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The Influence of Molecular Structure of Vapor Phase Chemisorbed Fatty Acids Present in Fractional Monolayer Concentrations on the Wettability of Cellulose Film

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THE INFLUENCE OF MOLECULAR STRUCTURE OF VAPOR PHASE
CHEMISORBED FATTY ACIDS PRESENT IN FRACTIONAL MONOLAYER
CONCENTRATIONS ON THE WETTABILITY OF CELLULOSE FILM

A thesis submitted by

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SUMMARY

It is well known that a single monomolecular layer of adsorbed molecules
can radically change the frictional and wetting properties of an underlying
solid. However, the relationship between fractional surface coverage and wetta-
bility has not been determined. This investigation examined the relationship
between the quantity of fatty acid present in fractional monolayer concentrations
and the resultant change in wettability of a cellulose film surface containing
fatty acid chemisorbed from the vapor phase. Fatty acids differing in molecular
structure were investigated in order to allow the development of a conceptual
model consistent with the wettability behavior.

Smooth cellulose film which was hand-cast from cellulose xanthate onto
pyrex glass plates and dried against Lucite was used as the adsorbent. Stearic,
behenic, and isostearic acids labeled with carbon-14 were vapor phase adsorbed
onto the cellulose film. These three fatty acids differ in molecular chain
length and branching but have similar vapor pressures so that the same adsorp-
tion conditions could be used to study the three adsorbates.

An adsorption apparatus closed to the ambient atmosphere which contained
an infinite reservoir of fatty acid was used. Adsorption was performed at
85 and 105°C. Higher adsorption temperatures changed the surface properties
of the cellulose film.

The wettability of the cellulose film surface containing the adsorbed fatty
acids was monitored with the water contact angle. A photographic method per-
mitted accurate measurement of an initial contact angle within one second follow-
ing placement of the liquid drop on the surface. Methylene iodide contact angles
were also measured so that a surface energy parameter for the cellulose film
could be calculated using the Owens-Wendt equations. The quantity of vapor phase
adsorbed fatty acid was measured using radiochemical counting techniques.

The three fatty acids were found to be physically and chemically adsorbed onto the cellulose. The physisorbed molecules were primarily dimeric while the chemisorbed species were linked to the cellulose by means of an ester bond. Extractions were used to separate and identify the various species of adsorbed acid. A benzene extraction removed physisorbed acid from the cellulose film surface; a water extraction removed physisorbed acid present in pores, crevices, etc.; and a 0.01$\underline{M}$ sodium methoxide-methanol extraction removed the chemisorbed molecules.

The quantity physisorbed onto the cellulose film surface reached a constant level quickly; this equilibrium quantity was present at all adsorption times studied. Increased total adsorption with time was due to continuing chemisorption and increasing physisorption into the pores and crevices. Chemisorption was very slow compared with physisorption. The rate of chemisorption was temperature dependent and independent of the molecular architecture of the fatty acid adsorbate.

The quantity of chemically bonded fatty acid determined the magnitude of the contact angle, even though the physically adsorbed species were generally present in much higher concentrations. The physisorbed dimers did not participate in the interfacial wetting and apparently lay on or near the cellulose surface.

Behenic acid decreased the wettability of the cellulose film more efficiently than either stearic acid or isostearic acid. Stearic acid was only slightly more efficient than isostearic aicd. An analysis of the wettability differences among the three acids resulted in the conclusion that the chemisorbed molecules sweep out an area far greater than their cross-sectional area. At low chemisorption levels the chemisorbed molecules sweep out the

projected area of a hemisphere. As chemisorption continues the chemisorbed molecules mask the projected area of a cone, with the angle between the surface perpendicular and the chemisorbed fatty acid decreasing with increasing chemisorption. An empirical relationship was obtained from the conceptual model of swept-out areas which related the water contact angle to the product of the quantity chemisorbed and the square of the molecular chain length of the adsorbate. This equation provided a quantitative relationship between fractional surface coverage and wettability for the adsorbate-adsorbent system investigated in this study.

INTRODUCTION

The properties of a surface represent a combination of many physical and chemical phenomena. Oftentimes it has been difficult to decide exactly which properties should be included in the field of surface chemistry. However, the interactions between a liquid and a solid have been universally recognized among the most fundamental properties of a surface. These interactions are collectively called wettability. They are omnipresent in the world around us and are as important to the housewife or industrial worker as to the scientist. Both the papermaker and the consumer of paper products are greatly concerned with wetting phenomena.

Cellulose is a very hydrophilic material. Furthermore, the very porous nature of paper often makes it act like a sponge, so that unsized paper soaks up or absorbs aqueous liquids rapidly and extensively. In spite of these physical properties, the end use of many paper products requires that they be resistant to the penetration of water and various aqueous liquids. The process of developing water resistance in paper and paperboard is called sizing. This process usually involves the addition of a chemical additive which provides paper and paperboard with resistance to wetting, penetration, and absorption of liquids.

The primary commercial methods of sizing are internal sizing, in which sizing agents are added to the aqueous pulp slurry, and surface sizing, in which surface coatings are applied to the formed sheet. Another possible method is surface sizing from the vapor phase. This would be a much cleaner sizing process involving less chemical loss. It would also provide more flexibility since it would eliminate the possible interference by other materials added to the pulp slurry. The vapor phase application eliminates

the requirement of a solvent. Furthermore the mandated antipollution effort accentuates the need for a chemically cleaner white water. Finally, since it is only necessary to make the surface of the sheet water repellent, this method of application would reduce the quantity of sizing material required. It is anticipated that this study will be a step toward the ultimate development of a commercial vapor phase sizing process.

