinc Chloride and Polymer

Results Obtained After Ten Minutes Treatment with the Solution

Polymer Concentration	P-1 (degrees)	P-2 (degrees)	P-3 (degrees)	P-4 (degrees)
10^2 γ/ml	zero	zero	152, 148	145, 145
10^3 γ/ml	zero	150, 145	150, 151	155, 145
10^4 γ/ml	123, 127	150, 152	145	151, 153

Results After 24 Hours Treatment

Polymer Concentration	P-1 (degrees)	P-2 (degrees)	P-3 (degrees)	P-4 (degrees)
10^2 γ/ml	zero	142, 142	153, 152	144, 141
10^3 γ/ml	140, 147	150, 141	147, 138	145, 143
10^4 γ/ml	145, 147	147, 147	138, 131	147, 148

Results of the Permanence Test

Polymer Concentration	P-1 (degrees)	P-2 (degrees)	P-3 (degrees)	P-4 (degrees)
10^2 γ/ml	zero	zero	115, 136	137, 135
10^3 γ/ml	146, 142	145, 152	156, 152	153, 152
10^4 γ/ml	146, 144	147, 142	148, 142	153, 143

Table 2.8

Contact Angles Measured on Apatite Surfaces After Simultaneous Treatment with Stannous Chloride and Polymer

Results Obtained After Ten Minutes Treatment with the Solution

Polymer Concentration	P-1 (degrees)	P-2 (degrees)	P-3 (degrees)	P-4 (degrees)
10^2 γ/ml	zero	zero	zero	zero
10^3 γ/ml	155, 152	149, 150	155, 154	zero
10^4 γ/ml	152, 157	154, 150	151, 151	155, 160

Results After 24 Hours Treatment

Polymer Concentration	P-1 (degrees)	P-2 (degrees)	P-3 (degrees)	P-4 (degrees)
10^2 γ/ml	45, 35	zero	zero	zero
10^3 γ/ml	148	85	75, 80	zero
10^4 γ/ml	166	144, 162	155, 147	112, 146

Results of the Permanence Test

Polymer Concentration	(degrees)	(degrees)	(degrees)	(degrees)
10^2 γ/ml	zero	zero	zero	zero
10^3 γ/ml	zero	zero	zero	zero
10^4 γ/ml	146, 145	146, 152	153, 153	152, 154

zinc chloride and polymer. All polymers gave favorable results. The experiments with stannous chloride (Table 2.8) are not interpretable because the 24-hour treatment resulted in the deposition of a stannous oxide layer on the solid surface.

2.4.3 Shorter Pretreatment Time. Table 2.9 gives the results of using a one-minute pretreatment of the 0.10 M metal salt solutions followed by 24-hour contact of the tablet with the polymer solution (10^3 γ/ml). The initial contact angles are high and do not appear to be significantly different from the ten-minute pretreatment. However, the permanence is not as good with the shorter pretreatment time. Permanence is still superior to that observed in the absence of metal ion pretreatment.

2.4.4 Effect of Polymer Solution pH. Table 2.10 gives the results when the pH of the hydroalcoholic solvent mixture was 4.0 instead of 4.85. The pH was limited in this range because of the high solubility of hydroxyapatite at lower values, and the poor solubility of the polymers at higher ones. At pH 4.0, the initial contact angles are comparable to those given in Tables 2.5 and 2.6. The permanence appears to be somewhat poorer at this lower pH for P-2 and zinc chloride, but about the same for P-2 and stannous chloride. The permanence of P-3 and zinc chloride appears to be better at this lower pH. In general, however, pH does not appear to be important in this range.

2.4.5 Contact Angle Results with Tooth Surfaces. Tooth treatment was carried out in the following manner. Tooth surfaces were etched in acetate buffer (pH = 4.6) for 30 seconds. They were then exposed for

Table 2.9

Contact Angles Measured on Apatite Surfaces After One-Minute Pretreatment with the Metal Salt Solution Followed by 24 Hours of Polymer Contact

Contact Angle Results

Treatment	P-1 (degrees)	P-2 (degrees)	P-3 (degrees)	P-4 (degrees)
$ZnCl_2$	140, 143	145, 140	157, 150	152, 148
$SnCl_2$	135, 137	158, 154	154, 151	147, 147

Results of the Permanence Test

Treatment	P-1 (degrees)	P-2 (degrees)	P-3 (degrees)	P-4 (degrees)
$ZnCl_2$	136, 133	129, 125	104, 98	87, 93
$SnCl_2$	136, 135	141, 131	114, 110	84, 88

The zinc chloride and stannous chloride concentrations were 0.1 M in aqueous solution and the polymer concentration was 10^3 γ/ml in the hydro-alcoholic solvent.

Table 2.10

Contact Angles Measured on Apatite Surfaces After Polymer Treatment at Low pH with and Without Pretreatment with $ZnCl_2$ or $SnCl_2$

Contact Angle Results

	P-1 (degrees)	P-2 (degrees)	P-3 (degrees)	P-4 (degrees)
No pretreatment	135, 137	133, 133	133, 138	132, 134
$ZnCl_2$	143, 140	137, 138	140, 145	144, 142
$SnCl_2$	144, 145	154, 153	138, 145	149, 142

Results of the Permanence Test

	P-1 (degrees)	P-2 (degrees)	P-3 (degrees)	P-4 (degrees)
No pretreatment	66, 69	129, 132	127, 122	115, 108
$ZnCl_2$	100, 106	131, 131	142, 146	132, 129
$SnCl_2$	90, 92	158, 151	108, 114	118, 114

Acetate buffer (pH 3.81) plus 20 percent absolute ethanol was used as a solvent (the measured pH of the mixture was 4.0). Polymer concentration was 10^3 γ/ml. The concentrations of $ZnCl_2$ and $SnCl_2$ were 0.1 M in aqueous solution.

ten minutes to 0.10 M aqueous solution of $SnCl_2$ or $ZnCl_2$, rinsed with water and dried. Polymers P-1 through P-4 were then adsorbed at two concentration levels from their aqueous-alcoholic solutions at 30°C for 24 hours. The teeth were then rinsed with the same solvent, dried at 55°C for one hour, and the contact angles measured.

The contact angles with and without the $SnCl_2$ or $ZnCl_2$ pretreatment are shown in Table 2.11. The data indicated lower values than those obtained on compressed synthetic apatite surfaces. This was probably due to the inefficiency of the etching in removing all the surface impurities. The data also indicated relatively higher contact angles with P-3 polymer.

Table 2.12 gives the contact angle results measured on tooth surfaces which received a simultaneous treatment of the polymers at 10^3 γ/ml concentration level together with zinc chloride 0.10 M in the aqueous-alcoholic solvent. The contact angles parallel those found in the pretreatment experiments. Again, the data indicate relatively higher values with P-3 polymers.

Table 2.13 shows the results of comparative studies on tooth surfaces, using P-3 polymer solution in hexane, acetone and ethanol-buffer solvents with and without the metal ion pretreatment. One group of the teeth was etched with 0.10 N hydrochloric acid solution for 30 seconds, which was sufficient to bring the angle of contact down to zero. The data demonstrate a dependency of the nature of the formed film on the initial surface conditions of the teeth prior to treatment. Also, it is shown that, with the perfect conditions and the

Table 2.11

Effect of Polymer Concentration and Metal-Ion Pretreatment on Contact Angle Measured on Tooth Surface

Contact Angle Results

Treatment	Contact Angles			
Polymer Conc.	P-1 (degrees)	P-2 (degrees)	P-3 (degrees)	P-4 (degrees)
10^3 γ/ml	92, 94	112, 98	111, 119	116, 119
$ZnCl_2$ + 10^3 γ/ml	124, 118	117, 122	122, 123	114, 101
$SnCl_2$ + 10^3 γ/ml	102, 96	108, 99	131, 129	98, 97
10^4 γ/ml	90, 95	101, 94	118, 113	115, 98
$ZnCl_2$ + 10^4 γ/ml	120, 123	118, 121	125, 125	112, 118
$SnCl_2$ + 10^4 γ/ml	118, 124	116, 111	134, 133	117, 112

Results of the Permanence Test

Treatment	Contact Angle			
Polymer Conc.	P-1 (degrees)	P-2 (degrees)	P-3 (degrees)	P-4 (degrees)
10^3 γ/ml	111, 106	88, 97	101, 94	111, 96
$ZnCl_2$ + 10^3 γ/ml	125, 115	112, 108	110, 117	104, 95
$SnCl_2$ + 10^3 γ/ml	105, 94	98, 100	108, 108	117, 103
10^4 γ/ml	91, 94	82, 89	102, 105	121, 113
$ZnCl_2$ + 10^4 γ/ml	116, 112	108, 114	123, 120	106, 109
$SnCl_2$ + 10^4 γ/ml	113, 118	108, 111	126, 127	109, 104

Table 2.12

Contact Angles Measured After Simultaneous Treatment of Teeth with Polymers (10^3 γ/ml) and Zinc Chloride 0.1 M in Aqueous-Alcoholic Medium

Treatment Time	P-1 (degrees)	P-2 (degrees)	P-3 (degrees)	P-4 (degrees)
10 minutes	98, 108	118, 116	130, 126	120, 120
24 hours	107, 105	118, 114	112, 125	116, 121
results after permanence*	97, 92	101, 106	128, 117	105, 110

* Permanence test was carried out following the 24 hour treatment.

Table 2.13

Contact Angles Measured on Teeth Surfaces Treated with P-3 Polymer Showing the Effect of Etching, Solvent Nature and Metal-Ion Pretreatment

Treatment	Acetate Buffer Etch		0.1 N HCl Etch	
	C. angle	Perm.	C. angle	Perm.
P-3/hexane	110, 106	88, 86	143, 142	126, 122
$SnCl_2$ - P-3/hexane*	143, 146	91, 87	146, 142	140, 137
$ZnCl_2$ - P-3/hexane			139, 137	128, 137
P-3/acetone	94, 98	94, 88	140, 147	127, 126
$SnCl_2$ - P-3/acetone*	154, 149	86, 98	142, 149	138, 134
$ZnCl_2$ - P-3/acetone			149, 151	124, 129
P-3/buffer	88, 86	96, 86	134, 142	121, 127
$SnCl_2$ - P-3/buffer*	140, 134	80,88	141, 144	135, 131
$ZnCl_2$ - P-3/buffer			142, 140	123, 121

* A thin layer of SnO has developed on the tooth surface during the treatment.

Note: In this experiment the concentrations of the polymer, $SnCl_2$ and $ZnCl_2$ were $10^3\gamma$/ml, 0.01 M and 0.10 M, respectively.

correct manner of treatment, a stable hydrophobic polymer film can be deposited on the tooth surface.

2.4.6 Results of Experiments on Polymers with Sarcosine Type End Groups. Compounds listed in Table 2.13 were tested for their film formation on compressed hydroxyapatite discs. These polymers were applied from acetate buffer-ethanol solvent systems at concentrations of 10^3 γ/ml for the indicated time. Table 2.14 shows contact angles measured after ten-minute and 20-minute treatment periods together with the permanence data obtained for each experiment. Table 2.15 summarizes the results of polymer treatments and simultaneous treatments with the polymer-zinc chloride solution mixture. The sequence of polymer treatment followed by the permanence test was repeated three times on the same samples. Treatment was maintained for ten minutes and the permanence was carried out as usual for 24 hours under the above-mentioned conditions. Very high contact angles with good permanence were obtained after the third treatment with S-3 polymer in the presence and absence of $ZnCl_2$, and with S-5 polymer-$ZnCl_2$ systems.

After the third treating period, S-3 polymer treatment without zinc chloride gave contact angles and permanence quite similar to S-3 with zinc chloride systems. The S-6 polymer showed poor permanence after two treatments but subsequent treatments led to improved permanence. The presence of zinc chloride did not increase the contact angle.

Table 2.14

Contact Angles Measured on Apatite Surfaces After Short-Time Treatment with S-3, S-5 and S-6 Polymers

Polymer*	10 Minute Treatment		20 Minute Treatment	
	C. Angle (degrees)	Perm. C.A. (degrees)	C. Angle (degrees)	Perm. C.A. (degrees)
S-3	138, 132	90, 106	138, 142	91, 88
S-5	132, 129	64, 69	124, 126	128, 124
S-6	138, 141	52, 61	133, 138	80, 84

* Polymer concentration was 10^3 γ/ml.

Table 2.15

Contact Angles Measured on Hydroxyapatite Discs After Several Treatments with Polymers S-3, S-5, and S-6

Polymer	First 10 Minutes		Second 10 Minutes		Third 10 Minutes	
	C. angle (degrees)	Perm. C.A. (degrees)	C. angle (degrees)	Perm. C.A. (degrees)	C. angle (degrees)	Perm. C.A. (degrees)
S-3	142, 136	86, 92	148, 146	114, 116	147, 147	146, 147
S-3/$ZnCl_2$	140, 137	129, 130	158, 148	155, 154	153, 148	148, 154
S-5	130, 134	56, 64	156, 157	72, 74	150, 154	68, 71
S-5/$ZnCl_2$	136, 146	97, 102	130, 133	122, 123	146, 151	144, 148
S-6	138, 131	67, 59	140, 140	71, 68	154, 150	150, 150
S-6/$ZnCl_2$	138, 140	63, 59	143, 141	62, 66	153, 152	70, 78

CHAPTER III. ADSORPTION ON HYDROXYAPATITE POWDER

3.1 Introduction

Adsorption isotherm experiments were conducted to delineate the factors influencing the adsorption and the configuration of polymers at the hydroxyapatite surface. The following aspects of this problem are presented:

1. Polymer adsorption from solvents of different polarities.

2. Adsorption of low and high molecular weight siloxane polymers with monoamine and diamine anchoring groups.

3. Adsorption of monomers chemically related to the polymers and having the same active groups.

4. Adsorption of siloxane polymers of different polar- and nonpolar-group ratios.

In the course of this study, the following two monomers were used:

n-octylamine $CH_3(CH_2)_7 NH_2$,

n-octylethylenediamine $CH_3(CH_2)_7 NH(CH_2)_2 NH_2$.

Also employed were the nine dimethylsiloxane polymers found in Table 2.2.

3.2 General Procedure

In a 100-ml measuring flask, 20 ml of polymer solution were added to 100 mg of dry hydroxyapatite powder. The flasks were then shaken for 20 hours in a constant temperature water bath which was maintained at 30°C by an Aminco relay system. The rate of shaking was maintained

constant in all the experiments. After equilibrium, the flasks were removed and their contents were centrifuged* in polyethylene tubes at 10,000 rpm for 20 minutes. An aliquot of the supernatant was then assayed by a nonaqueous titration method. The experimental concentration range of the polymers was limited by solubility considerations at the upper end and by assay sensitivity at the lower end.

3.3 Assay Method

The decanted portion of the polymer solution was evaporated in a 100-ml beaker. The residue was dissolved in 10 ml of glacial acetic acid (GAA) and titrated with freshly diluted 0.01 or 0.001 N perchloric acid solution in GAA using 0.1 percent crystal violet solution in GAA as an indicator. A magnetic stirrer was used during the titration to ensure rapid mixing in the beaker. The drying step proved to be unnecessary when n-hexane was used as a solvent but it gave more accurate endpoints when acetone or ethanol were the solvents.

All of the adsorption experiments were duplicated and the amounts of polymer adsorbed were plotted against the solution equilibrium concentrations.

3.4 Results

Adsorption experiments were first performed with a high molecular weight polydimethylsiloxane polymer** in n-hexane and cyclohexane using hydroxyapatite as the adsorbent. Atomic absorption spectroscopy was

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* Lourdes Instrument Corp., Brooklyn, N. Y.

** Dow Corning 200 fluid.

used to assay the polymer in the bulk. No measurable adsorption took place. This was also confirmed by measuring the water angle of contact on compressed apatite discs treated by this polymer and no change from the control was observed. The results indicate that the dimethylsiloxane polymers do not adsorb to the apatite surface unless a selective anchoring group is present in the polymer structure.

The first four polymers of Table 2.2 were used in the subsequent adsorption experiments to determine the amounts of the polymers adsorbed as a function of time from acetone and n-hexane solutions. The minimum time required for the polymers to reach equilibrium at the apatite surface was determined from Figs. 3.1 and 3.2 where the amounts adsorbed in milligram of polymer per gram of adsorbent are plotted versus the adsorption time.

In general, from two to six hours were required to establish equilibrium. The greater time dependency of adsorption when acetone is the solvent (Fig. 3.1) may be related to the better solvent nature of acetone which permits greater surface configuration rearrangement after initial adsorption. The hexane data (Fig. 3.2) suggest that the surface configuration of the polymer depends to a large extent upon the polymer configuration at the time of collision (or initial contact) of the polymer with the apatite surface. Only P-1 polymer adsorption from hexane showed relatively more time dependency which may be due to its longer hydrophobic chain and so higher solubility in hexane. On the basis of these results, twenty hours polymer treatment was followed in all the adsorption isotherm experiments to ensure sufficient time for equilibration.

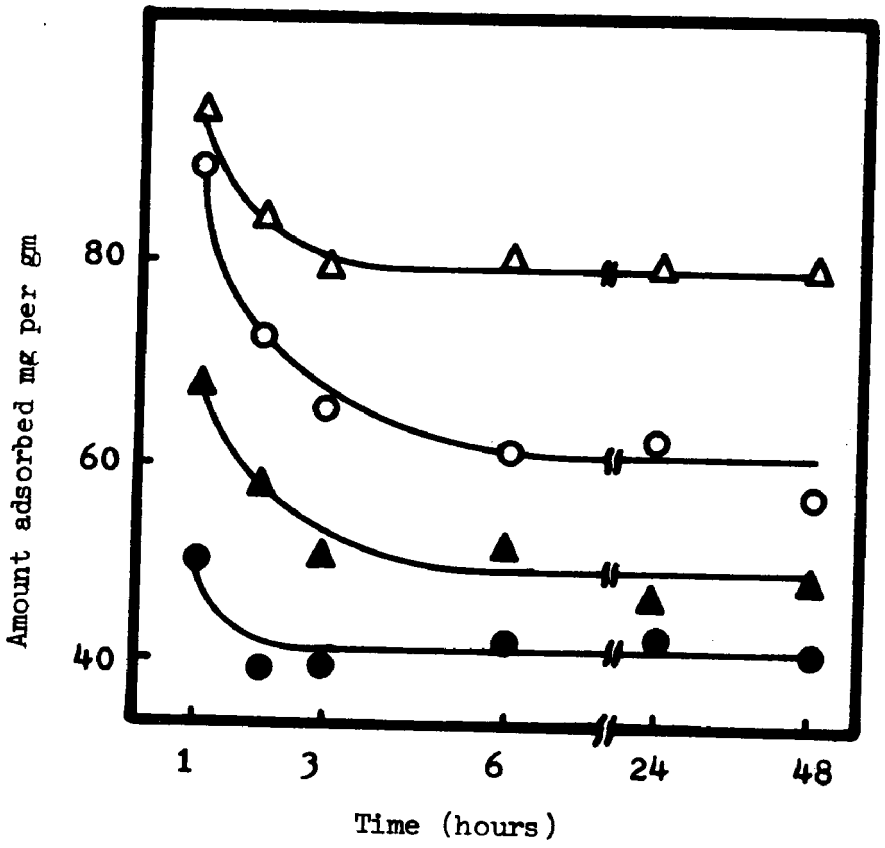


FIG. 3.1 THE RELATIONSHIP BETWEEN THE AMOUNT OF POLYMERS ADSORBED FROM ACETONE SOLUTIONS AND THE ADSORPTION TIME.

○ (P-1) , ● (P-2) , △ (P-3) , ▲ (P-4)

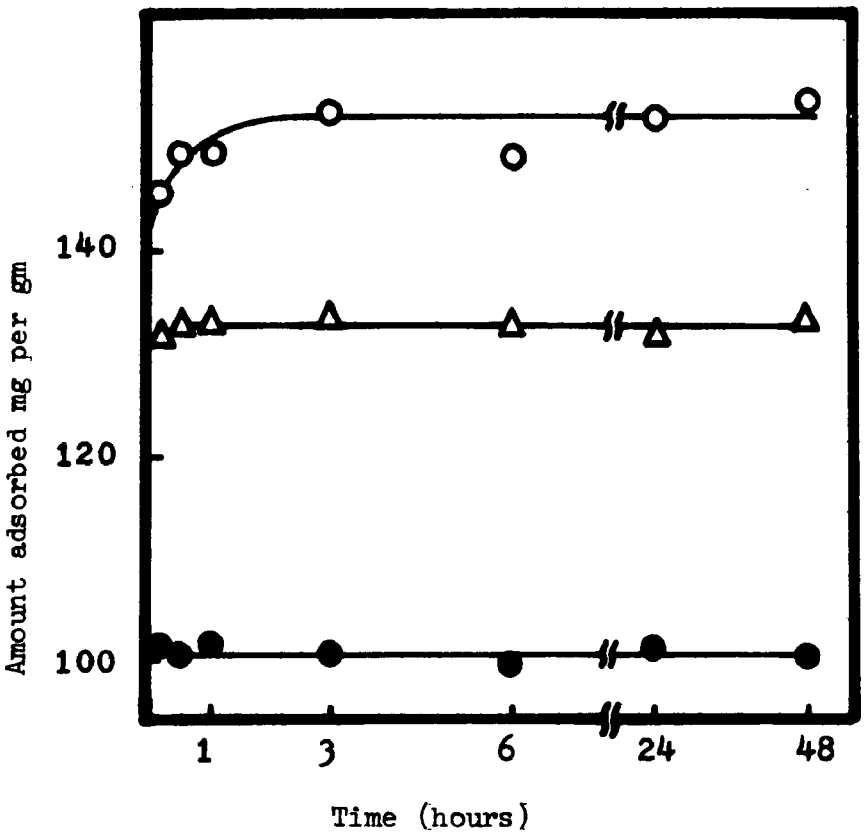


FIG. 3.2 THE RELATIONSHIP BETWEEN THE AMOUNT OF POLYMERS ADSORBED FROM HEXANE AND THE ADSORPTION TIME.