While it is well known that a single monomolecular layer adsorbed on a surface may profoundly alter the wetting properties of that surface, the relationship between fractional surface coverage and wettability is not well defined. This study investigates that relationship by examining the wettability of cellulose film as affected by the extent of chemisorption from the vapor phase of fatty acids present in fractional monolayer concentrations. By using fatty acid sizing compounds which differ in molecular structure, the orientation which these molecules assume when they are masking an underlying surface can be hypothesized. Knowledge of this orientation gives insight concerning how water repellency is produced as a surface is being covered and also what molecular configuration constitutes a good vapor phase sizing agent.

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LITERATURE REVIEW

THE SOLID SURFACE

The chemical composition of a solid allows a general classification of the surface properties of that solid to be made. For example, a hydrocarbon surface will be quite different than a cellulose surface. On the other hand, the surface of a solid may possess properties which are not characteristic of the bulk solid. Reactive groups may not be fully exposed or may be less reactive due to the presence of other bulky groups. The molecular composition of the surface may be quite different than the interior due to orientation of particular molecular groups. Surface molecules do not have neighbors in every direction, therefore the ubiquitous intermolecular forces of attraction are unbalanced in the direction normal to the bulk. The solid surface thus presents a distinct example of dissymmetry.

Solids and liquids differ primarily in that the molecules of liquid have much more mobility. Due to the limited mobility of the solid molecules, solid surfaces are likely to be much more complex in structure. The atoms and molecules remain in their original positions instead of forming a homogeneous surface, the result being that adjacent groups of atoms or molecules may possess different properties (1). This does not exclude the small degree of bulk and surface mobility exhibited by solids. The complexity of solid surfaces is further increased due to heterogeneity which may be chemical, physical, or induced from foreign matter adsorbed on the surface.

The presence of foreign molecules adsorbed onto the solid surface following its formation is the most common chemical heterogeneity. Impurities may also be present during the formation of the solid. Other causes of defective structures include lattice vacancies and the presence of interstitial atoms.

Physical heterogeneity is due to surface roughness and porosity. While a surface is never completely smooth when considered on an atomic scale, a greater problem is usually encountered from larger-scale roughness. The roughness manifests itself in a surface composed of edges or corners, crevices, declivities or acclivities, and other irregularities. The result is that each point of the solid surface may have a different adsorption potential which is dependent upon its location on the irregular matrix.

The induced heterogeneity arises from changes that occur when a surface is partially covered with an adsorbed layer. The initially adsorbed molecules can greatly affect the energy with which succeeding molecules are adsorbed. The interaction energy usually decreases with increasing coverage during chemisorption. Conversely, lateral attractions between adsorbate molecules have been reported to result in an increased energy of interaction between the adsorbate and the solid (2).

The study of solid surfaces is a formidable pursuit. A standard surface is difficult to obtain since complications arise from contaminants which may be adsorbed or deposited on the surface during or after its preparation. The magnitude of these problems increases with increasing surface energy of the solid.

SURFACE FORCES OF SOLIDS

The unbalanced intermolecular forces of attraction at the surface result in an inward attraction of the liquid or solid surface. The surface behaves as if it were under tension and resists expansion or extension. This resistance gives rise to the surface tension, which is responsible for such phenomena as the tendency for liquid drops and bubbles to be spherical (because the sphere is the geometric shape which has the smallest area for a given volume),

the rise of liquids in a capillary tube, and contact angles between liquids and solids.

Surface tension is the force in dynes acting perpendicularly to any line one centimeter in length in the plane of the surface. Surface energy is defined as the energy in ergs required to create one-square centimeter of non-stressed surface. Since energy must be consumed to create a new surface, the surface energy is always positive in sign. For all pure liquid and nonstressed pure solid surfaces, the surface tension is numerically equivalent to the surface energy (1).

In general the surface free energy of solids cannot be measured directly because of the elastic and viscous restraints of the bulk phase. In spite of this, the concept of surface energy of solids has been the basis for many theoretical as well as experimental investigations of surface wetting, and several experimentally simple methods have been designed to approximate it.

One method is the determination of the critical surface tension of the solid, denoted γ_c, which was proposed by Fox and Zisman (3). The critical surface tension is determined by the extrapolation to cos θ = 1.0 of a plot of cos θ (cosine of the contact angle) vs. γ_{lv} (the surface tension at the interface of the liquid and vapor phases) for various homologous liquids differing in surface tension.

The critical surface tension of an adsorbed layer of polar-nonpolar (amphipathic) molecules is dependent on the closeness of packing and on the chemical nature of the nonpolar and of the adsorbed molecules (4). Unbranched closely-packed molecules having terminal methyl or fluoromethyl groups have very low critical surface tensions. Branched and cyclic molecules have higher critical surface tensions. However, γ_c is not a fundamental property of a solid; it is

an interfacial parameter. Different series of liquids give different γ_c values. Nevertheless the critical surface tension is a valuable tool which permits a simple measurement of changes in surface constitution. The temperature dependence of γ_c has been studied (5,6).

Zisman classified as low energy solid surfaces those which have a γ_c of less than 100 ergs/cm^2 and those above this value as high energy solid surfaces. High energy solid surfaces may not always show perfect wetting by low energy amphipathic liquids because of autophobicity (7). This term refers to liquid molecules which adsorb on a solid to form a film whose γ_c is less than the γ_l of the liquid itself. Hence autophobic liquids are liquids that are unable to spread upon their own adsorbed oriented monolayer.

Bernett and Zisman (8) found that the surface energy of any clean, smooth high-energy surface, whether glass, metal, or metal oxide, was dependent upon the surface concentration of adsorbed water after being exposed to a humid atmosphere. The nature of the underlying surface had little effect on γ_c, indicating that the adsorbed layer of water completely masked the surface energies of the respective solids and produced surfaces of the same energy.

The critical surface tension has been useful in studies predicting adhesion of polyethylene to paper (9), adhesion of hot-melts on paperboard (10), and in studies of self-sizing and loss of absorbancy of wood pulp products (11). The wettability of cellulose films and films of various cellulose derivatives has also been studied using this method by Bartell and Ray (12) and Luner and Sandell (13). The γ_c obtained for regenerated cellulose films ranged from 35.5 to 49.0 dynes/cm.

Other methods relating contact angles to solid surface energy include that of Fowkes (14), Girifalco and Good (15), Owens and Wendt (16), and Wu (17).

These treatments have become increasingly sophisticated until they now specify dispersion and nondispersion components of the solid surface energy, and they are discussed in detail in a later section.

THE RELATIONSHIP OF SURFACE ENERGY TO WETTING

Wetting can be thought of as the process of achieving molecular contact. The molecular contact or interaction between a solid and liquid depends upon the surface forces of the interacting substances. Anything altering the magnitude or direction of these forces would change the wettability of the corresponding liquid-solid system. The secondary valence forces, which comprise the surface forces, act primarily in the range of atomic and molecular distances.

In a classical paper Langmuir ([18]) theorized that the surface forces depend almost entirely on the top layer of the groups of atoms which make up the surface, while the atoms below the top layer have a negligible effect on the surface forces. He disclosed that the surface properties of a substrate could be completely altered when covered with only one layer of foreign atoms or molecules. Langmuir ([19]) later observed that many of the physical properties of a homologous series of nonpolar organic substances are roughly additive. The addition of each methylene group to a hydrocarbon chain in most compounds increases the volume, raises the boiling point, and alters the solubility in approximately the same manner. Langmuir concluded that the force fields around any given group in a large organic molecule are characteristic of that group and are largely independent of the nature of the rest of the molecule. He submitted that the adsorptive properties of a surface were determined by the nature and packing of the atoms or groups of atoms in the surface of the solid or liquid, and he referred to this concept as the principle of independent surface action ([20]).

The scientific literature is rife with experimental examples that justify this postulate that only the atoms at the interface between a solid and liquid control the wettability of the system. The influence of adsorbed water on the critical surface tension of metals has already been mentioned. Initial contact angles of monolayers of fatty acids are independent of the substrate. Adsorbed monolayers of organic polar compounds radically change the frictional and wetting properties of solid surfaces, and monolayer masking of surface properties is fundamental to the fields of lubrication, adhesion, and paper sizing.

The contact angle formed by a sessile drop of a liquid on a solid surface is used as an inverse measure of wettability. Young (21), in 1805, suggested the following contact angle relationship between a solid and liquid as a mechanical equilibrium of three surface tensions:

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta \qquad (1)$$

The first component, γ_{sv}, represents the surface tension of solid in equilibrium with vapor; while γ_{sl} is the surface tension of the liquid surface in equilibrium with its own vapor. The solid-liquid contact angle is represented by θ. Equation (1) is applicable only when θ is greater than zero degrees. When $\theta = 0$, one may only deduce that $\gamma_{sv} > \gamma_{lv} + \gamma_{sl}$. A thermodynamic justification of Young's equation has been presented by Johnson (22). Deformation of the solid surface in the vicinity of the solid-liquid-vapor boundary has been theoretically considered by Lester (23).

In 1937 Bangham and Razouk (24,25) suggested that the γ_{sv} term is not generally equal to $\gamma_s o$, the surface free energy of the solid in a vacuum. The difference between these two quantities $(\gamma_s o - \gamma_{sv})$ is represented as π_e, the equilibrium film spreading pressure on the solid. It represents the amount by which the solid surface free energy is decreased due to adsorption of vapor.

This term has been neglected in many treatments, and a critical review of such an assumption has been given by Fowkes ([26]).

Dupre ([27]) defined the reversible work of adhesion at a solid-liquid interface as follows:

$$W_{sl} = \gamma_s{}^o + \gamma_{lv} - \gamma_{sl} \qquad (2)$$

All the symbols have the same meaning as was previously defined. The work of adhesion is the energy required to separate one-square centimeter of wetted solid surface into one-square centimeter each of liquid surface and solid surface. The equation was combined with Equation (1) and with $\gamma_s{}^o = \gamma_{sv} + \pi_e$, to give the following equation:

$$W_{sl} = \gamma_{lv} (1 + \cos \theta) + \tilde{\pi}_e \qquad (3)$$

If volatile liquids are used, the correction due to π_e can be quite significant. However, for water at 20°C the saturation pressure is so low that the correction becomes negligible unless the adsorbent is hygroscopic. When the correction is negligible, Equation (3) reduces to the following:

$$W_{sl} = \gamma_{lv} (1 + \cos \theta) \qquad (4)$$

In this case the work of adhesion is easily determined from a measurement of the surface tension and the contact angle.

A positive spreading coefficient has generally been employed as a thermodynamic requirement for a liquid to spread spontaneously on a solid. The spreading coefficient is defined as the difference between the work of adhesion and the work of cohesion $(W_A - W_C)$, where the work of cohesion of a liquid is equal to $2\gamma_{lv}$. The relation states that if a liquid has more attraction for the solid than it does for itself, it will spread on that solid.

The concept of contact angle and its equilibrium is important because it defines the notion of wettability and specifies the surface parameters needing measurement (7). A liquid wets a surface completely and spreads over the surface at a rate determined by the liquid viscosity, surface roughness, and the magnitude of the free energy change when the contact angle is 0°. A liquid is nonspreading when the contact angle is greater than 0°; the contact angle cannot equal 180° since this would imply no intermolecular forces of attraction between the liquid and the solid.

Although the wettability of a surface may be estimated by a simple contact angle measurement, the prediction of wettability for a real surface is complicated. Many apparently smooth surfaces have cracks, fissures, and other irregularities. The roughness and energy of a real surface varies from point to point, and this heterogeneity makes the prediction and interpretation of the contact angle very difficult.