○ (P-1) , ● (P-2) , Δ (P-3) ,

Figures 3.3 and 3.4 show the adsorption isotherms for n-$C_8H_{17}NH(CH_2)_2NH_2$ and n-$C_8N_{17}NH_2$ in several solvents. These compounds represent "monomers" having the same anchoring groups present in the siloxane polymers studied and provide baselines for the polymer adsorption data. Acetone, n-hexane, ethanol, cyclohexane and chloroform were tried as solvents representing different "solvent power." Results in Fig. 3.3 show that with n-$C_8H_{17}NH(CH_2)_2NH_2$, a much higher limiting value is reached in n-hexane and cyclohexane than in the three polar solvents. The large difference may indicate significant solvent competition of some of the sites for adsorption when a polar solvent is used. With the monamine, the same general trend was found (Fig. 3.4) except adsorption from ethanol approached the higher values at high solute concentrations. On a molar basis, the same limiting value of the amount adsorbed from hexane was obtained with both compounds, and this probably represents a monomolecular layer of molecules on hydroxyapatite surface consuming all of the available sites.

Figures 3.5 through 3.13 give the hydroxyapatite adsorption data for all of the polymers from n-hexane, acetone, ethanol and cyclohexane. The curves are similar in shape to Langmuir isotherms and give linear plots of C/A versus C where C is the equilibrium concentration and A is the amount adsorbed per gram of adsorbent. While certain generalizations may be immediately apparent, it is instructive to examine Table 3.1 where the limiting adsorption data have been summarized and analyzed. In Table 3.1 the limiting values have been presented on a weight adsorbed basis, on a molar basis, and finally, on a monomer equivalent basis using hexane adsorption as the reference (100 percent). Thus,

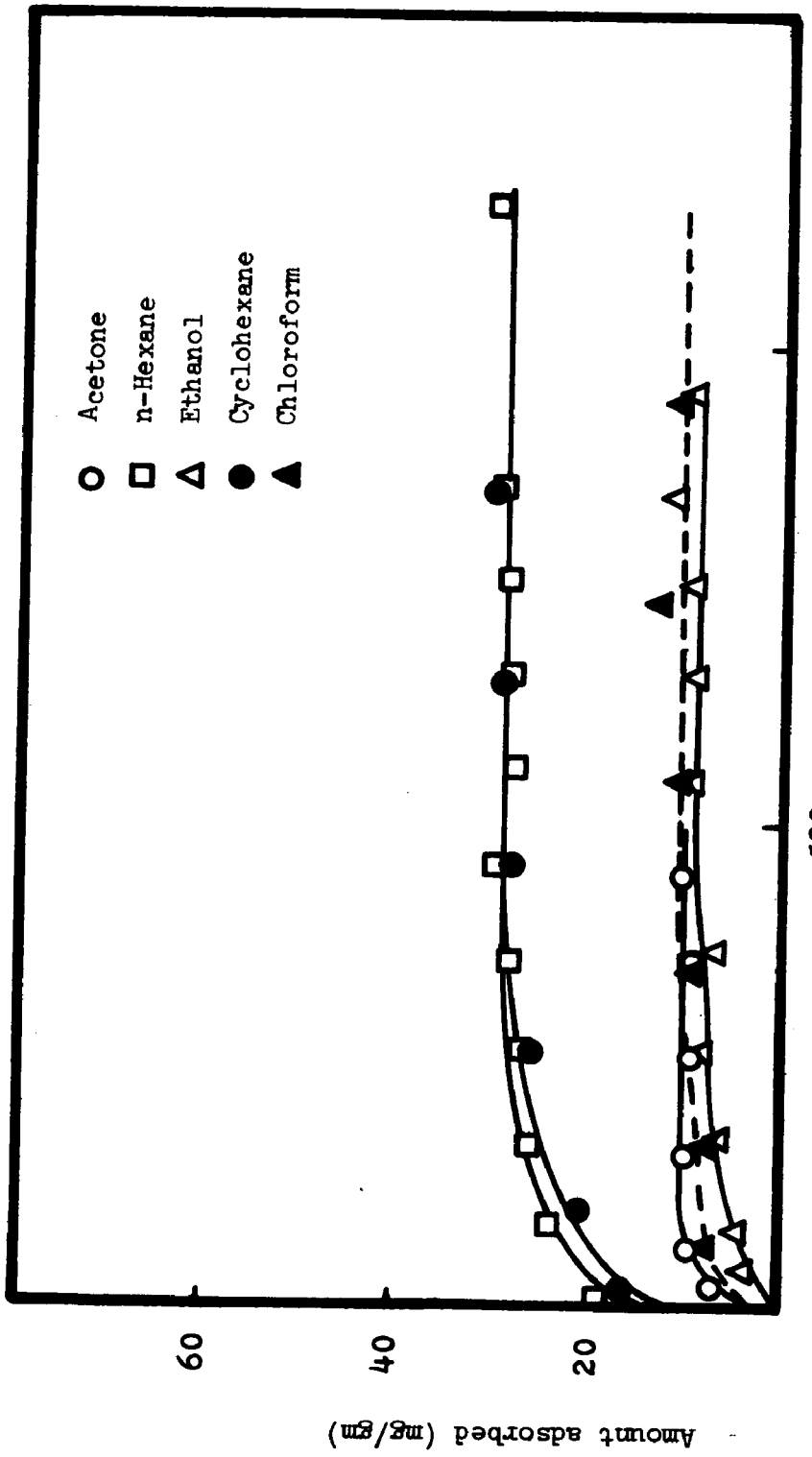


FIG. 3.3 ADSORPTION OF $n\text{-}C_8H_{17}NH(CH_2)_2NH_2$ ONTO HYDROXYAPATITE.

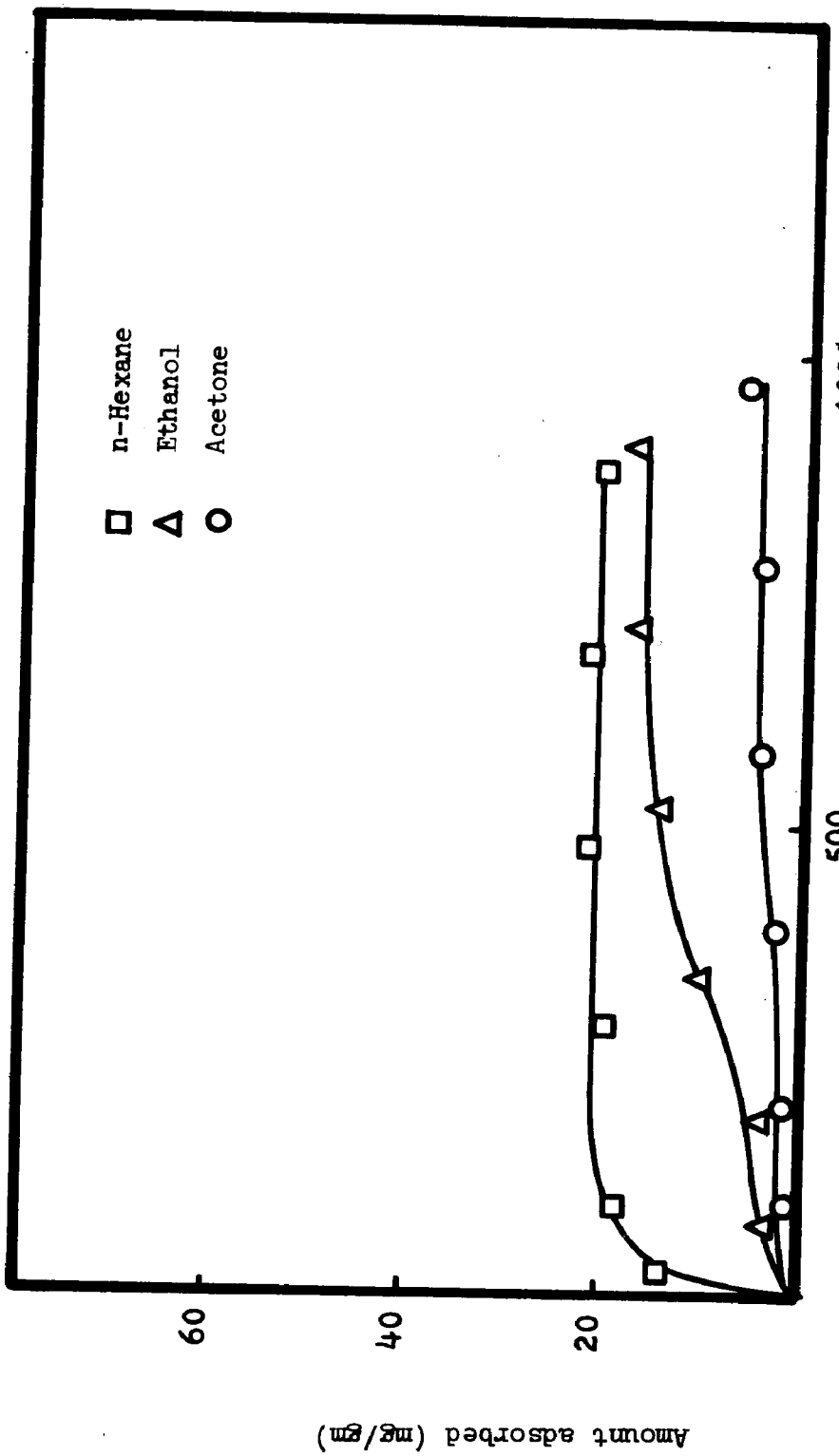
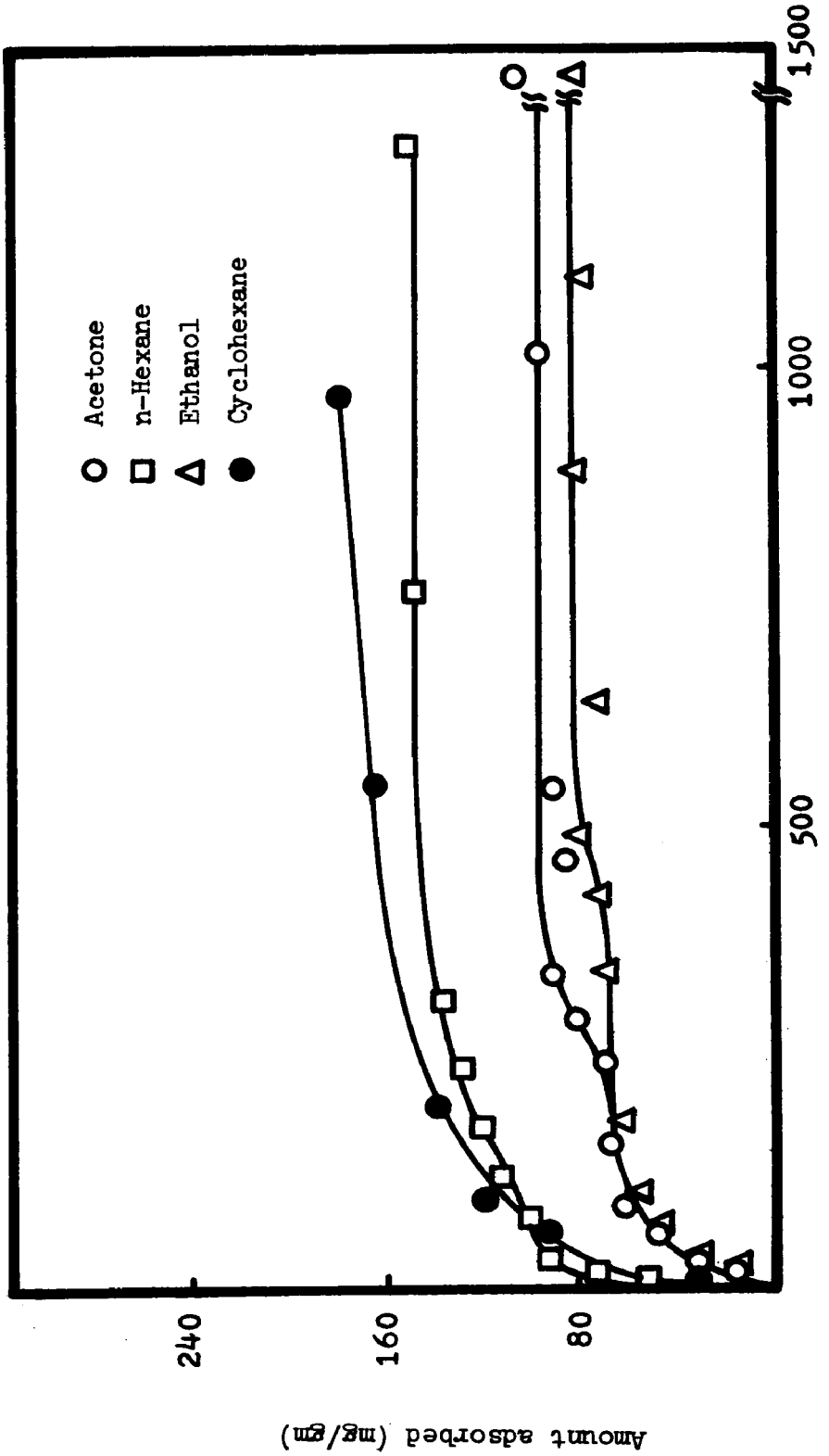


FIG. 3.4 ADSORPTION OF $n\text{-}C_8H_{17}NH_2$ ONTO HYDROXYAPATITE.



—FIG. 3.5 ADSORPTION OF P-1 POLYMER ONTO HYDROXYAPATITE.

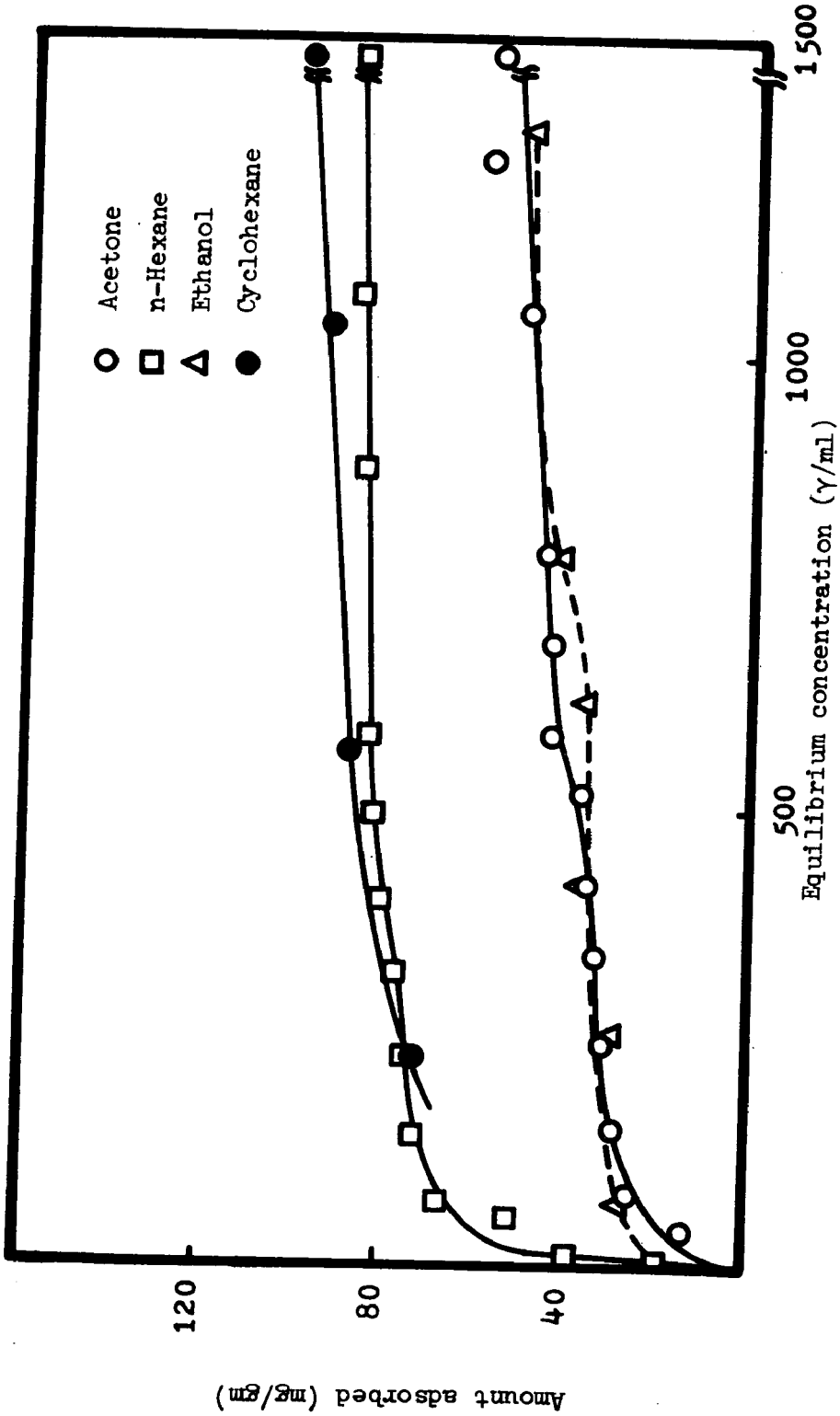


FIG. 3.6 ADSORPTION OF P-2 POLYMER ONTO HYDROXYAPATITE.

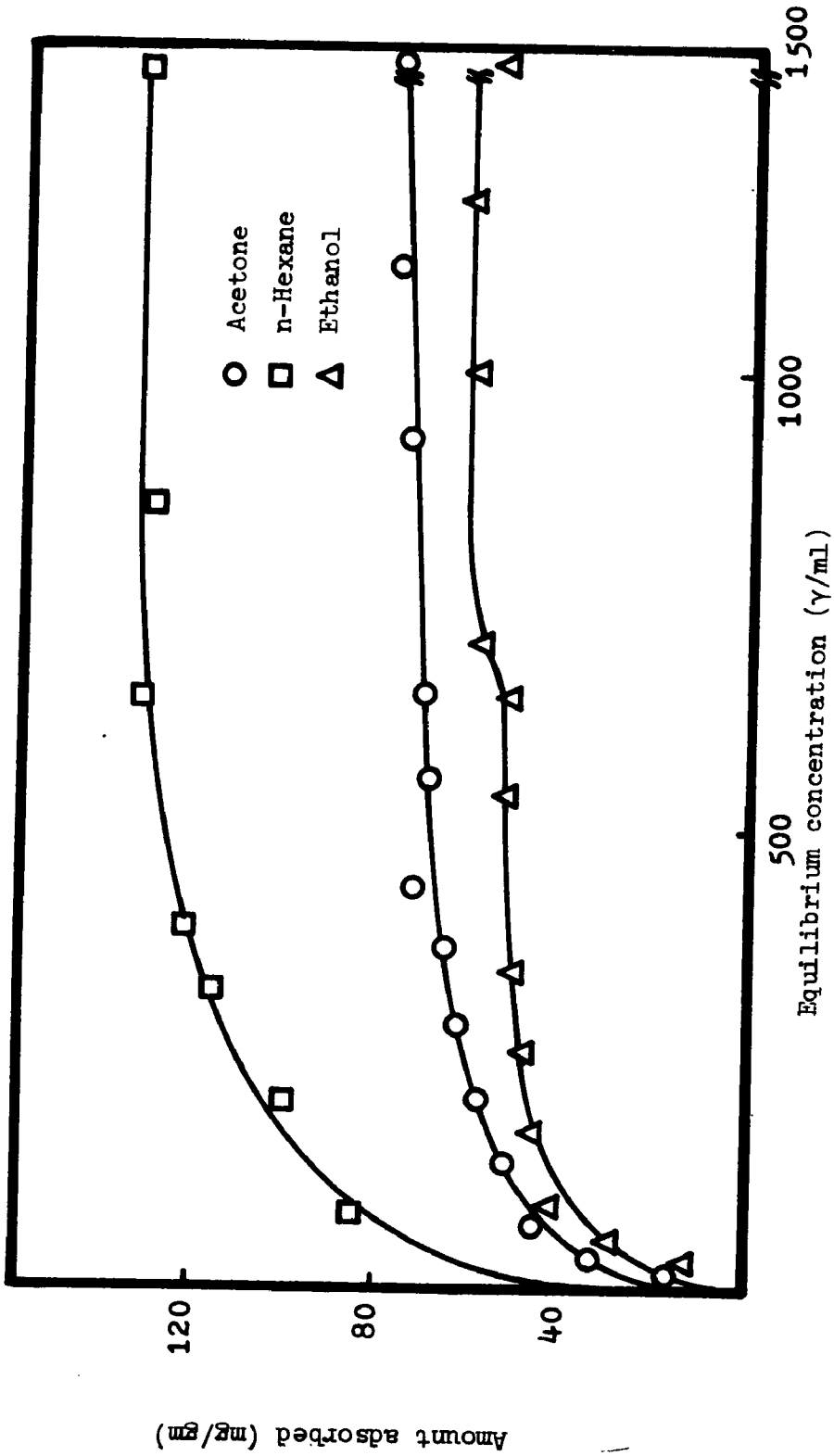


FIG. 3.7 ADSORPTION OF P-3 POLYMER ONTO HYDROXYAPATITE.

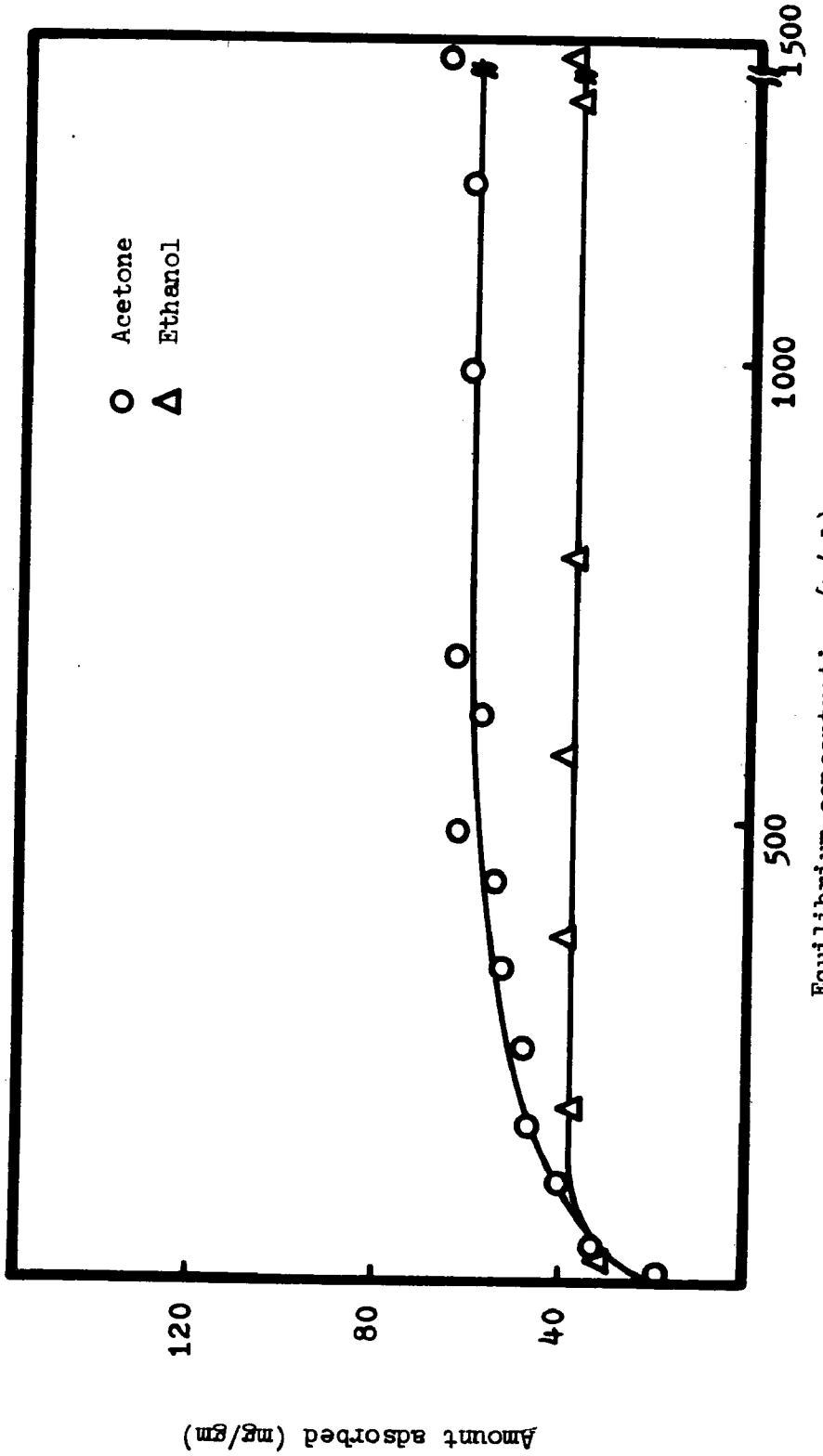


FIG. 3.8 ADSORPTION OF P-4 POLYMER ONTO HYDROXYAPATITE.

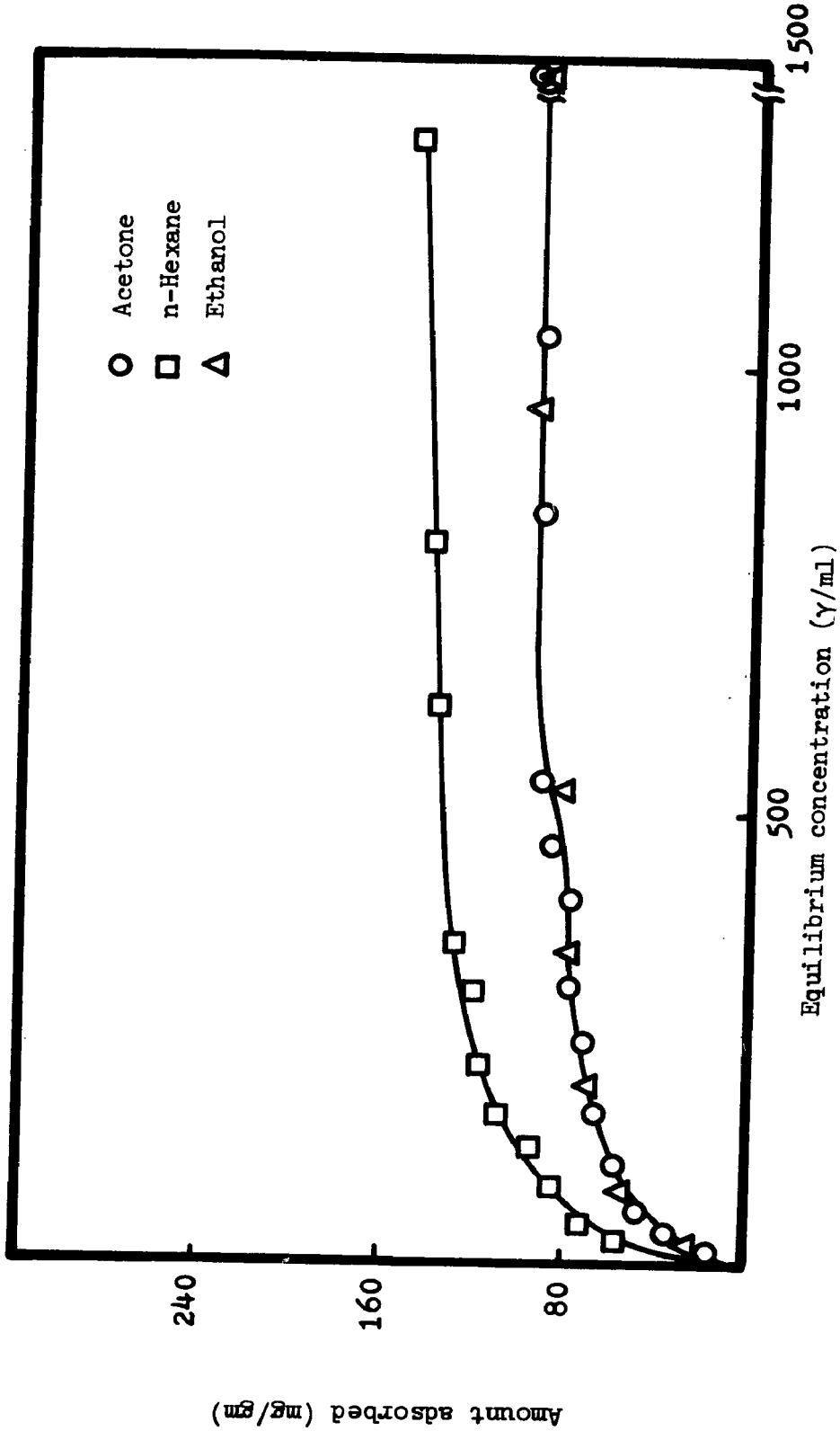


FIG. 3.9 ADSORPTION OF M-1 POLYMER ONTO HYDROXYAPATITE.

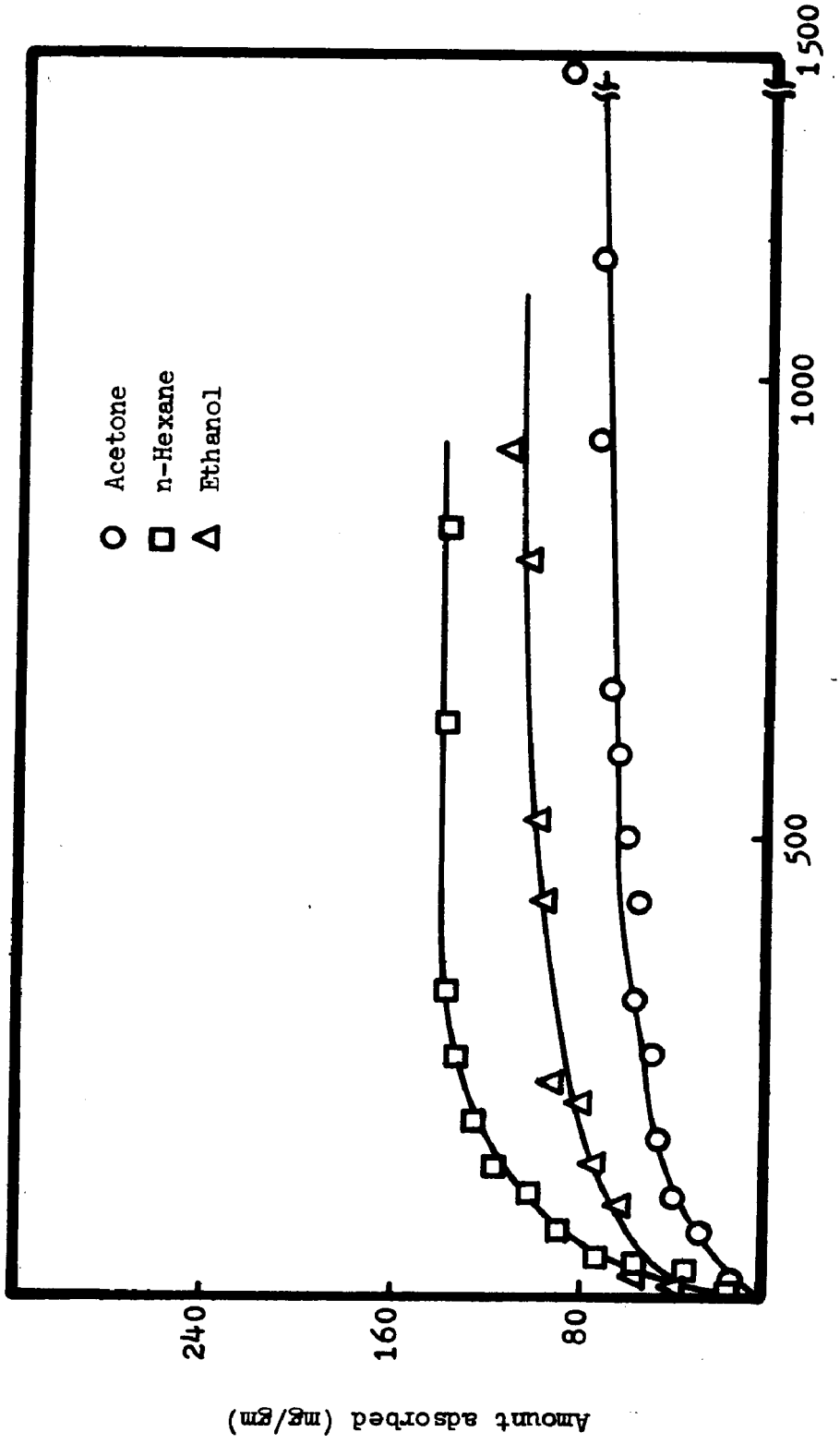


FIG. 3.10 ADSORPTION OF S-1 POLYMER ONTO HYDROXYAPATITE.

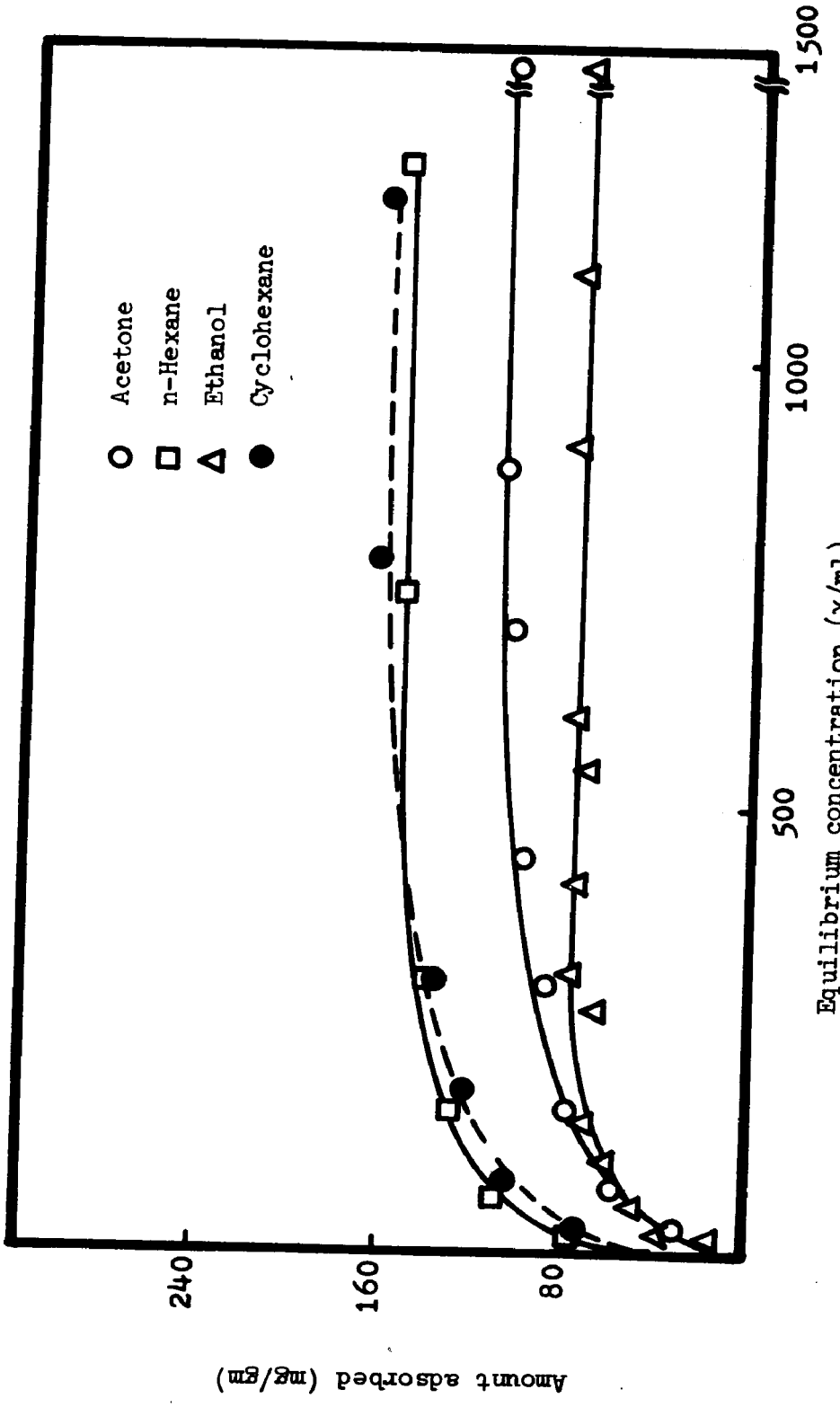


FIG. 3.11 ADSORPTION OF M-3 POLYMER ONTO HYDROXYAPATITE.

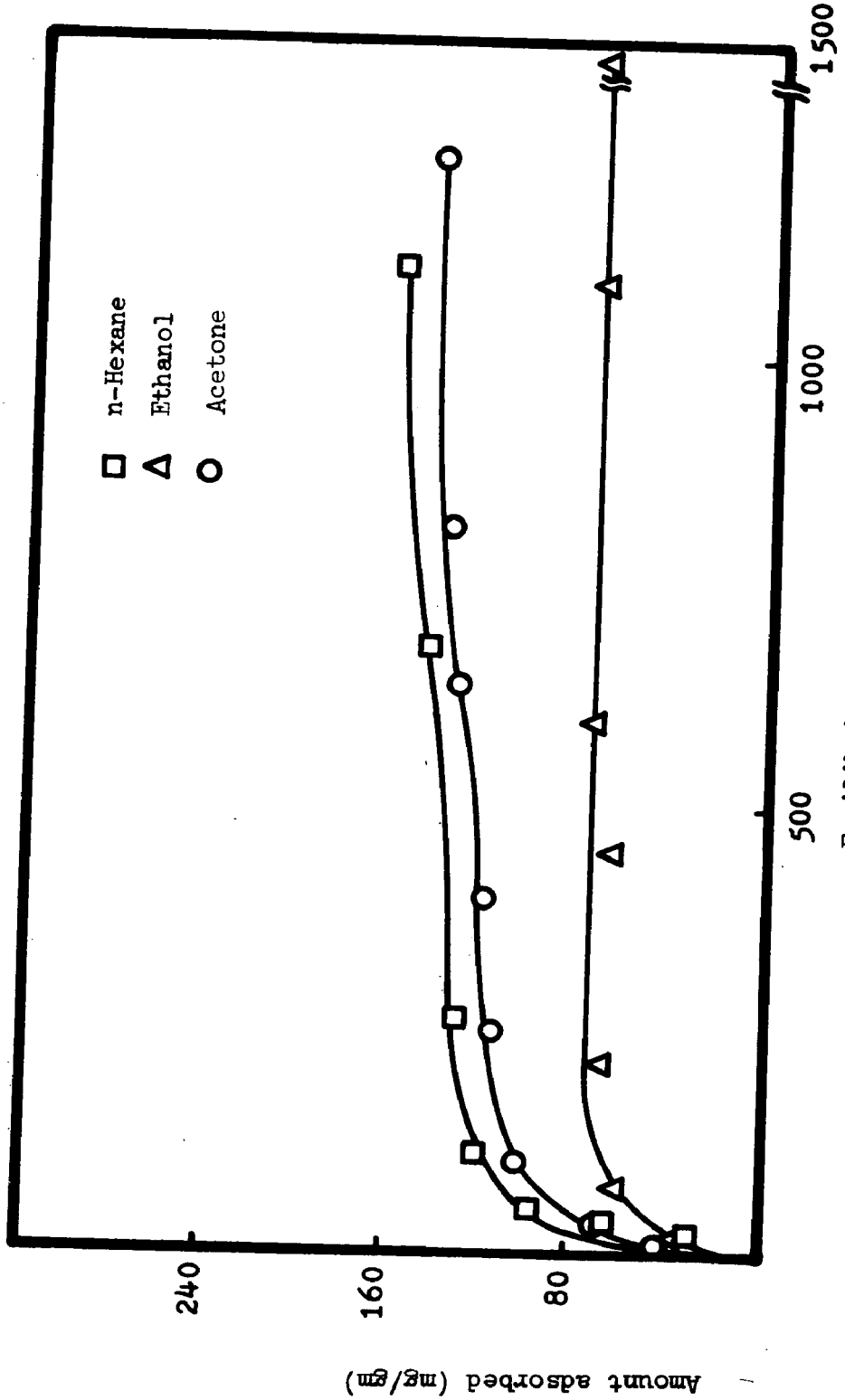


FIG. 3.12 ADSORPTION OF WM-3 POLYMER ONTO HYDROXYAPATITE.

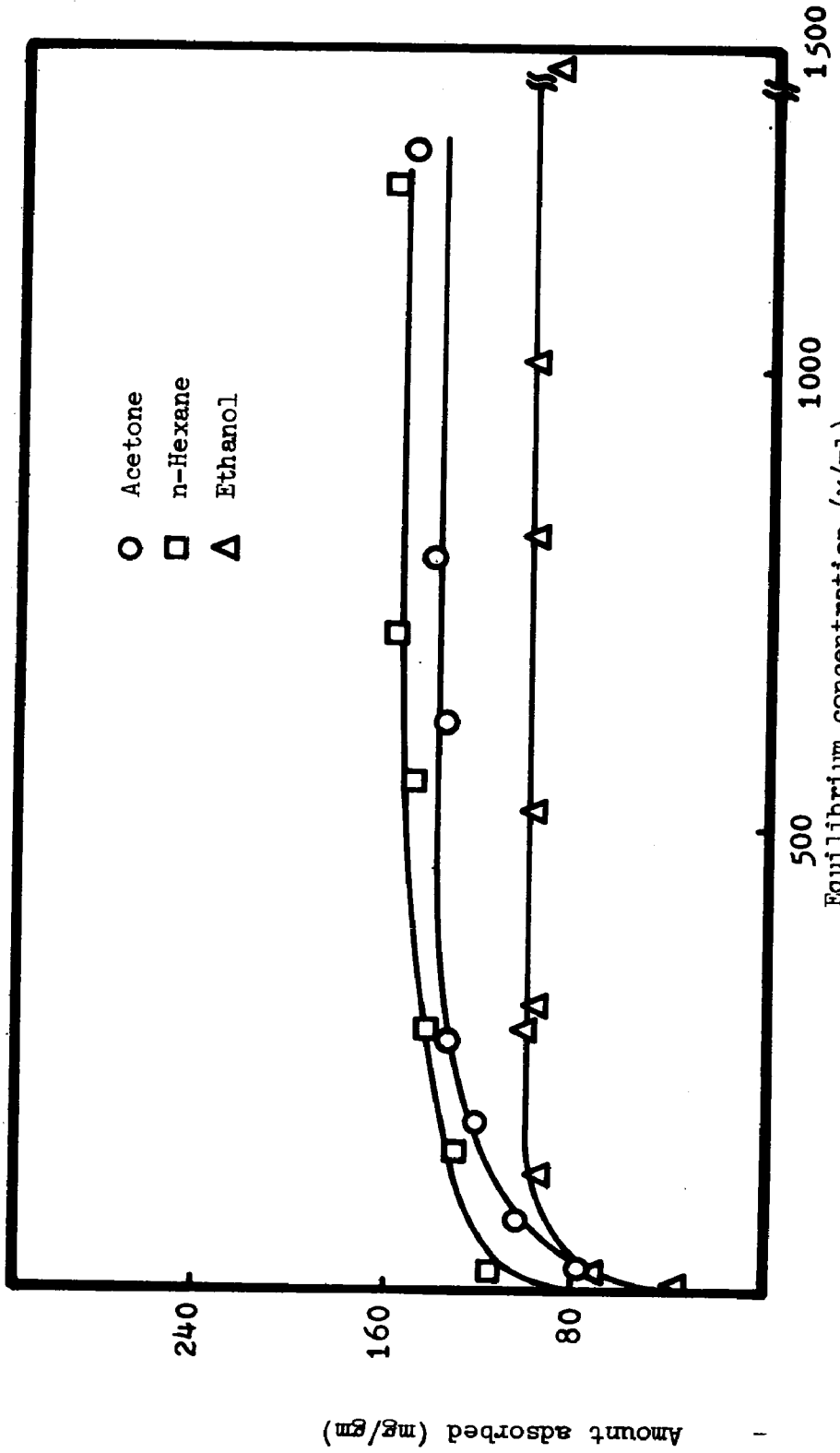


FIG. 3.13 ADSORPTION OF S-4 POLYMER ONTO HYDROXYAPATITE.