Modifications of Equation (1) to make it more applicable to real surfaces were made by Wenzel (28), who inserted a surface roughness factor, and Cassie and Baxter (29,30), who considered the influence of porosity of the solid surface on the contact angle. The contact angle was expressed by a linear combination of the solid-liquid and the liquid-vapor surface energies.

$$\cos \theta_A = \frac{f_1(\gamma_{s_1v} - \gamma_{s_1l})}{\gamma_{lv}} + \frac{f_2(\gamma_{s_2v} - \gamma_{s_2l})}{\gamma_{lv}} \qquad (5)$$

Cos θ_A is the apparent advancing contact angle; f_1 is the roughness factor, the ratio of the actual surface area to the geometric surface area; and f_2 is the porosity factor, the pore cross-sectional area divided by the geometric surface area. The second term on the right-hand side of the equation corresponds to the liquid-vapor (pore) interactions. The pores have no solid surface

area, hence γ_{s_2v} is equal to zero, and by the same reasoning, γ_{s_2l} is equal to γ_{lv}. The equation thus reduces to the following:

$$\cos \theta_A = f_1 \cdot (\gamma_{sv} - \gamma_{sl})/\gamma_{lv} - f_2 \qquad (6)$$

For a perfectly smooth solid, $f_1 = 1$ and $f_2 = 0$, and Equation (6) reduces to the Young equation. It is experimentally quite difficult to determine f_1 and f_2 for a solid. However, the general consequences of Equation (6) are important to all research concerning contact angles. The roughness factor can either increase or decrease θ_A, depending on whether the contact angle is obtuse or acute. This is more clearly seen when Equation (6) is put in the following form:

$$\cos \theta_A = f_1 \cos \theta_o - f_2 \qquad (7)$$

If θ_o (the real contact angle) is acute, surface roughness will always make the advancing contact angle smaller than the real contact angle, and liquids will spread more on a roughened surface. When θ_o is obtuse, the advancing contact angle is larger than the real contact angle. The porosity factor always increases θ_A, and the f_2 term is the primary cause of the extraordinary repellency of a duck's feathers.

Surfaces with a roughness (R or f_1) equal to 1.0 probably do not exist. The closest approximation to such a surface is freshly split mica or fire-polished glass. Carefully machined or ground surfaces have R values of 1.5 or greater. It has been shown that the effects of roughness are most important for contact angle measurements when θ_o is either small or large ([7]). Table I illustrates a numerical example. This consideration has rarely been given sufficient attention in work requiring the accurate measurement of θ_o.

TABLE I

THE EFFECT OF SURFACE ROUGHNESS ON THE CONTACT ANGLE

Real Contact Angle (θ_o)	Real Contact Angle (θ_o) Minus the Advancing Contact Angle (θ_A), $\theta_o - \theta_A$
15°	5° when $\underline{R}^a$ = 1.02
50°	5° when $\underline{R}$ = 1.1
85°	5° when $\underline{R}$ = 2.0

[a]$\underline{R}$ is the surface roughness.

The contact angle has been shown to vary with the angle the roughness makes with the plane of the surface, but it is independent of the height of the deformities on the surface (31,32).

It can be seen from the preceding discussion that the wettability of a solid depends primarily on the atomic groups which constitute the surface of that solid. If the groups of atoms of the solid surface change during the wetting process, the wettability of the solid also changes. Roughness and porosity complicate all of the above considerations and in some cases may be more important than the identity of the atomic groups in determining wetting behavior. Roughness and porosity are closely related terms as far as wetting is concerned since a liquid drop may not distinguish between surface asperities and pores.

THE CONTACT ANGLE — ITS SIGNIFICANCE AND MEASUREMENT

Since Young's proposal of the conceptually simple contact angle 170 years ago, its experimental determination has been widely practiced. Unfortunately, accurate measurement of the contact angle is not an easy task. Reproducibility requires scrupulously clean experimental conditions and meticulous surface preparation.

Probably the most difficult experimental aspect of the contact angle measurement is the existence of a hysteresis between a liquid advancing over a dry surface (larger contact angle) and the liquid receding from a previously wetted surface (smaller contact angle) (33). An extensive treatment of contact angle hysteresis has been given by Dettre and Johnson (34-37). They concluded that surface roughness has only a secondary effect on contact angle hysteresis and that it is caused primarily by surface areas of different intrinsic wettability or surface energy. Other authors have attributed hysteresis to differences in surface energy (38), penetration of the liquid into the solid surface (39), formation of an adsorbed layer from the liquid or liquids used (40), and the molecular cross-sectional area of the contact angle liquid (41). The latter postulate suggests that hysteresis will occur when the molecular cross-sectional area of the drop liquid is smaller than the pore size of the substrate. Timmons and Zisman (41) supported their theory by demonstrating that if a large enough molecule is used for the contact angle measurement, hysteresis is eliminated. Since the water molecule is quite small, hysteresis can be expected in most systems using water as the drop liquid.

A change in the contact angle (θ_o) can occur only by changing the individual and interfacial free energies involved. The means by which these quantities can be altered are numerous. Some of the considerations encountered in making contact angle measurements are: adsorption at any phase boundary, heterogeneity of the surface structure, reaction between phases, surface roughness and porosity, velocity of movement of the liquid over the solid, method of bringing the phases into contact, and vaporization from the liquid phase (42). While this list may give a pessimistic view concerning the significance of the contact angle, it certainly does not rule out the contact angle for systems where the conditions are carefully controlled or where comparative results

are desired. Contact angles of low energy homogeneous solids, where adsorption

of moisture and impurities is insignificant, are quite reproducible with a

confidence interval of ±2° being common.

The effect of drop size of the contact angle measuring liquid has been

studied by several workers. Herzberg and Marian (43) found that the water-

polymethylmethacrylate-air contact angle was not dependent on the size of

the sessile drop as the drop size was increased from 0.1 to 20 μl. Tamai and

Aratani (32) reported no variation in the mercury-glass contact angle for drops

ranging from 0.1 to 2.0 μl. When contact angles are calculated using geometric

dimensions of the drop, Mack (44) stated that the formula is applicable only

for small hemispherical drops (less than 1.0 mm in diameter) which are not

distorted by gravitational effects.