Table 3.1

Adsorption of Siloxane Polymers onto Hydroxyapatite

Polymer	Amount adsorbed (mg/gm)				Amount Adsorbed (mmole/gm) x 10^2				Amount Adsorbed in Percent Monomer Equivalent			
	Ac.	n-hex	eth.	cyc.	Ac	n-hex	eth.	cyc.	Ac.	n-hex	eth.	cyc.
Monomer (diamine)	10	30	9	30	5.8	17.4	5.2	17.4	33	100	30	100
Monomer (monoamine)	6	22	17		4.65	17.0	13.2		27	99	76	
P-1	100	152	80	200	3.32	5.05	2.66	6.64	38	58	31	76
P-2	54	88	46	104	5.23	8.52	4.46	10.08	60	98	51	116
P-3	80	132	60	136	2.64	4.35	1.98	4.48	91	150	68	155
P-4	62		40		1.64		1.06		141		91	
M-1	104	144	102		5.1	7.07	5.00		88	122	86	
S-1	80	170	110		4.29	9.13	5.90		74	157	102	
M-3	110	170	80	168	3.72	5.74	2.70	5.68	86	132	62	131
WM-3	150	170	76		2.76	3.13	1.4		177	144	64	
S-4	147.4	160	97		1.61	1.75	1.06		93	101	61	

Ac. : Acetone
n-hex.: n-hexane
eth. : Ethanol
Cyc. : Cyclohexane

for example, the limiting (plateau) for polymer P-2 in hexane is 88 mg/gm. This corresponds to approximately 8.52×10^{-2} millimoles per gram of apatite and 98 percent monomer equivalent adsorption. This suggests that both polar (diamine) anchors of P-2 have been utilized, and essentially all of the adsorption sites have been utilized at maximum adsorption in this system.

It can be seen from Table 3.1 that polymer P-3 gave 91 percent monomer equivalent adsorption from acetone and 150 percent monomer equivalent adsorption from hexane. This suggests that in acetone one obtains a rather efficient matching of the available polar groups with the available sites on the apatite surface, but in hexane the adsorption of P-3 results in the "stranding" of some of the polar anchors. This interpretation is in agreement with the contact angle work which showed that significantly higher water contact angles and therefore better hydrophobicity was obtained from acetone solution treatment (Fig. 2.5) than from hexane solution treatment (Fig. 2.6).

These data (Table 3.1) also help to explain why polymers P-1 and P-2 absorbed from acetone did not yield (high) contact angles (Fig. 2.5). In these cases sufficient polymer was not being adsorbed to fully utilize the adsorption sites. On the other hand these polymers yielded high contact angle when hexane was employed as the solvent.

Polymers M-1, M-3 and WM-3 are three of the branched type polymers with the same ratio of the nonpolar to the polar units. The results of the adsorption of these polymers are very useful in demonstrating the molecular weight dependence of adsorption of

polydimethylsiloxane polymers. The initial portion of their isotherms from n-hexane, acetone and ethanol is shown in Fig. 3.14. Except from ethanol, the initial amounts adsorbed increases with increasing molecular weight. At full coverage, the data (Fig. 3.15) shows that the dependence of polymer adsorption on molecular weight fits the empirical equation $A_e = \kappa M^{\alpha}$, where A_e is the amount adsorbed at equilibrium, κ and α are constants and M is the molecular weight; dividing through by M:

$$A_e/M = \kappa M^{(\alpha-1)} \quad .$$

Therefore:

$$\log \frac{A_e}{M} = \log \kappa + (\alpha - 1) \log M \quad .$$

The values of κ and α obtained from the graphs are given in Table 3.2.

The solvent effect with regard to the adsorption of the dimethylsiloxane polymers on hydroxyapatite is very significant. The data of Table 3.1 show that polymer adsorption decreases as the polarity of the solvent used increases. This may be related to either competition at the adsorption sites or change in the degree of polymer solvation.

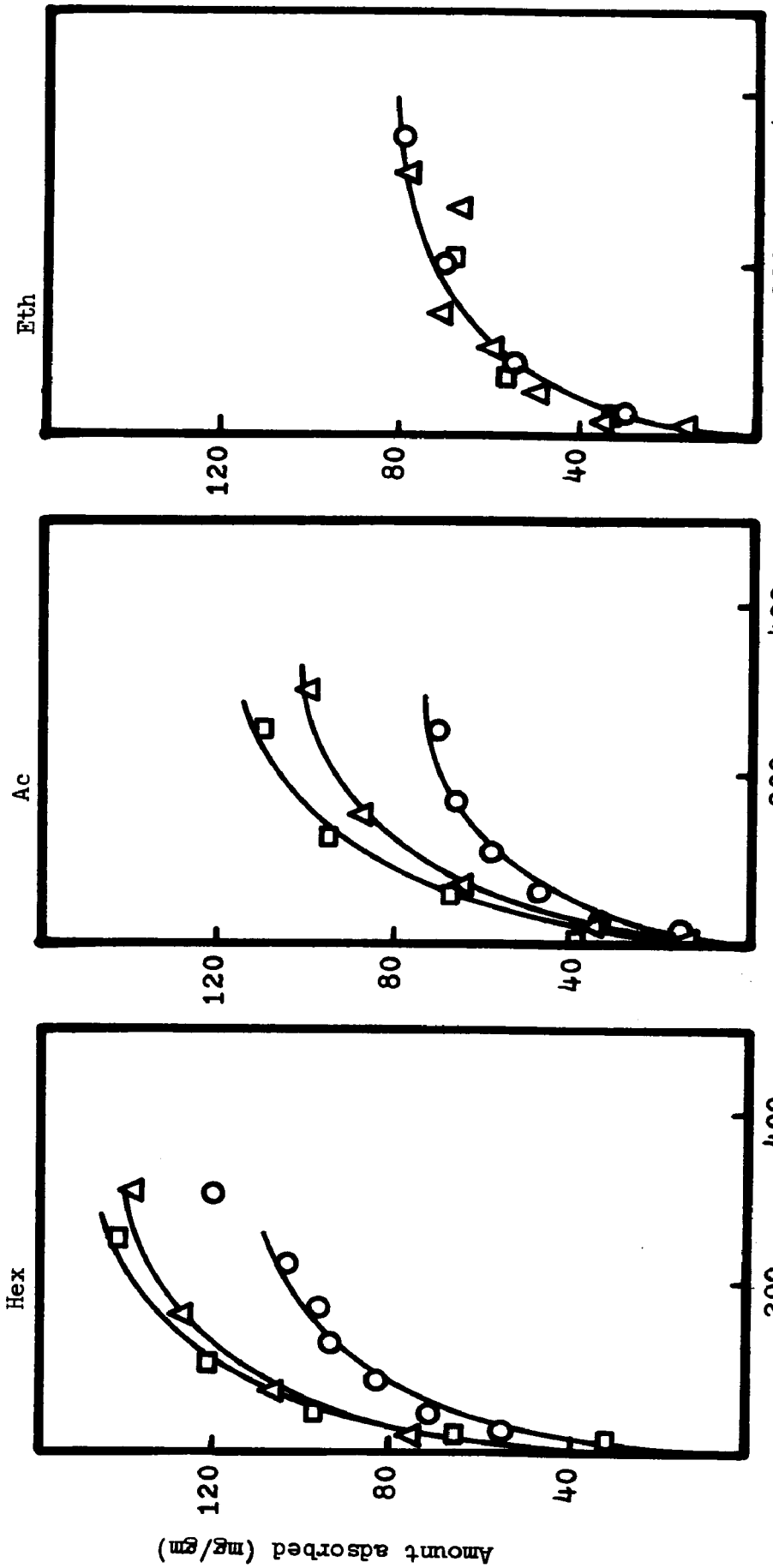


FIG. 3.14 ADSORPTION OF M-1, M-3 AND WM-3 POLYMERS ONTO HYDROXYAPATITE (INITIAL PORTIONS).

○ (M-1), △ (M-3), □ (WM-3)

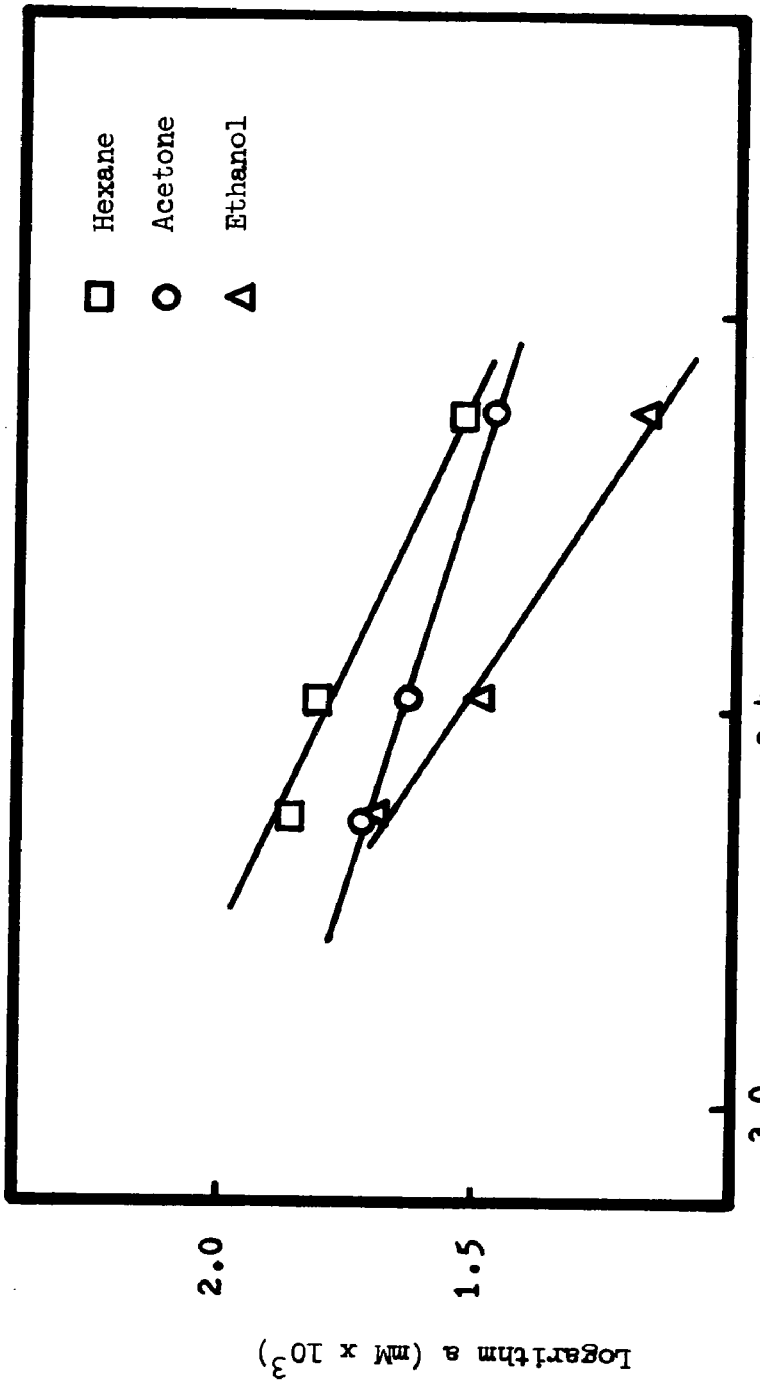


FIG. 3.15 RELATIONSHIP BETWEEN THE AMOUNTS ADSORBED AND THE MOLECULAR WEIGHT OF POLYSILOXANE POLYMERS.

Table 3.2

Experimental Results of κ and α for Polymers M-1, M-3, and WM-3 with n-Hexane, Acetone and Ethanol Solvents

Solvent	κ	α
n-Hexane	0.1053	0.025
Acetone	0.00398	0.425
Ethanol	1.32	- 0.350

Discussion

The studies carried out on contact angles and adsorption have answered some of the key questions regarding the adsorption of the polydimethylsiloxane polymers on hydroxyapatite. When the P-3 polymer was used in acetone solution, high contact angles were obtained and 91 percent monomer equivalent were adsorbed. These results point out the possibility of finding suitable film forming agents which will interfere with dental plaque adhesion to the tooth surface.

For this reason, an *in vitro* plaque growth experiment was carried out* to test the antiplaque activity of the P-3 films. Human teeth mounted in rubber were treated with the polymer solution in acetone and then incubated in *Streptococcus mutans* culture at 37°C. Inspection of the teeth surfaces during the incubation period indicated that the surface growth was significantly limited during the first two days. Later, surface growth was visible and no difference from the control was observed. Polymer desorption was confirmed on measuring contact angles on these teeth samples after cleaning.

The studies described in the preceding sections have given us important insight concerning the mechanisms whereby certain polymers are adsorbed onto hydroxyapatite and their potential effectiveness in inhibiting dental plaque development. These results are sufficiently encouraging to justify a more detailed mechanistic study on the

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* The experiments were carried out under the generous supervision of Dr. Lee Brown, Institute of Dental Research, Houston, Texas.

polydimethylsiloxane polymer adsorption with emphasis on the energetics and the configurations involved and the roles played by the solvent.

CHAPTER IV. SYSTEMATIC STUDIES ON THE ADSORPTION OF LINEAR POLYSILOXANE POLYMERS ON CALCIUM FLUORIDE

4.1 Introduction

As the result of the adsorption isotherm studies of polysiloxane polymers on hydroxyapatite powder, we have been able to identify several different factors involved in the adsorption process. But, because of the highly heterogeneous surface and the unidentified crystalline nature of hydroxyapatite, firm conclusions about the polymer configuration in the adsorbed layer cannot be reached. The experiments of this chapter are focused on the adsorption of the linear polysiloxane polymers P-1 and P-2 on calcium fluoride powder in an attempt to:

1. Study the solvent role in polymer adsorption and its effect on surface adsorbed layer.

2. Study the equilibrium configurations of the adsorbed polymer molecules.

3. Establish basis for the statistical treatment of the adsorption of linear molecules on solid surfaces.

4.2 Experiments

Preliminary experiments were carried out to assess the relative solvation and solubilities of the various polymers in the various solvents employed. This was done using intrinsic viscosity measurements. If the intrinsic viscosity of a polymer is higher in one solvent than in another, the higher intrinsic viscosity reflects (a) greater molecular expansion of the solute and (b) better solvation.

By means of a Cannon-Fenske Routine Viscometer* with viscometer constant (0.0038 centistokes/second), the viscosities of the P-1 and P-2 polymers were determined in n-hexane, acetone and ethanol solutions. The experiments were carried out at 30°C. Six viscosity readings were taken for each sample. The Viscometer constant was checked by measuring the viscosities of the two chemically pure samples of polyvinylpyrilidone,** (K-30 and K-60) with predetermined viscosities.

The intrinsic viscosity is given by:

$$[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c},$$

where η_{sp} is the specific viscosity and c is the polymer solution concentration. By plotting η_{sp}/c versus c, the intrinsic viscosity was deduced from the intercept at zero concentration.

In the experimental adsorption isotherm studies a calcium fluoride powder was chosen as the adsorbent because of its well-defined crystalline structure and because its purity and surface area can be controlled through synthesis. A sample of this material was prepared in this laboratory according to the method published in "Handbook of Inorganic Chemistry," (59). In this method a slurry of calcium carbonate*** in water (while boiling) was slowly titrated with 40 percent hydrofluoric acid**** solution with stirring. When effervescence ceased, the precipitated calcium fluoride was filtered while hot and washed with dilute acetic acid until carbon dioxide bubbles were no longer visible. The

* Cannon Instrument Co., Penn.

** Metheson Coleman and Bell, Northwood, Ohio.

*** J. T. Baker Co., Phillipsburg, N. J.

**** Allied Chemical, Morristown, N. J.

precipitate was then washed three times with boiling DDW and dried at 300°C. A 200-mesh sieve was used to break down the powder aggregates into small particles with narrow size distribution. The powder was then stored in a dry place for adsorption studies. X-ray diffraction* of the product (Fig. 4.1) were in good agreement with an optical grade sample calcium fluoride.** The surface area was 18.44 m^2/g when determined by BET nitrogen adsorption. The calcium content of the synthesized sample determined by flame photometry*** was (51.12%) (compared to (51.30%) of the optical grade sample).

The polymer adsorption procedure was the same as when followed with hydroxyapatite except 200 mg of the calcium fluoride powder were used instead of 100 mg.

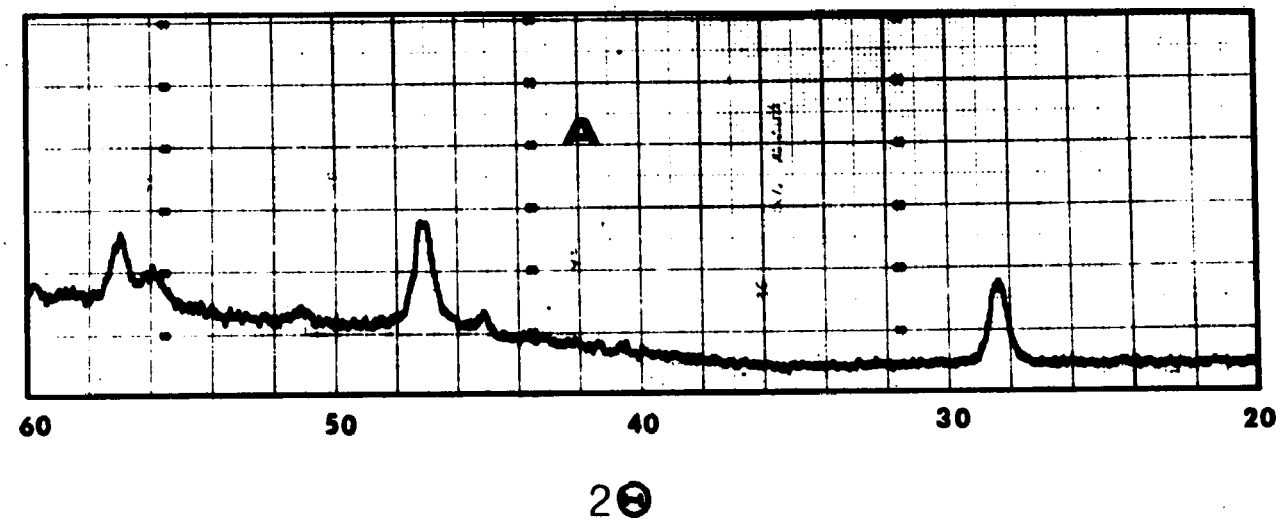
4.3 Experimental Results

4.3.1 Viscosity Measurements. Figures 4.2 and 4.3 show the specific viscosity of P-1 and P-2 polymers at different solution concentrations in each solvent. The P-1 solubility order as indicated from the intrinsic viscosity values is hexane>acetone>ethanol. The P-2 solubility order is just the reverse of this, viz., ethanol > acetone > hexane (Fig. 4.3). Probably, the relatively long dimethylsiloxane chain of P-1 polymer gives better solubility in the nonpolar solvent hexane, whereas the short-chained P-2 polymer was more soluble in the polar solvents, ethanol and acetone. These findings should be helpful in explaining some of the behavior observed on adsorbing P-1 and P-2 polymers on solid surfaces. A good solvent is known to cause expansion of the dissolved chains and so less polymer can pack into the surface layer.

*Philips Electronic Instruments.

**K and K Laboratories, Plainview, N. Y.

***Perkin-Elmer Atomic Absorption Spectrophotometer, Model 303.



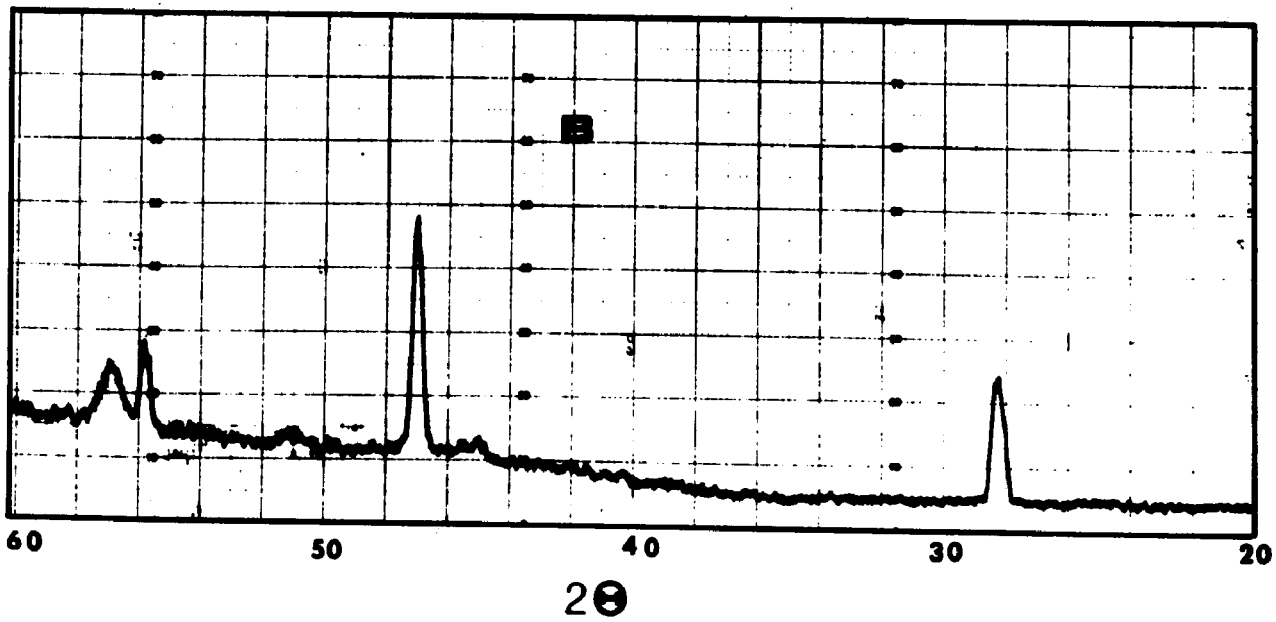


FIG. 4.1 X-RAY DIFFRACTION OF CALCIUM FLUORIDE. (A) THE SYNTHESIZED SAMPLE. (B) THE OPTICAL GRADE SAMPLE.

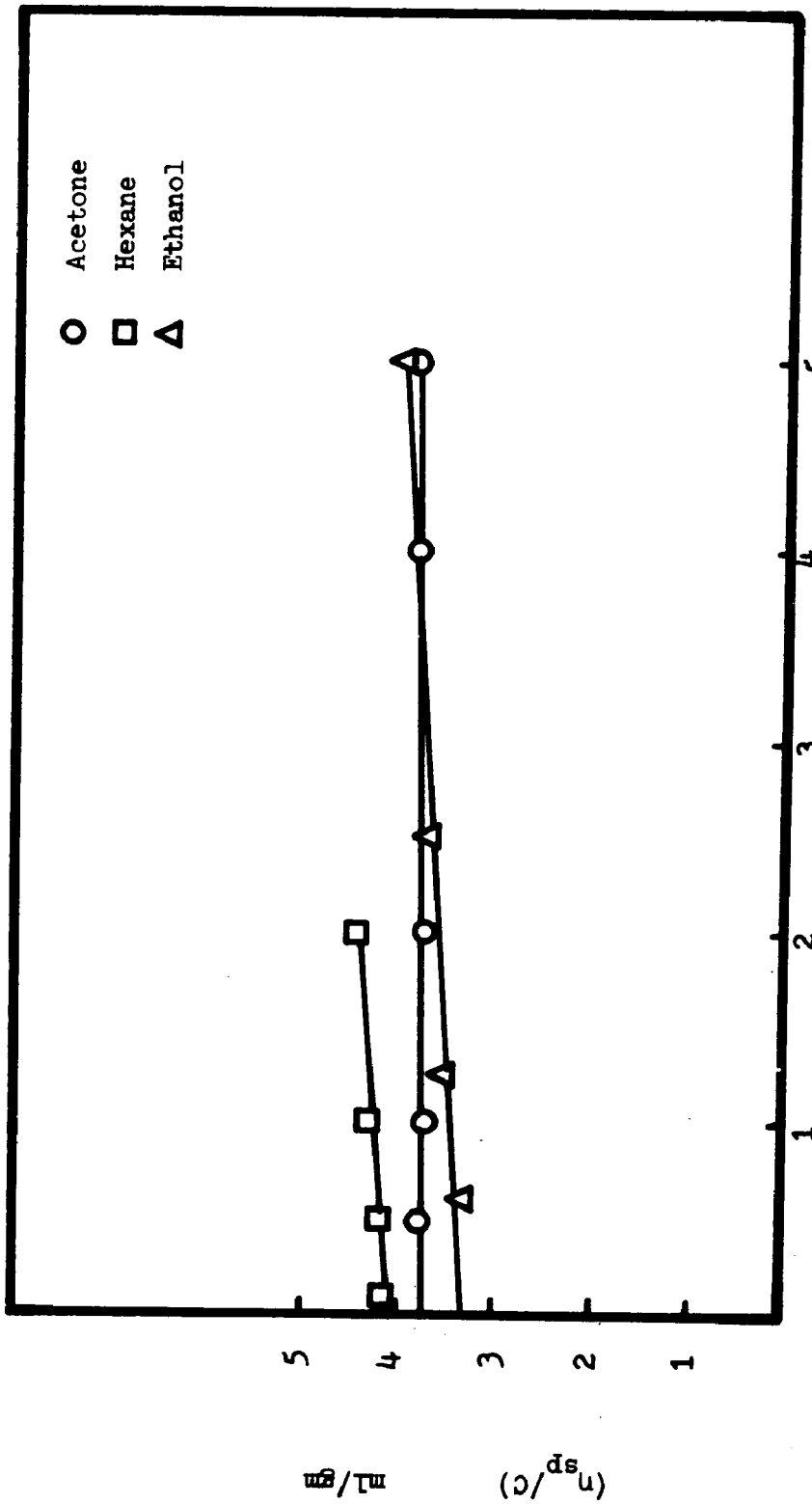


FIG. 4.2 VISCOSITY OF P-1 POLYMER.

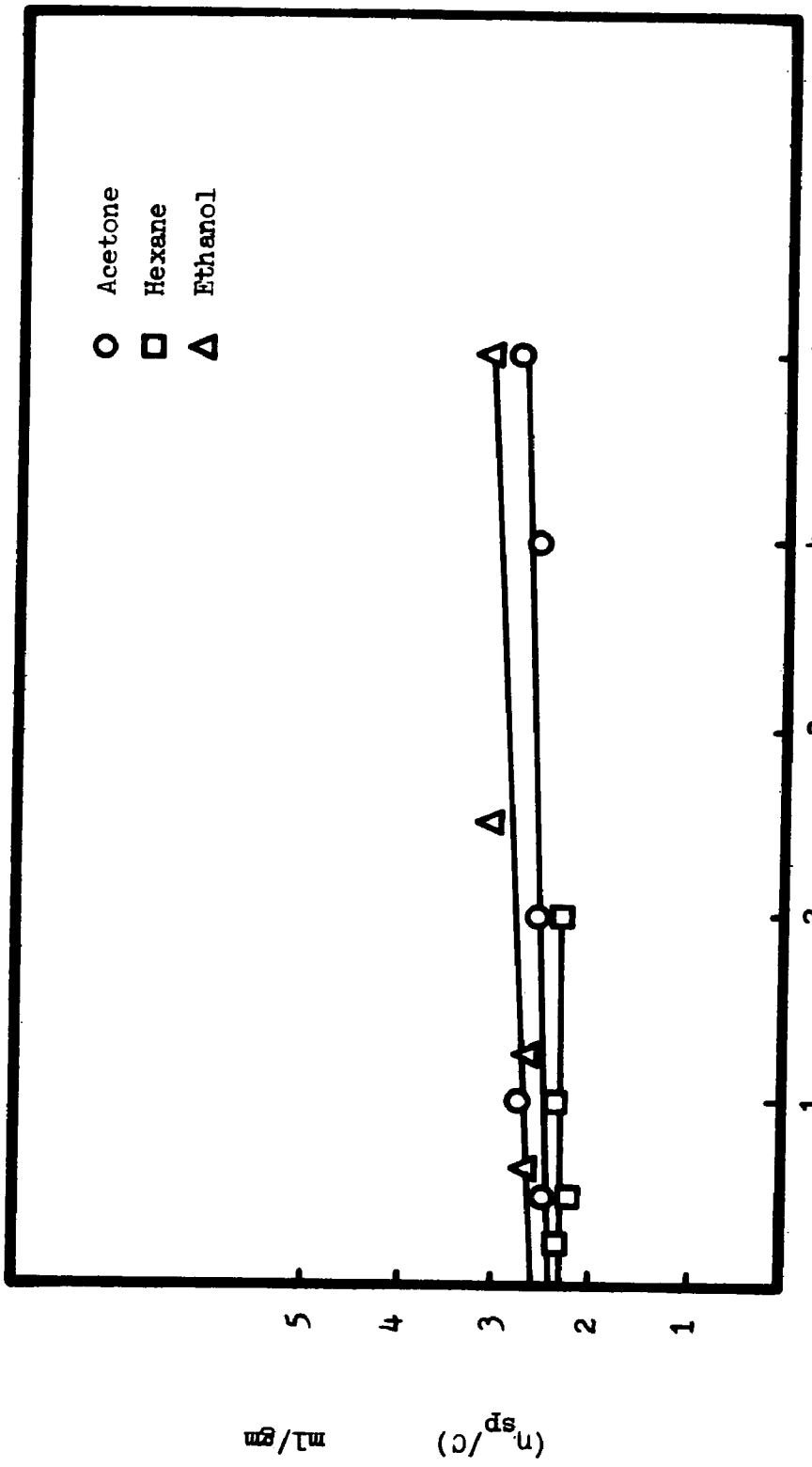


FIG. 4.3 VISCOSITY OF P-2 POLYMER.

4.3.2 Adsorption of P-1 and P-2 Polymers on Calcium Fluoride.

Preliminary adsorption experiments indicated that the polydimethylsiloxane polymer without the amine groups does not adsorb onto calcium fluoride. The amounts adsorbed of P-1 and P-2 polymers reached equilibrium after six hours of polymer contact with the calcium fluoride powder.

Figure 4.4 shows the adsorption isotherms of n-octylamine from n-hexane and acetone solutions. As was the case for hydroxyapatite adsorption, a limiting value of the monomer adsorption is obtained with n-hexane. From acetone, about half the limiting value was adsorbed. On a molar basis, 9×10^{-5} moles of the monomer are adsorbed from n-hexane solution to form a monomolecular layer on one gram of calcium fluoride. This value corresponds to a cross-sectional area of 34.1 $Å^2$ per monomer molecule using the BET value of calcium fluoride surface area. However, the effective surface area of calcium fluoride in the case of polymer adsorption appears to be much less than the value determined by gas adsorption. For this reason, the polymer adsorption data are compared to those of the monomer.

Figure 4.5 shows the isotherms of P-1 polymer adsorbed on calcium fluoride powder from n-hexane, acetone and ethanol solutions. Figures 4.6 and 4.7 show the data for P-2 polymer. The adsorption behavior of the two polymers is quite similar from n-hexane and acetone, whereas from ethanol, P-2 showed deviations from the Langmuirian adsorption isotherm.

Figures 4.8 through 4.12 show the isotherms of P-1 and P-2 polymers adsorbed from mixed-solvent systems. Figures 4.8 and 4.9 show the effect

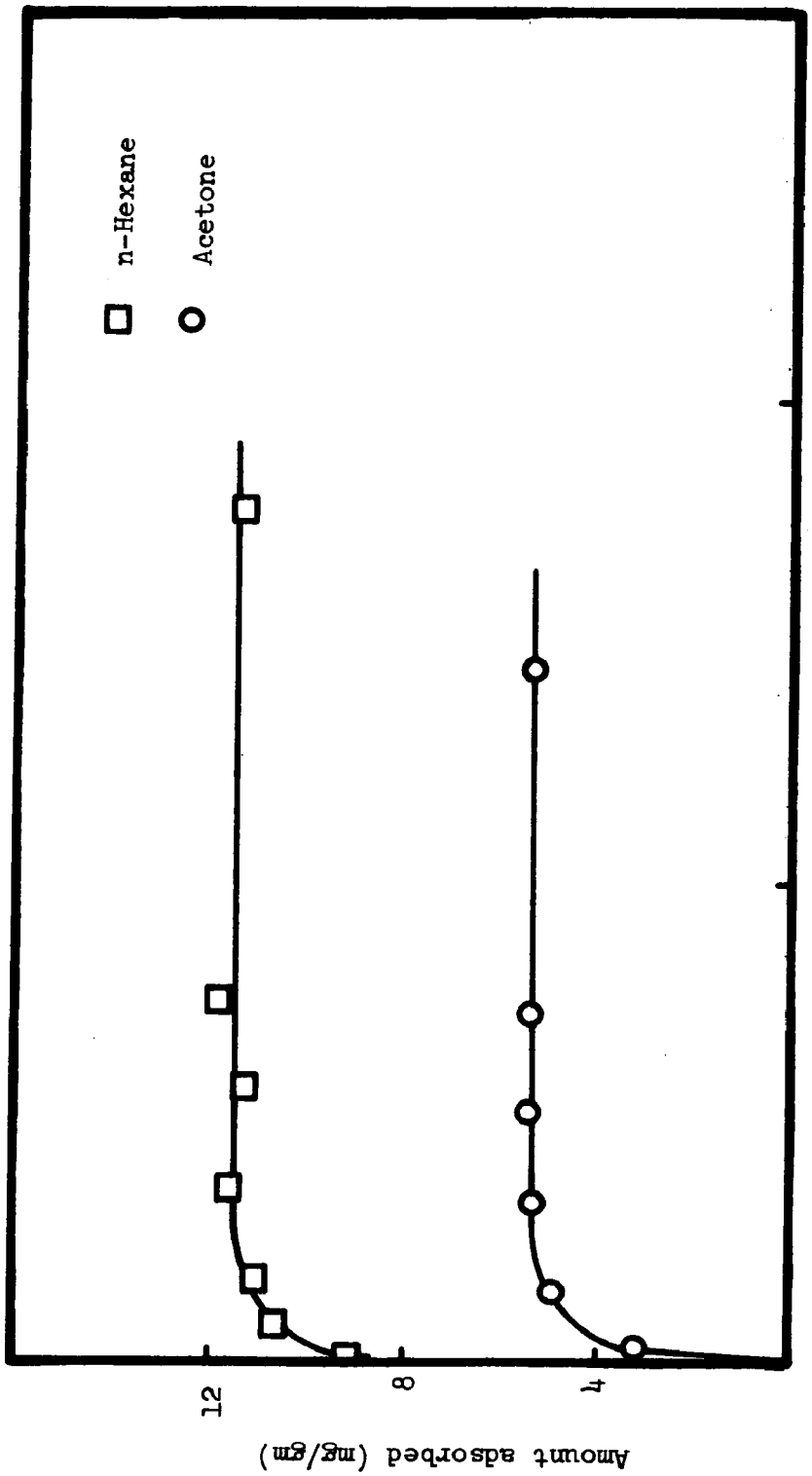


FIG. 4.4 ADSORPTION OF n-OCTYLAMINE ONTO CaF_2.

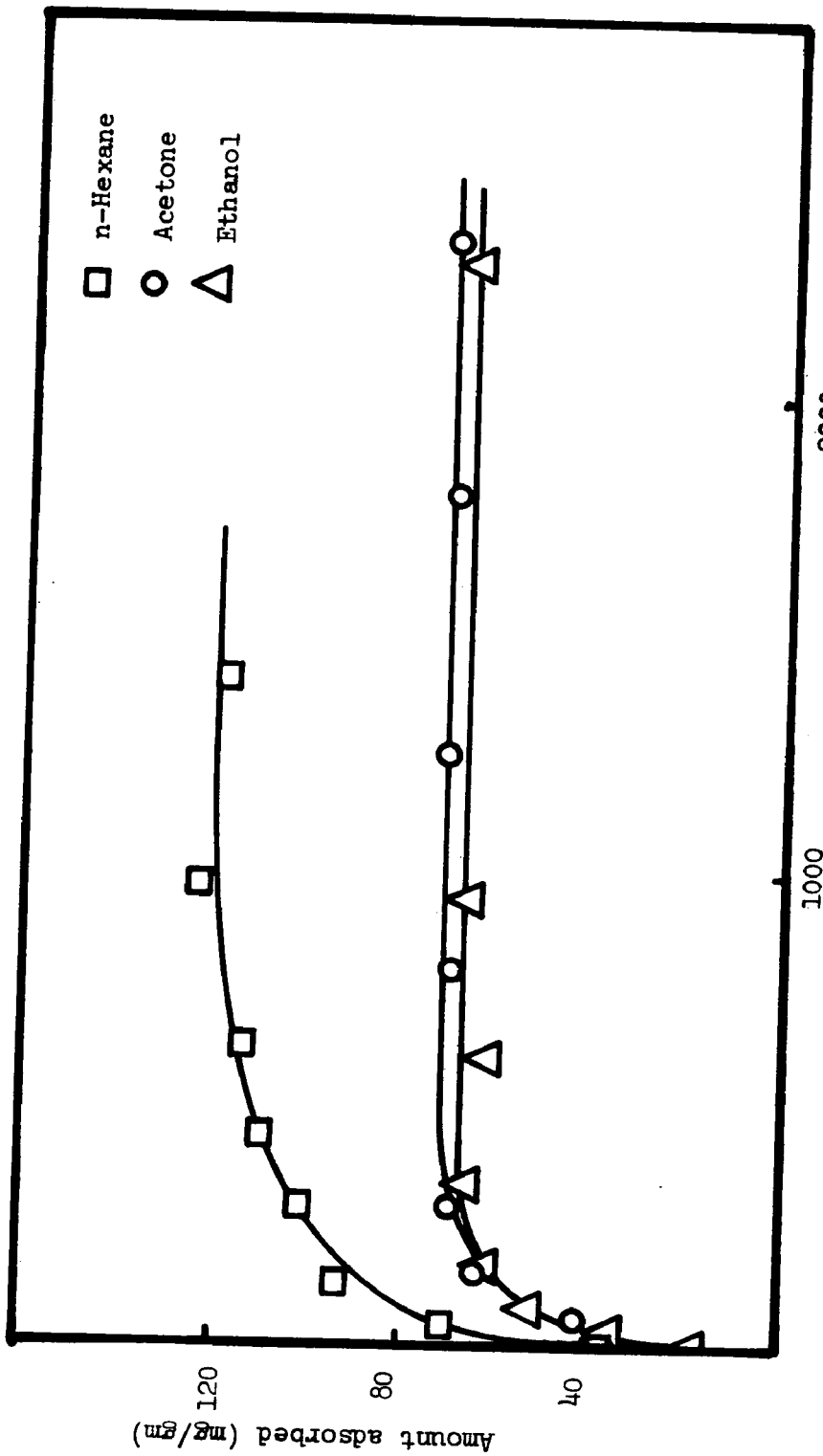


FIG. 4.5 ADSORPTIÕN OF P-1 POLYMER ONTO CaF_2.

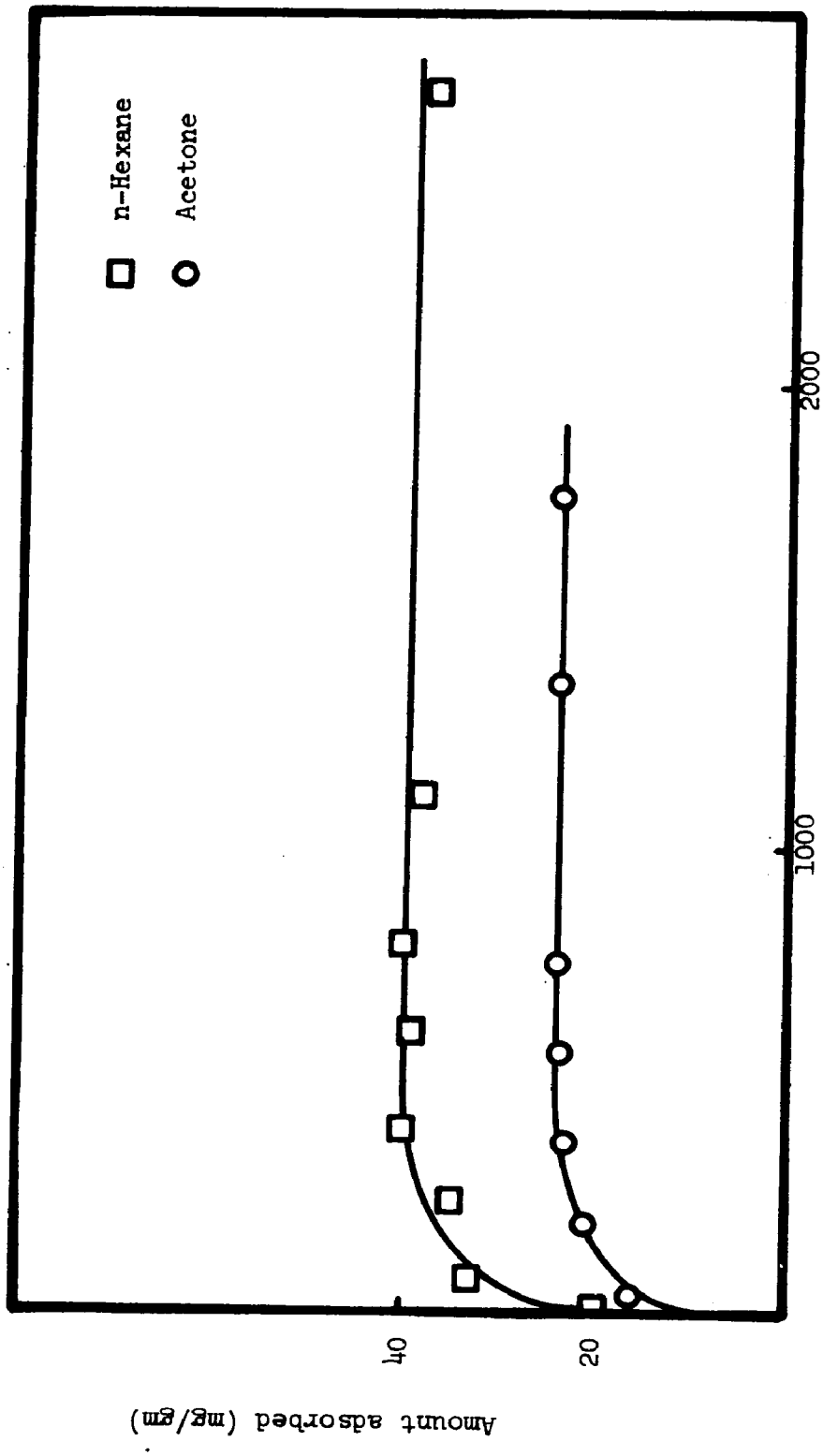


FIG. 4.6 ADSORPTION OF P-2 POLYMER ONTO CaF_2.