Due to the difficulty of holding other variables constant, the temperature

dependence of contact angles has been difficult to determine. The work that

has been done has resulted in conflicting conclusions. Neumann, et al. (45)

and Petke and Ray (5) found that the advancing contact angle has a negative

coefficient of ca. 0.1°/°C. Adam and Elliot (47) found no detectable variation

in the water contact angle on various solid hydrocarbons between 20 and 35°C.

Only Johnson and Dettre (48) have investigated temperatures sufficiently high

that advancing sessile drops of a liquid which had not spread at lower tempera-

tures began to exhibit spreading at higher temperatures.

Despite the inherent and procedural difficulties associated with the

measurement of contact angles, the contact angle has been successfully applied

to studies dealing with changes in the surface of solid substrates. Conveniently,

most of the problems involved in determining real contact angles cancel when a

relative angle is required. Zisman and Ellison (49) have shown that the contact

angle varies smoothly and predictably with the chemical composition of an organic substrate that is altered by substituting fluorine and chlorine for hydrogen. Contact angles have been shown to be sensitive to molecular packing (50), surface morphology (51), and chemical constitution (52). The preceding examples give an indication of the sensitivity and utility of the relative contact angle measurement. The contact angle is a good indicator of wettability and has been shown to be of great value in many studies, especially where only a relative angle was required.

FATTY ACID ADSORPTION

The adsorption of fatty acids onto various surfaces has received much attention in the literature. These adsorption studies involved adsorption from solution, while little attention has been given to vapor phase adsorption of long chain fatty acids.

Langmuir (53) suggested that the most likely configuration of adsorbed fatty acid molecules in a monolayer occurs when the hydrocarbon chains are in contact and directed normal to the solid surface. Since the cross-sectional area of the carboxylic group is somewhat greater than that of the hydrocarbon chain, the implication is that the molecules must tilt toward one another forming clumps of molecules which have been likened to corn shocks. Electron diffraction studies by Bigelow and Brockway (54) show an increasing average tilt of the molecules relative to the surface normal with decreasing length of the molecules, however, no apparent change in tilt occurred with variations in surface concentration. The tilt increased from ca. 2° for behenic acid to ca. 8° for myristic acid.

Brockway and Jones (55) observed a linear relation between the degree of coverage of a physisorbed fatty acid monolayer on a glass surface and the contact

angle. They found that adsorption occurred by the growth of patches or two-dimensional micelles of associated fatty acid molecules. Shafrin and Zisman (56) derived the following relation between the percentage coverage and the cosines of the contact angles for depleted monolayers:

$$X = (\cos \theta_p - \cos \theta_b)/(\cos \theta_c - \cos \theta_b) \qquad (8)$$

where $\underline{X}$ = the percentage coverage

$\cos \theta_p$ = the cosine of the contact angle of the partial monolayer

$\cos \theta_b$ = the cosine of the contact angle of the bare substrate

$\cos \theta_c$ = the cosine of the contact angle of the complete monolayer

Bartell and Ruch (39) depleted n-octadecylamine monolayers from platinum with boiling benzene and found that the contact angle remained constant until half of the monolayer had been removed. The contact angle then dropped off gradually to zero as the remainder of the monolayer was depleted. This was later explained by the same authors as a case in which the liquid used for the contact angle measurement (n-hexadecane) filled in the depleted areas. This process produced essentially a complete film at the higher fractional monolayer coverages (57).

The amphipathic fatty acid molecules are the most widely studied monolayer substituents. These types of molecules adsorb in such a manner that an outer surface with the lowest free energy is produced. The high energy polar end will adsorb at the solid surface while the low energy methyl group will project outward from the surface. As follows from Langmuir's findings, the low energy hydrophobic chain will determine the surface properties of the solid covered with a monolayer (58).

The interpretation of the wetting behavior of solids containing adsorbed amphipathic molecules is confounded by two important characteristics. First, it has been reported that the polar end of a physisorbed molecule will remain at the solid surface until a polar liquid is placed on the surface for the contact angle measurement, then the amphipathic molecule can overturn and reveal its polar end to the wetting liquid (59). The result is a decrease in contact angle which is dependent upon the number of overturned molecules (60). Yiannos (61) showed that 50% of a top molecular layer of a long-chain fatty acid will overturn when exposed to a water drop. The occurrence of molecular overturning has been used to explain time dependent contact angles on solids containing physisorbed fatty acids. The preceding observations present a simplified picture concerning molecular overturning. These physisorbed surface molecules actually comprise a dynamic situation in which evaporation, condensation, vibration, etc., are occurring. Molecular overturning is a response to an applied stress (the presence of a polar liquid) so that the effects of that stress are reduced (the equilibrium is shifted so that statistically the polar end of the amphipathic molecule is much more likely to be adjacent to the polar liquid).

The second important confounding factor concerning the wettability of solids involves the ability of amphipathic molecules to chemically bond with the substrate. Chemisorption, accompanied by a high heat of adsorption, has been distinguished from the process of physical adsorption. Physisorption pertains to condensation and other related physical processes. Various fatty acids on numerous substrates have shown evidence of chemical bonding. Most of the evidence is based on the observation that part of the adsorbed monolayer can be easily desorbed while the remainder can only be removed by quite harsh treatment (62). The difference in severity of treatments is believed to represent the distinction between the energy required to break chemical bonds and that required to disrupt physical interactions.

Contact angle measurements on surfaces containing adsorbed amphipathic molecules must always be interpreted in light of these two characteristics (molecular overturning and chemisorption). The chemically bonded fraction is anchored and therefore unable to overturn while the physisorbed fraction may overturn and hence change the surface energy.