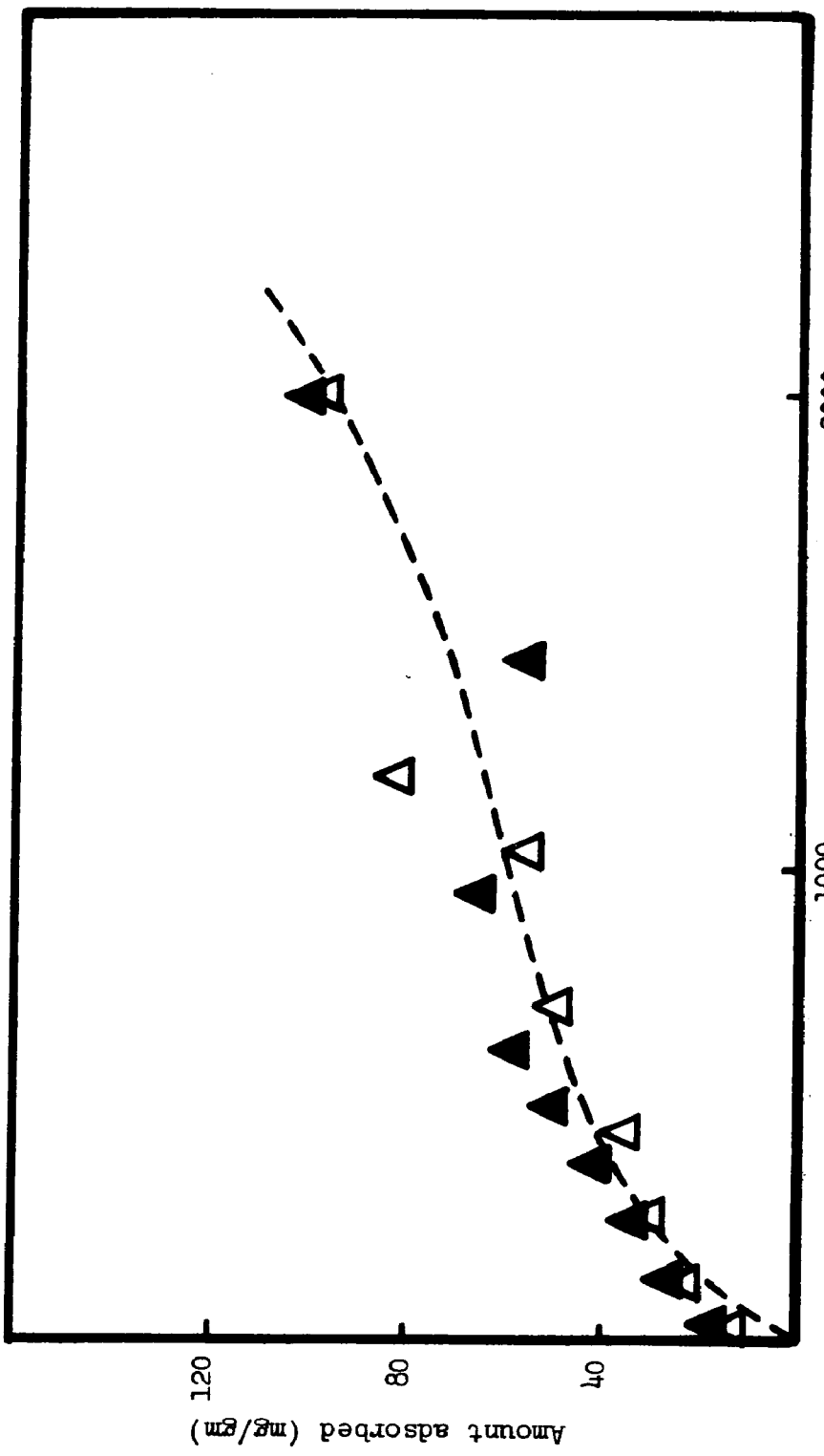


FIG. 4.7 ADSORPTION OF P-2 POLYMER ONTO CaF_2. Δ, ▲ TWO SETS OF DATA FOR ETHANOL AS SOLVENT.

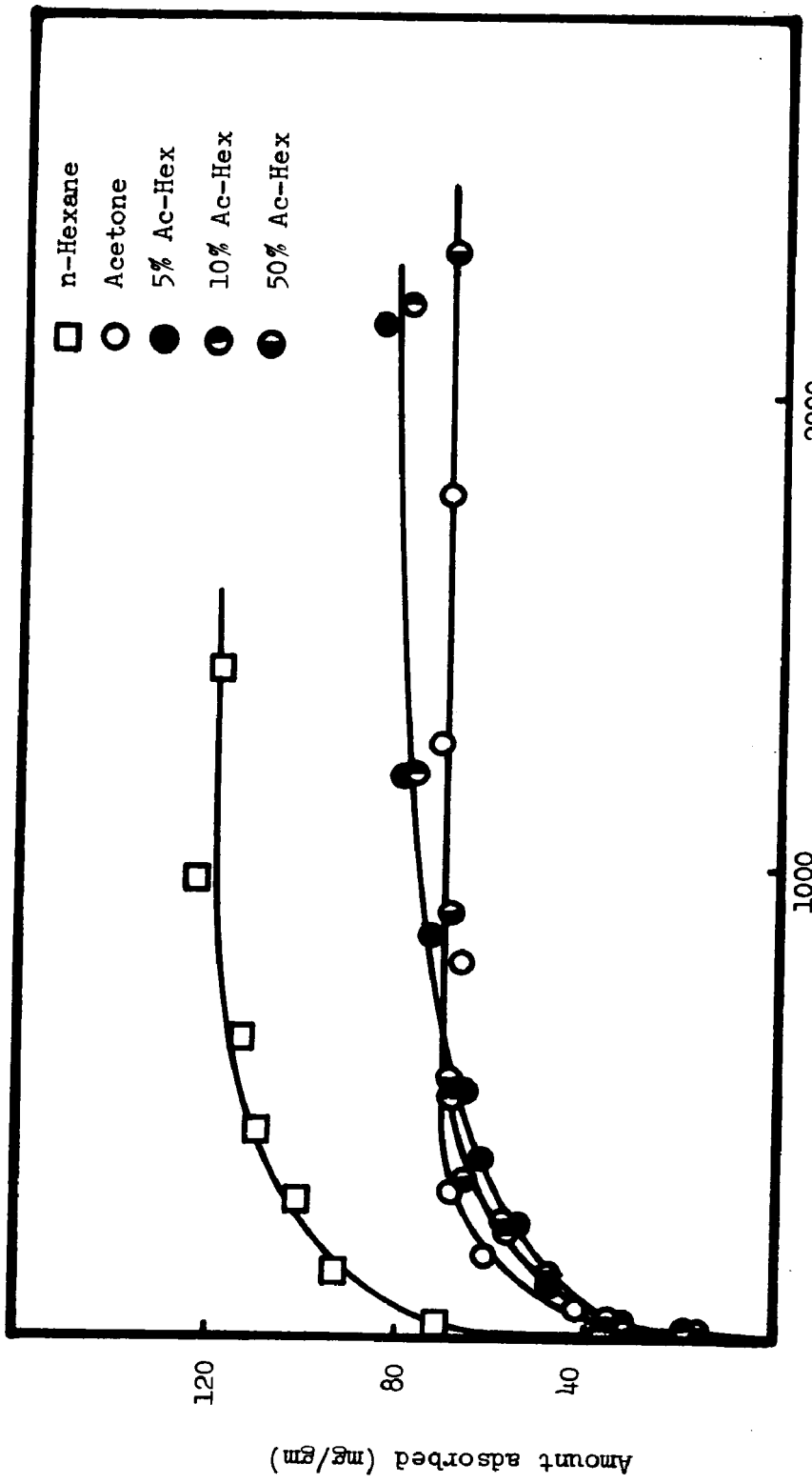


FIG. 4.8 ADSORPTION OF P-1 POLYMER ONTO CaF_2.

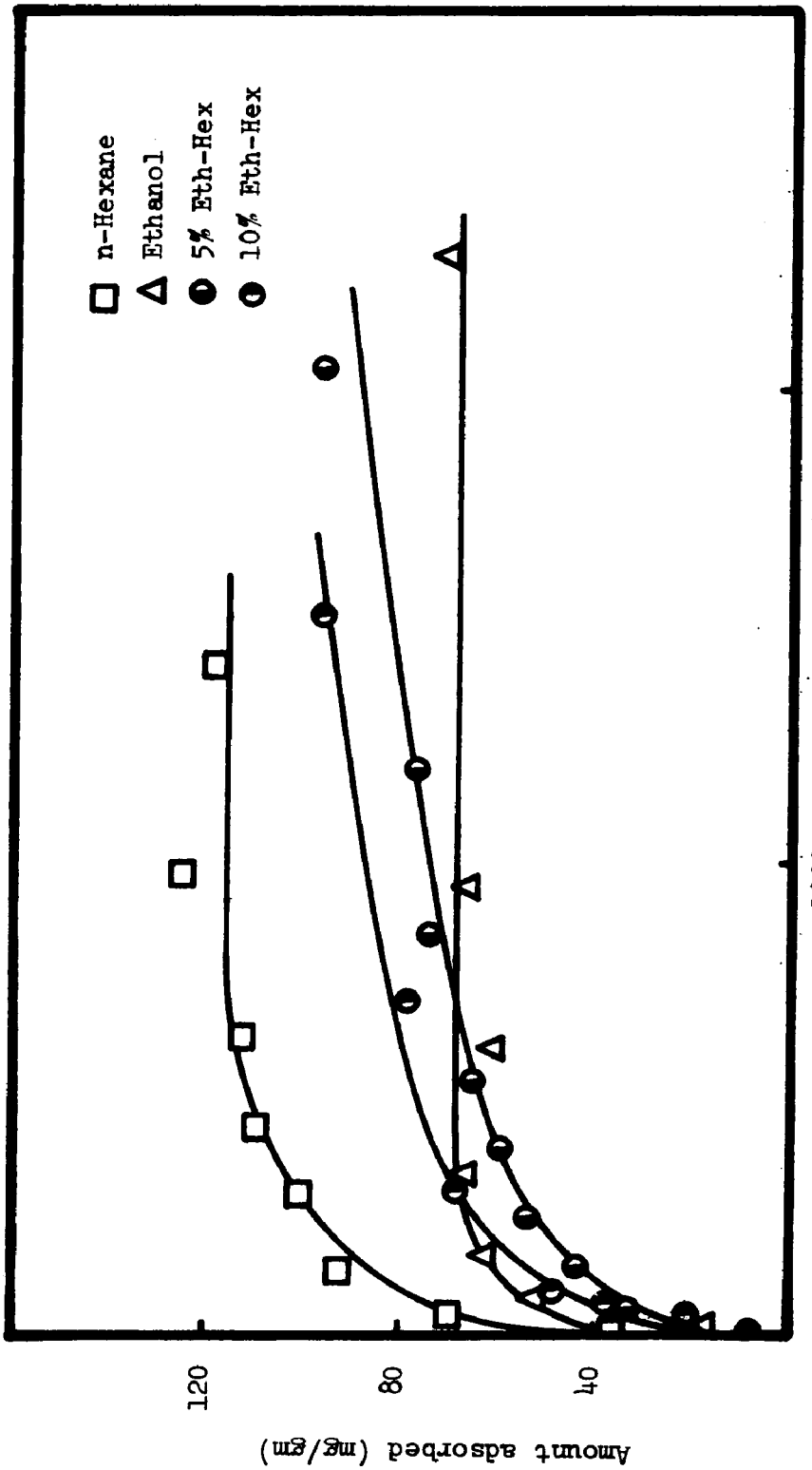


FIG. 4.9 ADSORPTION OF P-1 POLYMER ONTO CaF_2.

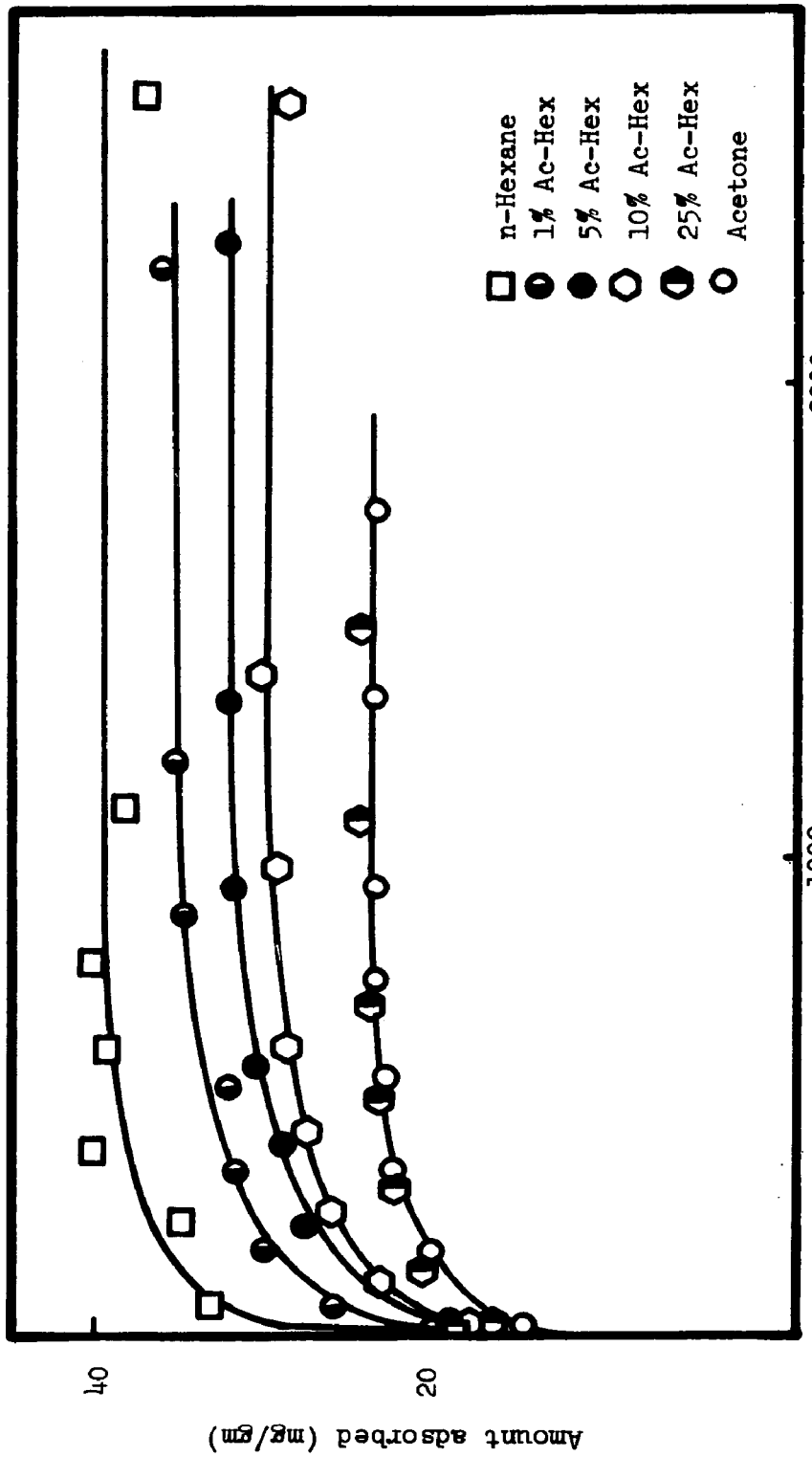


FIG. 4.10 ADSORPTION OF P-2 POLYMER ONTO CaF_2.

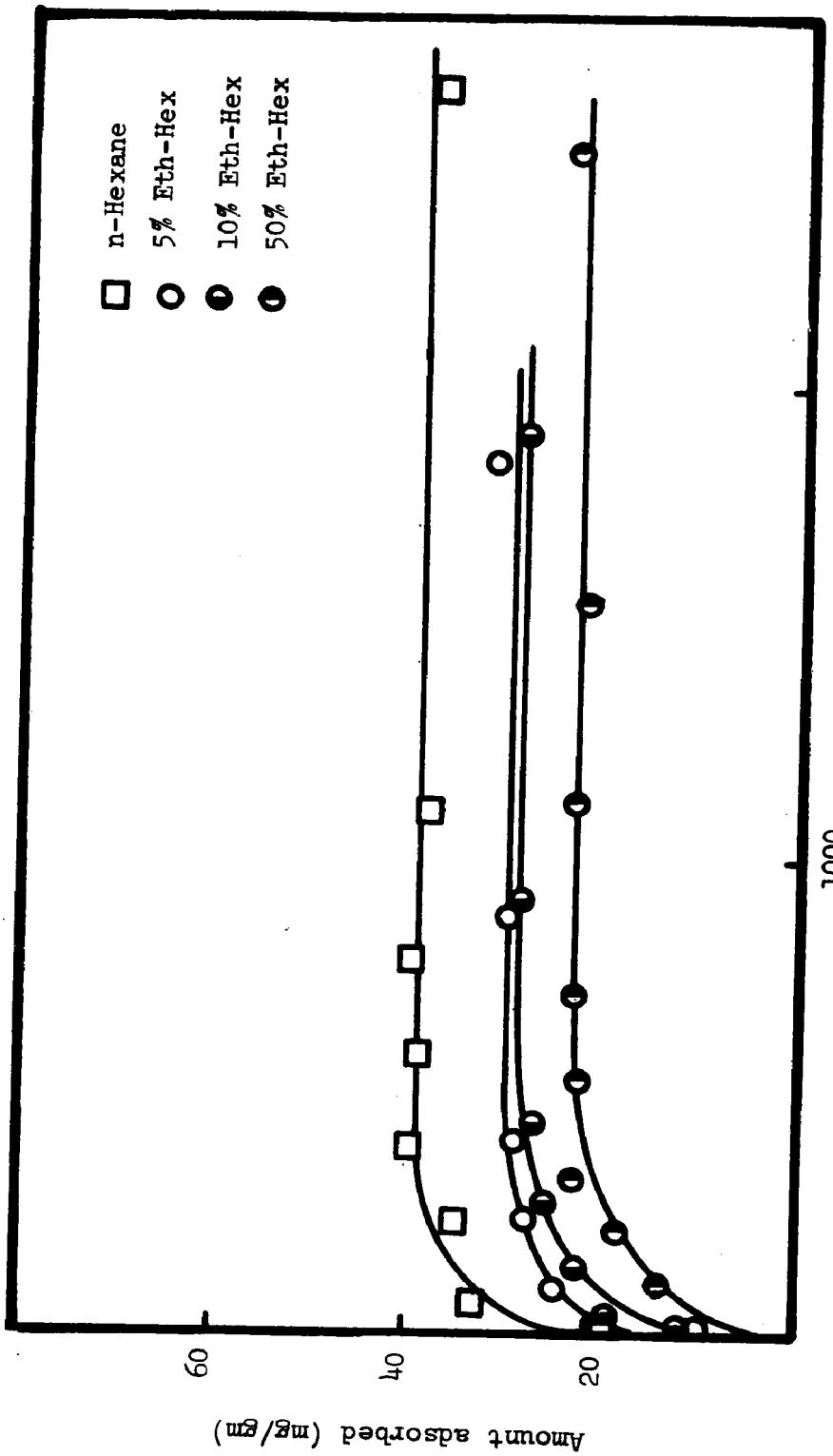


FIG. 4.11 ADSORPTION OF P-2 POLYMER ONTO CaF_2.

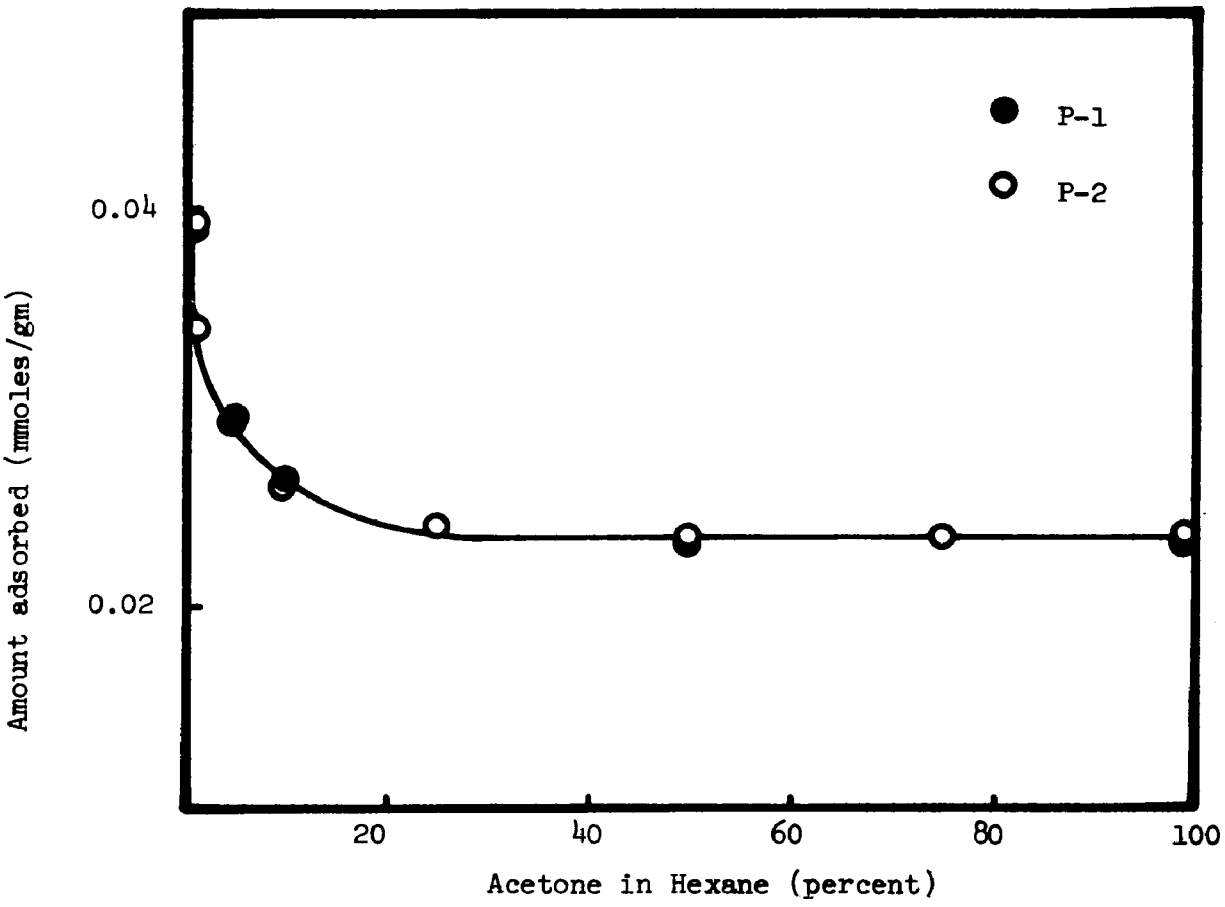


FIG. 4.12 THE MAXIMUM AMOUNTS ADSORBED OF P-1 AND P-2 POLYMERS ON CaF_2 FROM ACETONE-HEXANE SOLVENT MIXTURE.

of adding various proportions of acetone and ethanol to n-hexane on P-1 polymer adsorption. Figures 4.10 and 4.11 show the same effect on P-2 polymer adsorption. In general, the addition of these polar solvents to hexane, even in small percentages, interfered with the polymer adsorption. With the exception of P-1 adsorption from the ethanol-hexane system, the amounts adsorbed of the polymers generally decreased upon increasing the polar solvent percentage in the system. The equilibrium amounts adsorbed of P-1 and P-2 polymers from the 50-percent acetone in hexane solvent are exactly the same as those adsorbed from pure acetone. This means that the acetone effect on P-1 and P-2 adsorption reached the maximum value at the 50-percent level.