A recent infrared spectroscopy study concerning the physisorption of fatty acids onto metal oxides indicated that fatty acids adsorbed from solution formed a surface layer that was regularly packed and oriented similarly to that of a solid fatty acid ($\underline{63}$). Adsorption from the gas phase occurred as monomers, with these species rapidly dimerizing as the surface concentration increased. This resulted in adsorbed dimers which were deposited randomly over the surface. The interaction between the gas phase adsorbed dimers and the surface was much weaker than the interaction between the surface and fatty acid adsorbed from solution.

Clint ($\underline{64}$) studied the adsorption of $\underline{n}$-alkane vapors (C_5-C_{12}) on Graphon and concluded that the alkanes in the first layer lie flat on the surface.

TREATMENTS RELATING CONTACT ANGLE TO INTERFACIAL TENSION

The contact angle method as a means of measuring the surface energy or surface tension of a solid suffers from the difficulty that $\gamma_{\underline{sv}}$ cannot be expressed as a function of variables which can be experimentally measured. The difference, $\gamma_{\underline{s}}{}^o - \gamma_{\underline{sv}}$, which is the equilibrium film spreading pressure, can be measured by means of adsorption studies. However, it is not possible to experimentally determine $\gamma_{\underline{s}}{}^o$.

Zisman's concept of the critical surface tension of wetting permits ranking solids in terms of a value ($\gamma_{\underline{c}}$) which is related to the solid surface energy. In addition several other semiempirical treatments relating contact angles to

interfacial tensions have been developed. Girifalco and Good (15,65,66) advocated the use of a geometric-mean relationship to describe the system of combined molecular forces acting across an interface. Assuming that the two phases are immiscible, have the same molecular volume, and interact through Van der Waals forces whose constants obey the geometric-mean law, they proposed the following relationship:

$$\gamma_{ab} = \gamma_a + \gamma_b - 2\Phi(\gamma_a\gamma_b)^{\frac{1}{2}} \qquad (9)$$

The constant Φ, which is a property of the particular liquid-solid system, can be calculated from the molar volumes of the two substances.

Fowkes (14,67,68) began with the concept that surface and interfacial tensions are manifestations of the intermolecular forces and that the measured tension is comprised of several components due to the several kinds of forces involved. Most of these forces, such as the metallic bond or the hydrogen bond, are a function of specific chemical nature. On the other hand, London dispersion forces exist in all types of matter and always give an attractive force between adjacent atoms or molecules no matter how dissimilar their chemical natures may be (69). The London dispersion forces arise from the interaction of fluctuating electronic dipoles with induced dipoles or other fluctuating electronic dipoles in neighboring atoms or molecules. Since the dispersion forces are not appreciably influenced by other intermolecular forces, the dispersion forces are additive to the other types of intermolecular forces. Thus, the surface tension of water (γ_{H_2O}) can be divided into two parts,

$$\gamma_{H_2O} = \gamma_{H_2O}^d + \gamma_{H_2O}^h \qquad (10)$$

where $\gamma_{H_2O}^d$ is the London dispersion force contribution and $\gamma_{H_2O}^h$ is the hydrogen bond contribution. Similarly, in the case of mercury,

$$\gamma_{Hg} = \gamma_{Hg}^d + \gamma_{Hg}^m \qquad (11)$$

where γ_{Hg}^d and γ_{Hg}^m are the contributions of the dispersion forces and metallic bonds, respectively. Similar equations may be written for other polar liquids.

Fowkes then used the geometric-mean relationship to summarize the interfacial force field at the interface between any two liquids as:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{\frac{1}{2}} \qquad (12)$$

In this equation the subscripts identify liquid 1 and liquid 2.

These treatments assume that the correction due to π_e (the decrease in the solid surface free energy due to adsorption of vapor) is negligible.

The use of the geometric-mean relationship to predict intermolecular forces is based on various assumptions which contribute limitations. Generally the interaction energies due to dispersion forces at an interface can be reliably predicted by the geometric mean of the dispersion force components of the two substances. Combining Equation (1) with Equation (12), where liquid 2 is considered to be a solid, gives

$$\gamma_2 - \gamma_1 \cos \theta = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{\frac{1}{2}} \qquad (13)$$

Rearrangement of Equation (13) leads to a more easily graphed relation.

$$\cos \theta = -1 + 2(\gamma_2^d)^{\frac{1}{2}} (\gamma_1^d)^{\frac{1}{2}}/\gamma_1 \qquad (14)$$

Plotting $\cos \theta$ versus $(\gamma_1^d)^{\frac{1}{2}}/\gamma_1$ gives a straight line with an intercept of -1 and a slope of $2(\gamma_2^d)^{\frac{1}{2}}$. The latter quantity (γ_2^d) is the dispersion force contribution to the surface free energy of the solid. Since the origin is fixed, one contact angle measurement is sufficient to determine γ^d of the solid surface energy when Equation (14) is used. Fowkes reported that $\gamma_{H_2O}^d$ varies with the molecular weight

of the reference n-alkane (70). Since the value is dependent on the probe

liquid, the dispersion component determined by this method is an interfacial

parameter and not a fundamental property.