Figure 4.12 presents the maximum amounts (i.e., plateau values) adsorbed of P-1 and P-2 polymers on calcium fluoride as a function of the percentage of acetone in the hexane solvent. The data indicates that on a molar basis, the amounts of the two polymers adsorbed from the pure solvents or from mixtures of acetone and hexane are exactly the same.

Table 4.1 summarizes the limiting adsorption data of Figures 4.4 through 4.11 and presents it in milligrams, millimoles and, finally, as a percentage equivalence to monomer adsorption using the octylamine-hexane adsorption as the reference (100 percent).

Table 4.1

Equilibrium Adsorption of P-1 and P-2 Polymers on Calcium Fluoride

Solvent	Amount Adsorbed (mg/gm)			Amount Adsorbed (mmole/gm) x 10^2			Monomer Adsorbed Equivalent (%)		
	P-1	P-2	M	P-1	P-2	M	P-1	P-2	M
n-Hexane	118	40	11.5	3.9	3.88	9.00	87	86	100
Acetone	70	24	5.4	2.3	2.33	4.18	51	52	47
Ethanol	67	80↑		2.21	7.75↑		49	172 ↑	
Ac/Hex (%)									
1		35			3.4			76	
5	90	30		2.96	2.91		66	65	
10	80	27		2.63	2.62		59	58	
25		25			2.43			54	
50	70	24		2.3	2.33		51	52	
Eth/Hex (%)									
5	100 ↑	32		3.3 ↑	3.1		73 ↑	69	
10	120 ↑	29		3.95 ↑	2.81		88 ↑	63	
50		23			2.23			50	

Ac.: Acetone
Eth: Ethanol
Hex: n-Hexane
M: $CH_3(CH_2)_7NH_2$

4.4 Discussion of P-1 and P-2 Adsorption on Calcium Fluoride

This investigation on the adsorption of the two linear polydimethylsiloxane polymers has led to certain general conclusions These are:

1. The quantity of polymer adsorbed at the liquid-solid interface is far in excess of that calculated assuming a flattened configuration in which all segments of the polymer are in contact with the surface.

2. The shape of the adsorption isotherm with the exception of P-2/ethanol system is characteristic of monolayer formation.

3. The amount adsorbed at equilibrium is greater for the higher molecular weight polymer.

4. Adsorption from a poor solvent is greater than from a good solvent, except in those cases when the poor solvent was competing with the polymer for adsorption sites.

An adequate model that explains the adsorption of linear polymers with two terminal polar groups has been formulated in accord with these facts. In this model the polymer is allowed to adsorb onto all the available adsorption sites through one or both polar terminals. Two energetically different types of sites are assumed to be present in the calcium fluoride surface.* The unadsorbed segments of the adsorbed polymer chain extend into the surrounding solution and have configurations dependent on the polymer-surface and polymer-solvent interaction energies.

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*Ross, et al., (60) has reported for calcium fluoride powder the presence of two homotatic crystallographic surfaces that behave as two or more energetically homotatic surfaces toward certain adsorbates.

By gathering the information obtained from the instrinsic viscosity studies (Figures 4.2 and 4.3) and the equilibrium adsorption on calcium fluoride (Table 4.1), the P-1 and the P-2 adsorption data may be explained as follows.

Primarily, the monomer adsorption data (Table 4.1) shows that, while the utilization of the adsorption sites when hexane was the solvent was 100 percent (by assumption), this value dropped to 47 percent when hexane was substituted with acetone. This may indicate that the monomer was able to adsorb onto both surface sites from hexane, whereas it was adsorbing onto only one of the sites from acetone, because acetone molecules displace it from the other site. The results also indicate that the total surface sites are divided about equally between the two types.

The intrinsic viscosity of P-1 (Figure 4.2) is higher in hexane than in acetone or ethanol, and, presumably, if the solvent did not interact with the surface, the polymer adsorption would be less from hexane than from acetone or ethanol. In fact, the reverse is true (Figure 4.5). The only explanation is that the acetone and ethanol are adsorbing to the calcium fluoride surface and actively compete with the polymer for some sites, most probably the higher energy sites. The P-1 adsorption data (Table 4.1) indicated that 87 percent monomer equivalent were adsorbed from hexane, 51 percent from acetone and 49 percent from ethanol. This supports the monomer data in which it was found that acetone strongly competes for about one-half of the sites. The hexane figure is probably less than 100 percent because of a larger area being occupied by a polymer segment as compared to the

monomer molecule. The acetone and ethanol values are slightly greater than half the hexane value. This might be related to the better solvation of the polar groups in these solvents with more of the polymer molecules attaching to the surface through one end only.

The adsorption of P-2 polymers from hexane and acetone (Fig. 4.6) can be explained on the same basis as P-1. Again, the monomer equivalent data for P-2 (Table 4.1) are very much in support of the discussion. However, the P-2 polymer was found to behave differently than P-1 when ethanol was used as the solvent (Fig. 4.7). The following arguments may be presented to explain this difference. First, ethanol, being a relatively poor solvent for the P-1 (see Fig. 4.2), is able to force the molecules toward the solid surface and the behavior would be expected to be similar to that for P-1 in acetone. However, ethanol is a relatively better solvent for P-2 (see Fig. 4.3) probably because there are much fewer dimethylsiloxane groups in P-2 and ethanol is able to solvate the diamine groups, primarily through hydrogen bonding. Therefore, P-2 in ethanol may (i) adsorb onto sites already covered with ethanol, (ii) adsorb with a single polar group attachment to the surface and (iii) form multilayers that are well solvated by ethanol.

The mixed solvent studies in general agree with the model and the previously discussed results. Moreover, they emphasize the fact that the role played by the solvent in P-1 and P-2 adsorption involves solvent interactions with:

(a) the solid surface sites,

(b) the polar groups in the polymer molecule and

(c) the nonpolar chain.

Net polymer adsorption from these mixed solvents was found to result from two driving forces. The first force is the solid surface site occupation on adding polar solvents to the system. This tends to decrease the maximum adsorption of the polymer. The second force is polymer solvation. If the polymer solubility increases on adding the polar solvent, the polymer adsorption tends to decrease and vice versa; hence, decreasing the polymer solubility in the bulk will tend to increase its adsorption.

With both P-1 and P-2 (Figs. 4.8 and 4.10), the adsorption is generally lowered when acetone is added to hexane. However P-2 shows a significant solvent composition dependence (see Fig. 4.10) while P-1 does not (see Fig. 4.8). This might be explained on the basis that, for P-2, the addition of acetone to hexane increases site competition and <u>improves</u> solvent quality--both of which tend to oppose P-2 adsorption. On the other hand, for P-1, the addition of acetone to hexane probably lessens solvent quality (Fig. 4.2) even though it increases site competition. It is therefore likely that the two effects tend to cancel each other and relatively little solvent composition dependence is found (Fig. 4.8).

The results with the ethanol-hexane system is somewhat different. The incorporation of small amounts of ethanol in hexane gives greater adsorption of the P-1 polymer at the higher coverages than from pure

ethanol (Fig. 4.9). It is probable that the five percent or the ten percent ethanol-hexane solvent is a better solvent for P-1 than pure hexane. Solvation of the nonpolar chain as well as the polar head can be visualized for these compositions. In this case, a significant amount of the polymer molecules may adsorb onto the surface through only one polar anchor and consequently the maximum adsorption will increase as was found for P-2 in pure ethanol (Fig. 4.7). The larger amount adsorbed from the ten percent ethanol-hexane mixture suggests that it is a better solvent than the five percent mixture. However, the intrinsic viscosity measurements have indicated that the incorporation of 5 or 10 percent ethanol in the hexane solvent did not change the polymer solubility. Most probably hydrogen bonding between the polar groups of the polymer and the ethanol molecules in the solvent is responsible for the adsorption behavior from these two mixed solvent systems.

The P-2 adsorption from the ethanol-hexane system (Fig. 4.11) shows many similarities to the acetone-hexane system. The spread of the isotherms is similar to that for the acetone-hexane case.

Studies on the adsorption of pure solvents onto calcium fluoride powder were attempted. C^{14} labeled ethanol and acetone in unlabeled hexane were allowed to adsorb onto the powder surface. Unfortunately, counts before and after adsorption could not be interpreted in a meaningful way. Apparently, losses from the volatile solvents were very high.

CHAPTER V. THEORETICAL TREATMENT AND MODEL USED TO PREDICT POLYMER CONFIGURATION AT THE SOLID-LIQUID INTERFACE

5.1 Introduction

Adsorption from solution onto solid surfaces (in particular, the adsorption of macromolecules) has received great attention. Many attempts have been made to correlate experimental adsorption measurements with theory. However, most of these attempts have yielded limited results because the theoretical treatments have often had so many assumptions and restrictions that are difficult to evaluate either theoretically or experimentally.

The present theories have been largely based on the lattice model (61-69) in which the liquid bulk phase as well as the adsorbed phase are viewed as an array of lattice sites. Each site is occupied by a segment of the polymer molecule or by a monomer molecule. Mackor and van der Waals (61) derived adsorption isotherms for rod-shaped polymers with one active end group. The theory was considered poor because of its restrictions on molecular flexibility. The model also neglected the effect of the solution interaction energies on the configuration of the adsorbed molecules. Flexible macromolecules were treated by Frisch, Simha and Eirich (62-66). In their approach, they first considered the equilibrium of the isolated macromolecules at the surface and derived parameters characterizing its shape. Generally, it was suggested that the molecules are only attached to the surface with very few of its segments, and the remaining segments form large loops whose size increase with the square root of the molecular weight. Higuchi (67) used the same model to

evaluate the train-loop distribution as a function of the short-range anchor segment interaction energies. Silberberg (68,69) predicted by his theory on polymer adsorption that for the high molecular weight polymers, only the adsorption energy (energy change per segment brought into contact with the surface) can affect the polymer molecule shape at the surface. He viewed the polymer molecules to be more flattened on the surface. These treatments by Silberberg and Frisch et al. were restricted only to the lower range of concentrations and did not account for the individual polymer configurations at the surface.

It was not until 1970 when Ash, Everett and Findenegg (70) published their multilayer theory for adsorption from solution, that one was theoretically able to determine the area of the solid surface covered by each individual polymer configuration. This theory is applicable over the entire range of concentration and over a wide range of surface-solution and solution-solution interaction energies. It requires no prior assumption with regard to surface configurations and the influence of the adsorption is allowed to extend a large distance into the solution. Ash and co-authors applied their theory to mixtures of monomers and flexible trimers or tetramers with the possibility of extending the calculations to cover higher r-mers.

In the present study, their techniques have been extended to cover higher interaction energies among the components in the solution and at the solid-liquid interface. The calculations were carried out to show and define the energetic conditions necessary for converting a hydrophilic solid surface into a highly hydrophobic one when linear hydrophobic agents with terminal polar groups such as P-1 or P-2 polymer are employed.

The approach here is based upon the model and equations developed by Ash et al. (70). The adsorbing species is taken to be a tetramer with terminal polar groups which are able to act as "anchors" for the adsorption process.

5.2 Model Description and Parameters

For the system of a solution of monomers and flexible tetramers in contact with a solid adsorbing surface, a general expression for the configurational free energy is available (70). By minimizing this expression, a set of simultaneous equations may be obtained. These equations may then be solved to give the concentrations of the expected polymer configurations.

Figure 5.1 shows the possible tetramer configurations and each has been identified by a certain number. The first subscript (n) refers to the layer number in which the first segment is located, the second subscript(s) defines each particular configuration. Ten possible tetramer configurations are to be considered, two of them "1" and "5" having both their active groups attached to the surface. Configuration "5" is the one in which the polar groups are embedded under the nonpolar part of the molecule.

In a statistical treatment, a lattice extending number (t) of layers from the surface is considered with $A\nu$ sites in each layer where "A" is the area and "ν" is the number of sites per unit area. The number of tetramers and monomers in any layer is related to the number of sites by

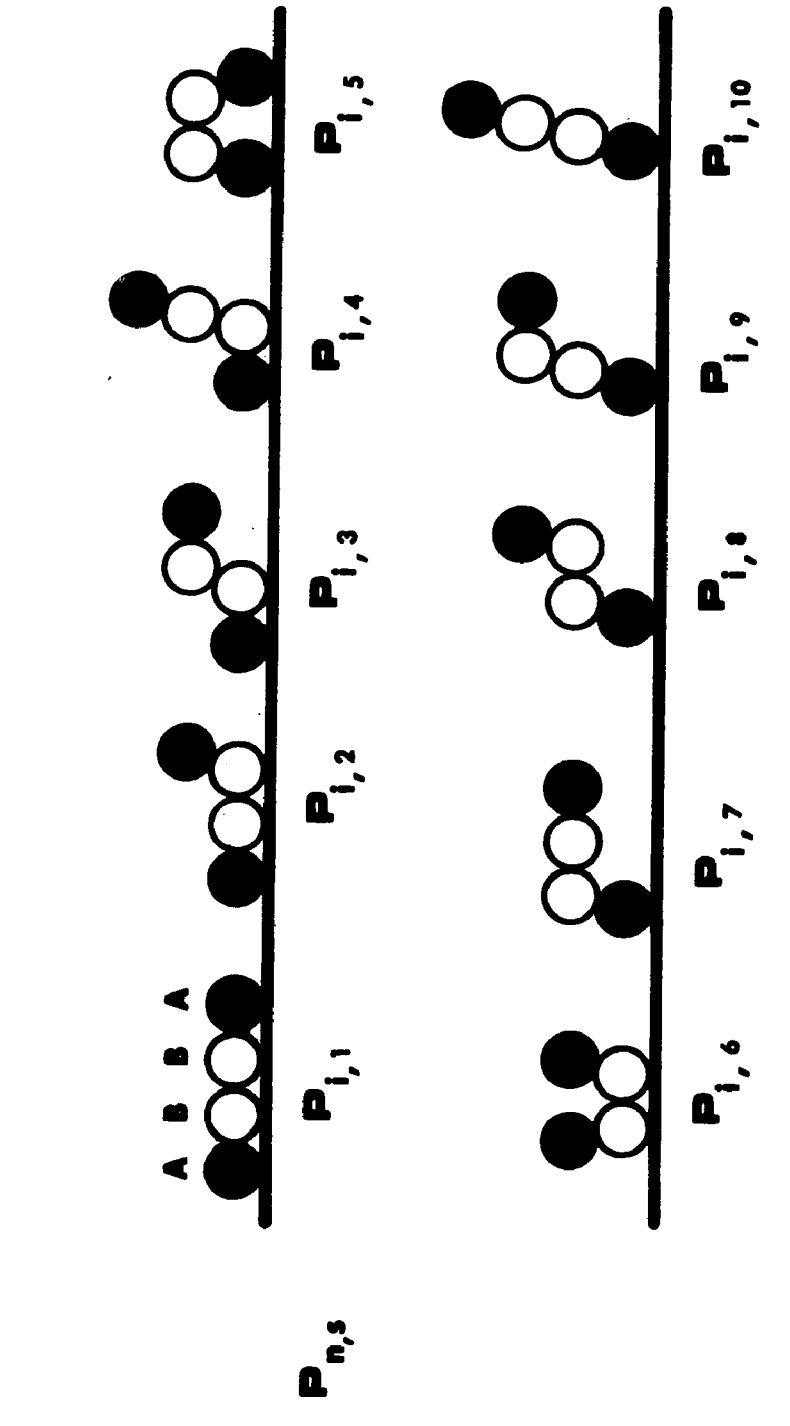


FIG. 5.1 CONFIGURATIONAL SPECIES OF THE SYMMETRIC TETRAMER. (A: POLAR SEGMENT. B: NONPOLAR SEGMENT)

$$A\nu = N_M^i + N_T^i \quad ,$$

where N_M^i is the number of sites occupied by monomer molecules in the ith layer, N_T^i is the total number of sites occupied by tetramer segments in the same layer.

The free energy of the system F_c is a function of the surface area (A) and the number of molecules ($N_{n,s}$) for each configuration in each of the t-layers. By minimizing F_c with respect to changes in $N_{n,s}$ keeping the sum of $N_{n,s}$ over the t-layers constant, this gives 10-t equations of the form

$$\left(\frac{\partial F_c}{\partial N_{n,s}}\right)_{A,N_{1,1},\ldots,N_{t,10}} = \mu \quad ,$$

which for given μ are solvable simultaneously for all $N_{n,s}$.

Three main parameters were introduced to vary the conditions of the system. These were:

1. ϕ_T^{ℓ}, the volume fraction of the tetramer in the bulk.
2. w , the net solution interaction energy. Defined by

$$w = z\left(\epsilon_{ab} - \frac{1}{2}\left(\epsilon_{aa} + \epsilon_{bb}\right)\right) \quad ,$$

where z is the coordination number, ϵ_{ab} is the interaction energy between a polar segment (A) and a nonpolar one (B), ϵ_{aa} is the interaction energy between two polar segments and ϵ_{bb} is the interaction energy between two nonpolar ones.

3. K, the parameter involving the differential free energies of adsorption of the polar and the nonpolar segments. It is defined by

$$K = \exp\left\{-\left[\left(\chi_a - \frac{mz}{2}\epsilon_{aa}\right) - \left(\chi_b - \frac{mz}{2}\epsilon_{bb}\right)\right]\Big/kT\right\},$$

where χ_a and χ_b are the interaction energies of segments (A) and (B) with the surface, mz is the number of the nearest neighbors of each lattice site in each of the adjacent layers. The ranges covered for these parameters are given in Table 5.1.

5.3 Results

Figures 5.2, 5.3 and 5.4 show the effect of independently varying ϕ_T^{ℓ}, w and K, respectively. The data of Fig. 5.2 indicate that at the lower ϕ_T^{ℓ} range, the volume fraction adsorbed for all the configurations increases by an almost constant rate on increasing ϕ_T^{ℓ}. While at the higher ϕ_T^{ℓ} values the volume fractions of some configurations begin to increase more rapidly than the others. These are the configurations which occupy the minimum surface sites and have at least one of their polar groups directly attached to the surface.

Figure 5.3 shows the effect of increasing the solution energy, w, on adsorption. The higher the value of w, the lower is the interaction energy between the polymer molecules and the solvent. The increase in w/2.3 kT was limited below 1.96, the value at which the solution begins to separate into two phases (70). The data indicate that as w increases, more polymer molecules are forced to the surface; especially those that anchor through both of their end groups.

Table 5.1

Values of the Parameters for Which Numerical Solutions Were Evaluated

ϕ_T^l	w/2.3 kT	Log K		
		1	2	3
0.002	0	+	+	+
0.002	0.4	+	+	+
0.002	1.0	+	+	+
0.02	0	+	+	+
0.02	0.4	+	+	+
0.02	1.0	+	+	+
0.1	0	+	+	+
0.1	0.4	+	+	+
0.1	1.0	+	+	-

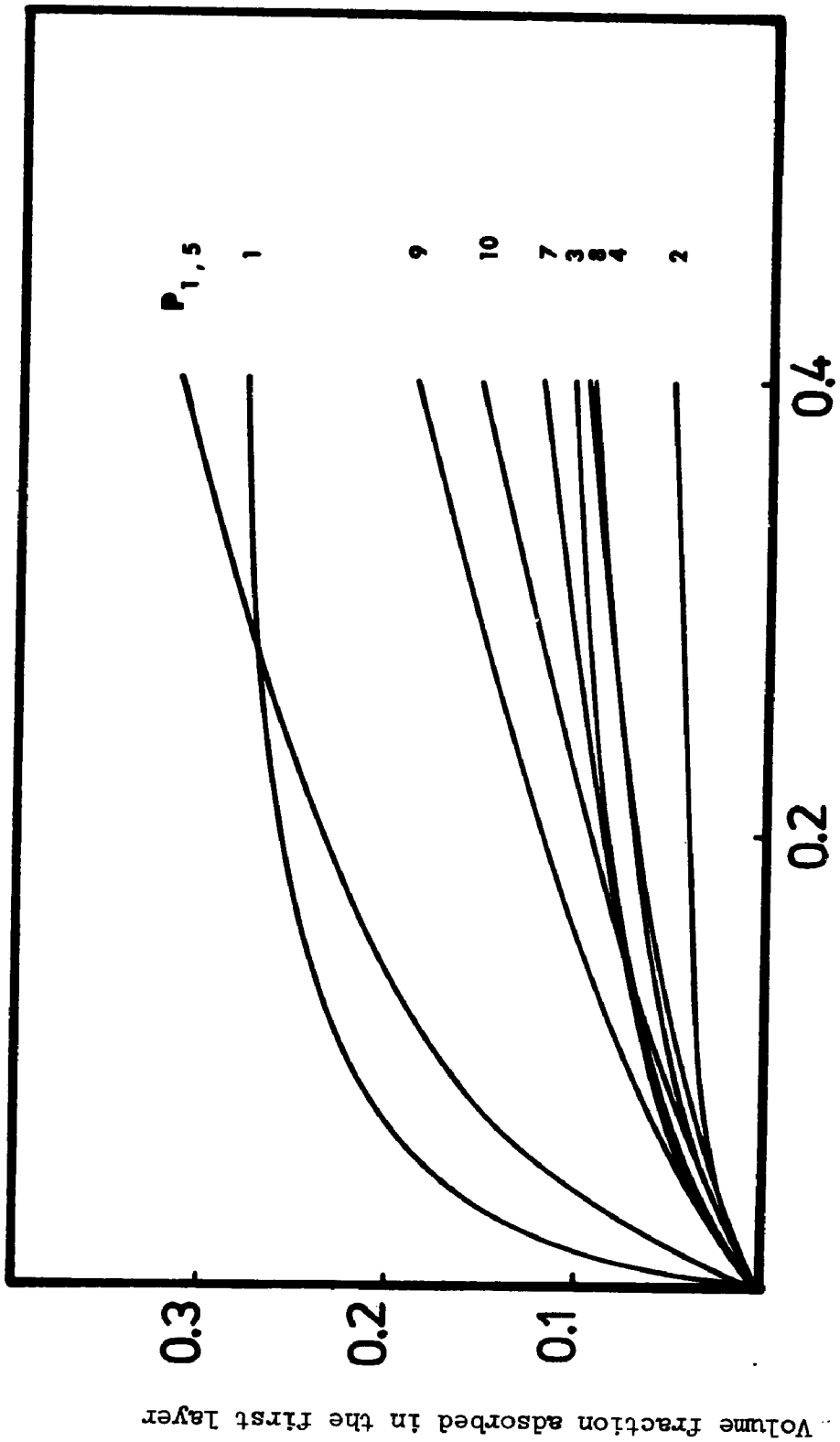


FIG. 5.2 TETRAMER ADSORPTION AS A FUNCTION OF BULK CONCENTRATION.