Owens and Wendt (16) introduced a method for measuring the surface energy

of solids and the contributions of dispersion forces and dipole-hydrogen bonding

forces by generalizing Fowkes' concepts of the interfacial tension. For a

liquid in contact with a smooth solid surface, Equation (12) has the more general

form,

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2(\gamma_s^d \gamma_l^d)^{\frac{1}{2}} - 2(\gamma_s^h \gamma_l^h)^{\frac{1}{2}} \tag{15}$$

where γ_s^d and γ_l^d are the parts of the surface energies of the designated phase

resulting from London dispersion intermolecular forces and γ_s^h and γ_l^h are the

corresponding parts of the surface energy resulting from dipole-hydrogen bond

type forces. When combined with Young's equation, Equation (15) becomes for a

solid-liquid system:

$$\cos \theta = -1 + 2(\gamma_s^d)^{\frac{1}{2}}(\gamma_l^d)^{\frac{1}{2}}/\gamma_{lv} + 2(\gamma_s^h)^{\frac{1}{2}}(\gamma_l^h)^{\frac{1}{2}}/\gamma_{lv} \tag{16}$$

The γ_l^d values have been published for numerous liquids (14). The γ_{lv} values

are present in several handbooks and γ_l^h values can be calculated using Equation

(17).

$$\gamma_{lv} = \gamma_l^d + \gamma_l^h \tag{17}$$

By measuring the contact angle of two different liquids against a solid and

using Equation (16), simultaneous equations are obtained which can be solved

for γ_s^d and γ_s^h. Thus the components of the surface free energy due to various

forces can be approximated, and the sum of these components, as expressed in

Equation (18), which is analogous to Equations (10) and (11), should yield a

reasonable approximation of the total solid surface energy γ_s.

$$\gamma_s = \gamma_s^d + \gamma_s^h \qquad (18)$$

Another approach to the estimation of the interfacial tension has been given
by Wu (17). He states that when the sizes of the volume elements are nearly
equal, the geometric-mean treatment by Fowkes and by Owens and Wendt is applica-
ble. However, a geometric-mean polar term is not applicable to polar-polar systems.
Wu's equation contains a reciprocal-mean polar term based on empirical grounds
and a reciprocal-mean nonpolar term based on the assumption that the polarizabili-
ties of the interacting elements of the two phases are not too different.

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - \frac{4\,\gamma_s^d\gamma_l^d}{\gamma_s^d + \gamma_l^d} - \frac{4\,\gamma_s^p\gamma_l^p}{\gamma_s^p + \gamma_l^p} \qquad (19)$$

The terms have the same meaning as previously described. When combined with
Equation (1), Equation (19) becomes for a liquid-solid system,

$$\cos\theta = -1 + \frac{4\,\gamma_s^d\gamma_l^d}{(\gamma_s^d + \gamma_l^d)\gamma_{lv}} + \frac{4\,\gamma_s^p\gamma_l^p}{(\gamma_s^p + \gamma_l^p)\gamma_{lv}} \qquad (20)$$

Since the $\gamma_{\underline{l}}^d$, $\gamma_{\underline{l}}^p$, and $\gamma_{\underline{lv}}$ values are known, measurement of the contact angle on
a solid for two different liquids will result in simultaneous equations which can
be solved for $\gamma_{\underline{s}}^d$ and $\gamma_{\underline{s}}^p$ (the dispersion and polar components of the solid). Equa-
tion (20) has been applied to both polar and nonpolar systems of organic polymers
in the molten or solid state, organic liquids, and water.

Other methods attempting to estimate the solid surface energy, which do
not involve the measurement of contact angles, have been described in the litera-
ture and have been reviewed by Adamson (71). Many of these methods are peculiar
to special solids or situations. Examples include heats of solution and relative
values from equilibrium shapes of crystals.

Good (72) and Panzer (73) state that the Fowkes method is useful in providing a reliable measure of the dispersion component of the solid surface free energy for solids of low polarity. However the extension of Fowkes' ideas by Owens and Wendt and Wu to include polar components of the solid surface free energy has resulted in numerous criticisms. One of the most fundamental criticisms concerns the additivity of the interactions of permanent dipoles. Fowkes indicated that permanent dipoles are not additive because adjacent dipoles tend to cancel each other's fields (70). For example, the assumption of equal additivity predicts that dipole-dipole interactions account for 69.5% of the intermolecular forces in acetone (74), while actual measurements by Meyer (75) show that only 14% of the attractive forces in acetone are contributed by dipole-dipole interactions. However, other polar compounds appear to obey the assumption of equal additivity of permanent dipoles. The two-parameter approaches also ignore π_e. If either reference liquid is partially soluble or reacts chemically with the measured substrate, large errors are introduced. The roughness of the substrate has also been neglected. The contact angles of each liquid will be affected by the roughness to a different extent.

Panzer (73) studied a wide range of solids with various liquid pairs and showed that for a given solid widely different γ_s^p and γ_s^d values were obtained that were dependent upon the liquid pair. It appears that semiempirical techniques like those of Owens and Wendt and Wu are capable of determining only those components of the solid surface free energy which are present in the probe liquids. The components of the surface energy as determined by these approaches are not fundamental properties of the surface, but, analogous to γ_c, are interfacial parameters.

CELLULOSE FILM — PROPERTIES AND PREPARATION

Cellulose films are characterized by a smoothness and purity which make them far superior to paper for cellulose surface studies. Surfaces of the finest papers are still fibrous, resulting in larger-scale roughness and porosity which makes contact angle values difficult to interpret. Cellulose films are esentially non-fibrous, and extremely smooth surfaces may be produced from them.

In an extensive electron microscopic study of cellulose films, Jayme and Balser (76) demonstrated that the production technique strongly affected the surface features of the film. A tension-free hand-cast film presented an isotropic surface structure without any preferential orientation. On the other hand, machine-cast films exhibited parallel streaks in the machine direction which had an average width of 100-200 A. The striations were present regardless of the velocity of film casting. The tensile stress and shrinkage during machine casting also produced a highly oriented thin skin or cuticle on the surface.

The conditions under which the films were dried greatly affected the structure and hence the properties of the cellulose film. Slow drying under natural stress provided the smoothest surface, while quick drying under tension resulted in blistery irregularities in the surface.

Stone, et al. (77) employed the technique of solute exclusion to determine a median pore size of 40 A for a previously dried hand-cast cellulose film. The maximum pore size was 165 A for never-dried films and 110 A for dried and reswollen films.

From a surface study viewpoint the most important chemical characteristic of regenerated cellulose is that the free hydroxyl groups are responsible for its chemical behavior. Cellulose reactions are similar to those of alcohols

with esterification, etherification, and oxidation to carboxyl or aldehyde groups common to both.