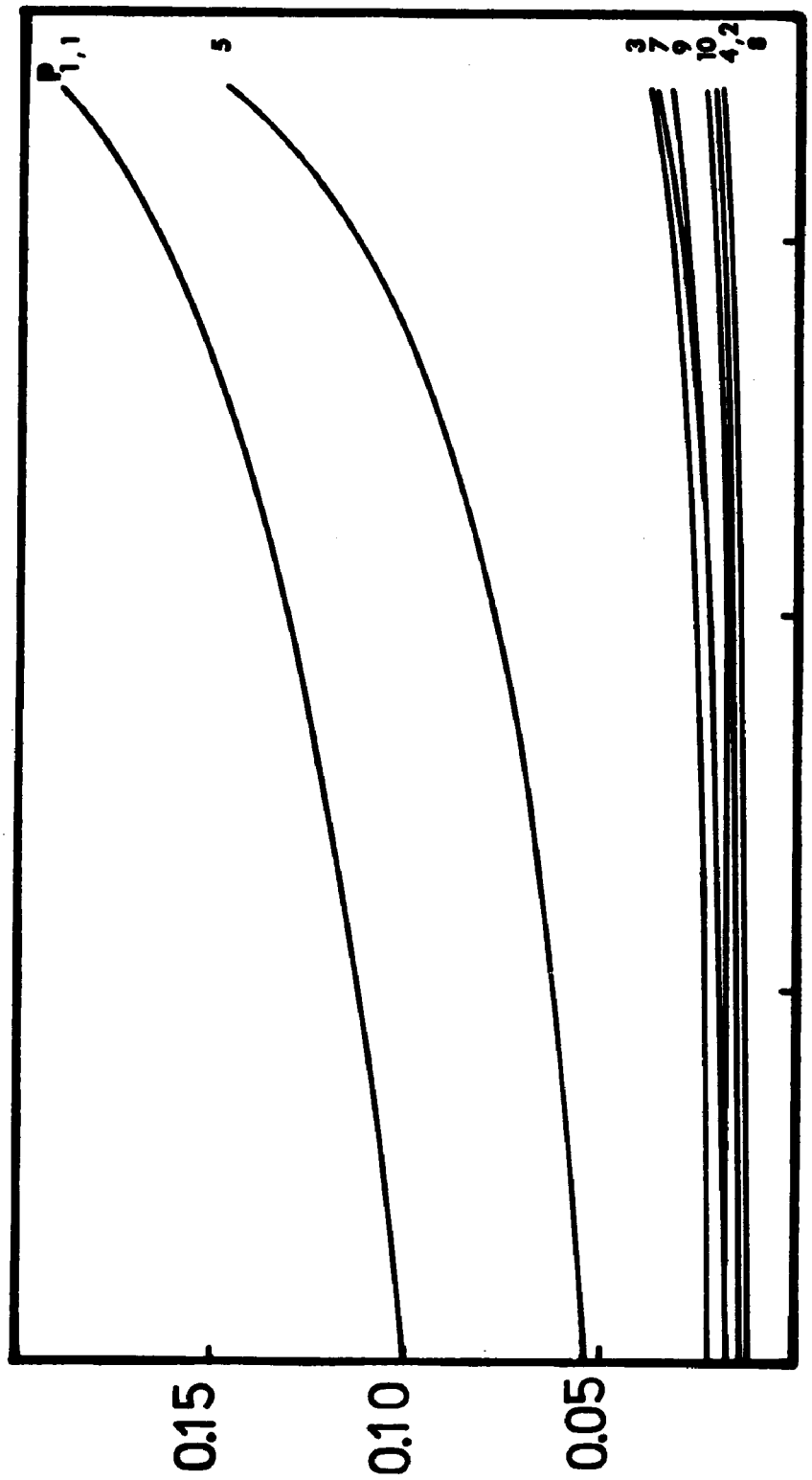


FIG. 5.3 TETRAMER ADSORPTION AS A FUNCTION OF w/2.3 kT.

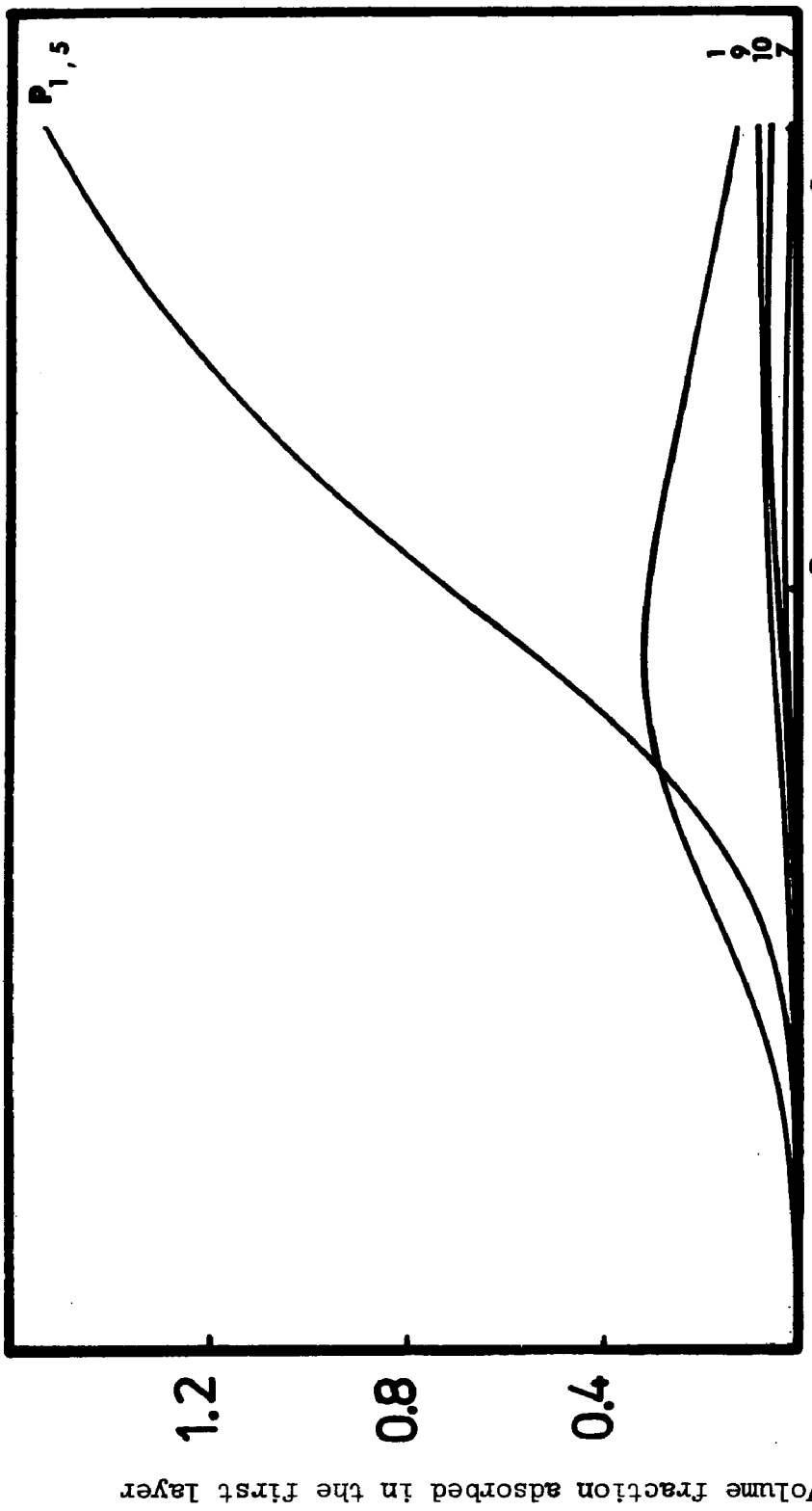


FIG. 5.4 TETRAMER ADSORPTION AS A FUNCTION OF log K.

Figure 5.4 shows how the polymer adsorption changes on increasing the interaction energy between the polar segments and the solid surface. As expected, the volume fraction of all the configurations adsorbed increases. But, at some log K, values which vary from 1.5 to 2.5, the adsorption starts to drop or remains almost constant for all the species except configuration 5 which predominates under these conditions.

This last result is of great significance since it defines the conditions at which the linear polymer molecules with terminal polar groups can orient themselves like configuration 5. It appears that the high interaction energy with the solid surface overwhelms both the bulk concentration and the solution solvation effect on the adsorbed polymer molecules.

The next group of calculations were aimed at covering different combinations of low, medium and high values of ϕ_T^{ℓ}, w and K (Table 5.1). The data are illustrated in Tables 5.2, 5.3 and 5.4. From Table 5.4, the percentages of the surface covered by configurations 1, 5 and 10 are plotted as functions of log K (Fig. 5.5). Similar plots can be made from Tables 5.2 and 5.3. The results may be summarized as follows. At low log K values neither the increase of the bulk polymer concentration nor the decrease of the interaction energy between the solvent and the polymer would effectively characterize the nature of the surface adsorbed layer. While, at high log K values (high interaction between the polymer polar groups and the solid surface) there is a tendency for configuration 5 to cover from 54 to 85 percent of the surface sites depending upon the ϕ_T^{ℓ} and the w values. This limit of the surface

Table 5.2

Effect of Log K and w/2.3 kT at Conc. 0.002

w/2.3 kT	log K	Volume Fraction in the First Layer									
		1	2	3	4	5	6	7	8	9	10
	1.0	0.0168	0.0024	0.0032	0.0024	0.0080	0.0001	0.0024	0.0016	0.0024	0.0018
0.0	2.0	0.2642	0.0050	0.0106	0.0091	0.2605	0.0002	0.0079	0.0062	0.0112	0.0084
	3.0	0.2616	0.0010	0.0031	0.0048	1.0728	0.0	0.0058	0.0079	0.0222	0.0172
	1.0	0.0171	0.0024	0.0032	0.0024	0.0081	0.0001	0.0024	0.0016	0.0024	0.0018
0.4	2.0	0.2972	0.0053	0.0107	0.0083	0.3165	0.00002	0.0116	0.0081	0.0145	0.0110
	3.0	0.2330	0.0007	0.0027	0.0036	1.2479	0.0	0.0060	0.0073	0.0269	0.0206
	1.0	0.0177	0.0024	0.0032	0.0024	0.0082	0.00008	0.0025	0.0016	0.0024	0.0018
1.0	2.0	0.3261	0.0042	0.0111	0.0072	0.5881	0.00001	0.0168	0.0097	0.0201	0.0151
	3.0	0.1619	0.0003	0.0015	0.0018	1.5263	0.0	0.0049	0.0052	0.0307	0.0234

Table 5.3

Effect of Log K and w/2.3 kT at Conc. 0.02

w/2.3 kT	log K	Volume Fraction in the First Layer									
		1	2	3	4	5	6	7	8	9	10
0.0	1.0	0.1012	0.0148	0.0217	0.0169	0.0530	0.00054	0.0176	0.0123	0.0191	0.0146
	2.0	0.3241	0.0087	0.0212	0.0221	0.5481	0.00005	0.0292	0.0274	0.0562	0.0437
	3.0	0.1983	0.0010	0.0041	0.0092	1.3086	0.0000	0.0099	0.0189	0.0827	0.0639
0.4	1.0	0.1105	0.0157	0.0234	0.0177	0.0605	0.00056	0.0195	0.0131	0.0206	0.0156
	1.5	0.2820	0.0152	0.0305	0.0241	0.2843	0.00021	0.0344	0.0242	0.0432	0.0331
	2.0	0.3105	0.0068	0.0197	0.0190	0.7334	0.000037	0.0324	0.0277	0.0661	0.0513
	3.0	0.1584	0.0006	0.0029	0.0059	1.4610	0.000001	0.0085	0.0155	0.0896	0.0704
	3.2	0.1341	0.0003	0.0018	0.0046	1.5424	0.0000	0.0061	0.0132	0.0917	0.0721
1.0	1.0	0.1314	0.0177	0.0274	0.0193	0.0789	0.00059	0.0241	0.0151	0.0240	0.0179
	2.0	0.2501	0.0035	0.0138	0.0117	1.1071	0.0000	0.0317	0.0237	0.0820	0.0640
	3.0	0.1056	0.0002	0.0016	0.0028	1.6960	0.0000	0.0064	0.0102	0.0956	0.0762

Table 5.4

Effect of Log K and w/2.3 kT at Conc. 0.1

w/2.3 kT	log K	Volume Fraction in the First Layer									
		1	2	3	4	5	6	7	8	9	10
0.0	1.0	0.2051	0.0345	0.0568	0.0479	0.1402	0.0015	0.0529	0.0396	0.0662	0.0516
	2.0	0.2837	0.0094	0.0280	0.0366	0.7730	0.000077	0.0470	0.0546	0.1408	0.1133
	3.0	0.1460	0.0009	0.0042	0.0126	1.3920	0.00	0.0119	0.0312	0.1826	0.1474
0.4	1.0	0.2238	0.0355	0.0618	0.0492	0.1713	0.0014	0.0607	0.0429	0.0737	0.0571
	2.0	0.2533	0.0066	0.0229	0.0284	0.9547	0.000042	0.0455	0.0501	0.1562	0.1275
	3.0	0.1160	0.0005	0.0029	0.0081	1.4970	0.0	0.0098	0.0243	0.1882	0.1562
1.0	1.0	0.2648	0.0360	0.0716	0.0501	0.2687	0.0012	0.0813	0.0505	0.0945	0.0725
	2.0	0.1937	0.0031	0.0144	0.0162	1.2286	0.00001	0.0386	0.0385	0.1766	0.1502
	2.7	0.1045	0.00045	0.0031	0.006	1.534	0.00000	0.0122	0.0211	0.1914	0.1665

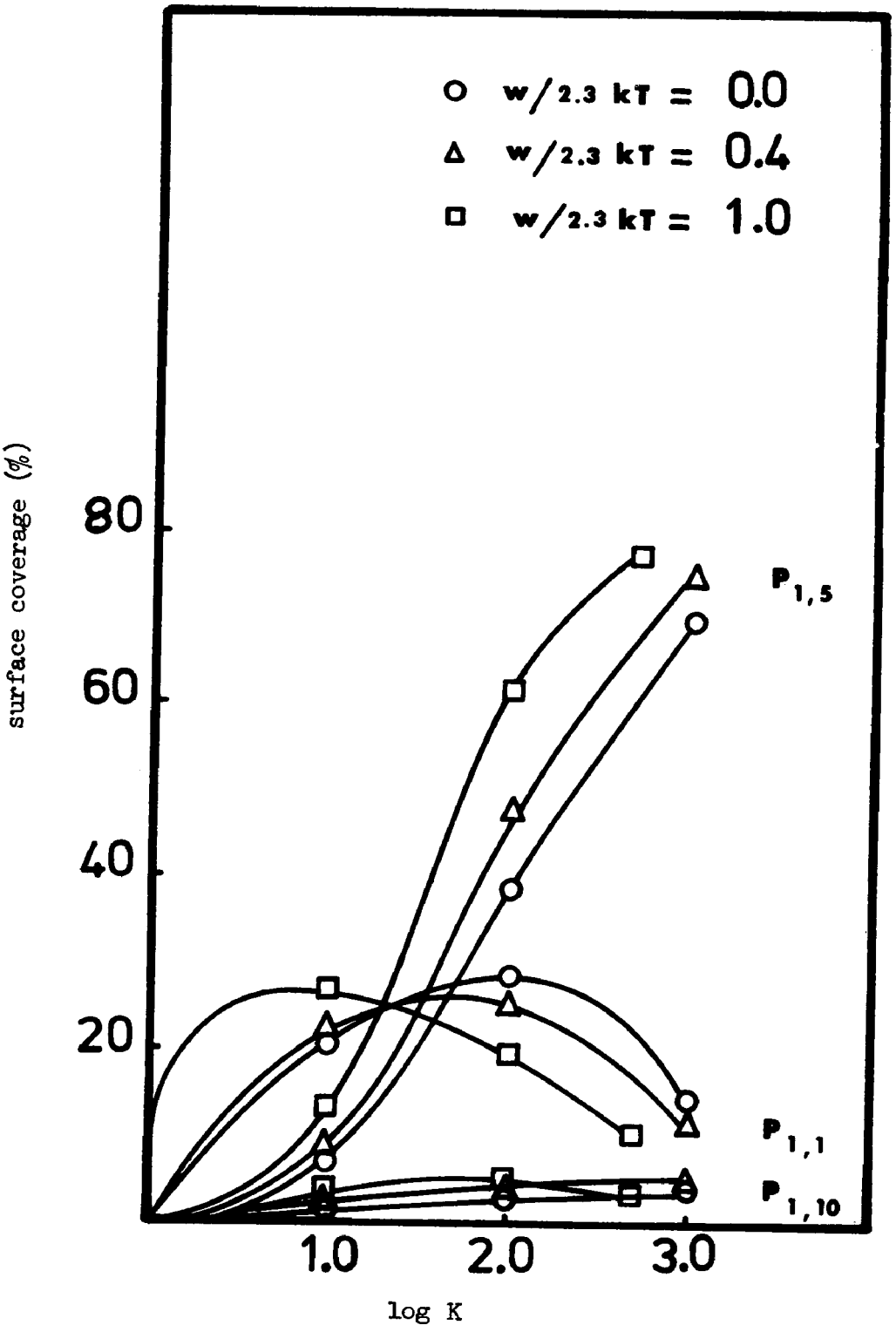


FIG. 5.5 EFFECT OF log K AND w ON THE SURFACE COVERAGE BY CONFIGURATIONS 1, 5 AND 10. ($\phi_T^{\ell} = 0.1$)

coverage could still be increased at higher log K values which require further improvement of the computing techniques.

5.4 Discussion

The essential contribution of this analysis is an improvement in the technique to compute adsorption values developed by Ash et al. (70). Initiating this improvement, the calculations were extended to cover high K values where the significant effect of K upon the configurations was demonstrated. Ash and co-authors covered log K values up to 1.5 (Figure 5.4) where there was no overwhelming preference shown for configuration 5.

We are now interested in modifying the model from ABBA-B solvent to ABBA-C solvent so that the specific effect of the solvent on both segments A and B may be independently studied. It is anticipated that from a suitable solvent, close to 100 percent of the surface sites might be covered by configuration 5. Indeed, it would be interesting to note how ϵ_{aa}, ϵ_{bb}, ϵ_{cc}, ϵ_{ab}, ϵ_{ac} and ϵ_{bc} collectively determine the adsorption behavior.

Work is continuing in this laboratory (71) to study the system ABBA-C and to date it appears that the formulation of the new equations and the programming would not entail a great deal of additional time. Therefore, it is anticipated that the solvent effect upon adsorption could be more critically evaluated.

SUMMARY AND CONCLUSIONS

The adsorption of a group of polydimethylsiloxane polymers on hydroxyapatite has been studied in an attempt to find a model compound that could protectively form a film on human teeth and thereby prevent the adhesion of dental plaque. Contact angle measurements were used to determine the wettability of the formed films. The equilibrium adsorption data were analyzed and possible adsorption mechanisms were considered taking into account the molecular configurations of the polymers and the effects of solvent.

In order to obtain a better understanding of the adsorption behavior of these compounds, detailed systematic studies were carried out on the adsorption of the two linear polymers P-1 and P-2 on calcium fluoride. A physical model that explains the adsorption data and the solvent effect was proposed. The experiments with hexane, acetone and ethanol solvents showed a large dependence of the adsorption upon the solvent used. These data were interpreted on the basis of either quality of the solvent and/or solvent competition for adsorption sites. Adsorption of P-1 and P-2 from mixed solvent systems indicated that the polar solvents are competing with the polymer molecules for some of the solid surface sites. Acetone and ethanol were found to effectively "poison" about one-half of the calcium fluoride surface sites.

The results of the studies with P-1 and P-2 polymers have indicated that the polymer configuration on a solid surface is essentially a function of (a) the strength of the polymer adsorption to the surface;

(b) the degree of polymer solvation by the solvent and (c) the extent to which the solvent is able to compete with the polar anchoring segments of the polymer molecules for the surface sites.

Theoretical studies in this area were conducted and calculations on the extent of adsorption of linear polymers on a solid surface were carried out. The multilayer theory of polymer adsorption proposed by Ash, Everett and Findenegg (70) was used and the calculations were extended to cover higher interaction energies among the components of the solution and at the solid surface. The studies on the individual polymer configurations established the necessary energetic conditions for converting a hydrophilic solid surface into a highly hydrophobic one when a linear hydrophobic agent with terminal polar groups is employed.

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