The importance of obtaining a chemically pure and reproducible film of maximum smoothness indicated that hand-cast films were required. Ferris (78) concluded that the simplest method of cellulose film preparation, the use of copper-based solvents, is excluded due to the introduction of copper ions. The copper ion can react with fatty acids and thus cause serious experimental errors if it is not completely removed from the film. Ferris also rejected a cellulose acetate approach with subsequent saponification of the acetyl groups due to weakness of the film during handling. Casting from cellulose xanthate was found to result in the formation of smooth durable films of negligible metal ion content.

The preparation of cellulose xanthate involves essentially four steps (79): (a) treatment of the cellulose with strong alkali, (b) aging of the alkali cellulose, (c) addition of carbon disulfide to form the xanthate, and (d) ripening to the xanthate solution. The viscose is then cast onto glass plates and the film is regenerated in a coagulating solution.

CONTACT ANGLES ON CELLULOSE FILM

Borgin (80-83) performed an extensive study on the measurement of contact angles on regenerated cellulose film and concluded the following:

1. The change in contact angle with time was considerable. An apparent equilibrium was reached after 10 to 15 minutes. A true equilibrium, corresponding to stable contact angles after a considerable length of time (i.e., from 1 to 24 hours), could only be obtained by using air of 100% RH. The data are shown in Fig. 1.
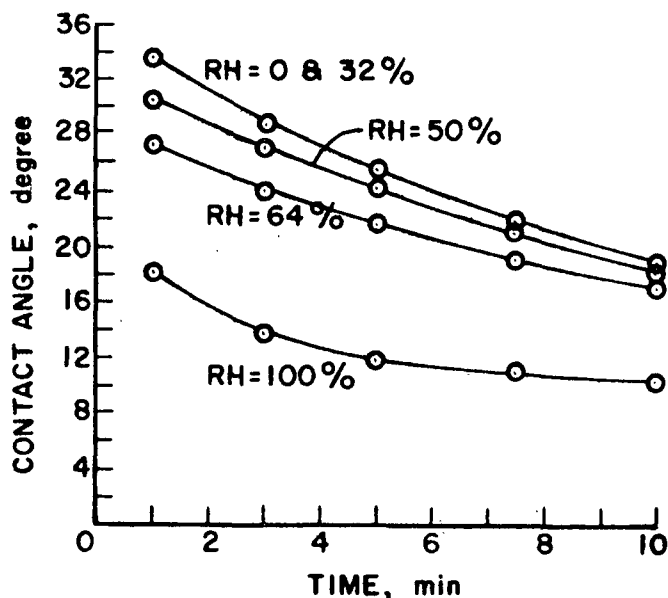
Figure 1. Water-cellulose-air Contact Angle as a
Function of Time (81)

2. At lower relative humidities evaporation had a negligible effect
on the contact angle if the time for measurement was not extended
beyond 30 minutes.

3. The contact angle did not vary with relative humdity up to ca. 40%
RH, after which the contact angle decreased proportionately with
the relative humidity up to 100% (see Fig. 2). The percentage
relative humidity refers to both the cellulose film preconditioning
atmosphere and the contact angle measuring atmosphere. Borgin
interpreted this to mean that the first 12% water taken up is bound
in such a way that it is not reactive or accessible, and therefore
this quantity of water contributes little or nothing to the surface
properties of cellulose. Additional water is adsorbed as layers and
therefore contributes to the surface properties. The minimum contact
angle of 10.2° at 100% RH indicates that the water taken up from the
air never completely covers the surface of the cellulose to such an
extent, or in such a way, that the properties of cellulose are

completely masked. He interpreted this to mean that water must be

taken up only at active sites, resulting in a nonuniform distribution

of water molecules at the surface. The actual concentration of water

on the fiber surfaces is quite low because conditioning cellulose at

higher relative humidities results in swelling and exposure of

additional sorption sites. The result is that the bulk of the sorbed

water is that which is absorbed (penetrated into the cellulose).
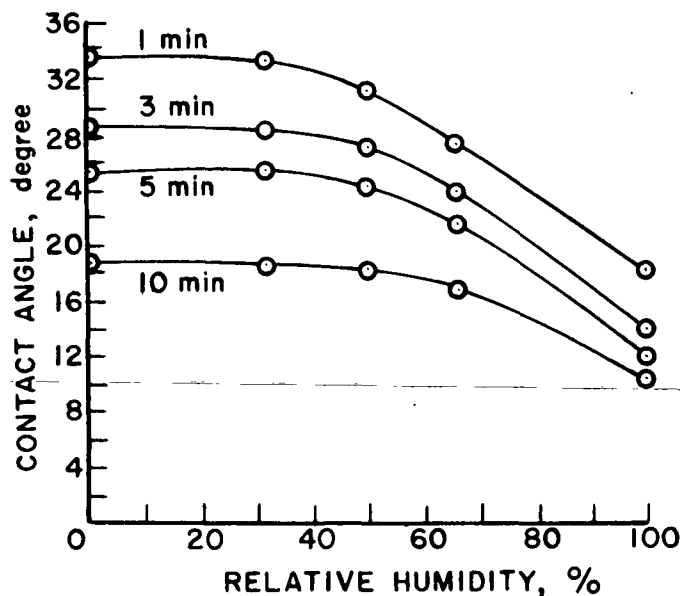
Figure 2. Water-cellulose-air Contact Angle as a
Function of Relative Humidity (81)

4. The contact angle decreased with increased vapor temperature during

the measurement.

5. The cellulose film in equilibrium with 50% RH water vapor contained

ca. 12% water; see Fig. 3.

6. High storage temperatures affected the contact angle of the

cellulose film. A film stored at 110°C showed no effect during

the experiment, but at 140°C the contact angle increased signifi-

cantly (especially at low relative humidity); see Fig. 4.
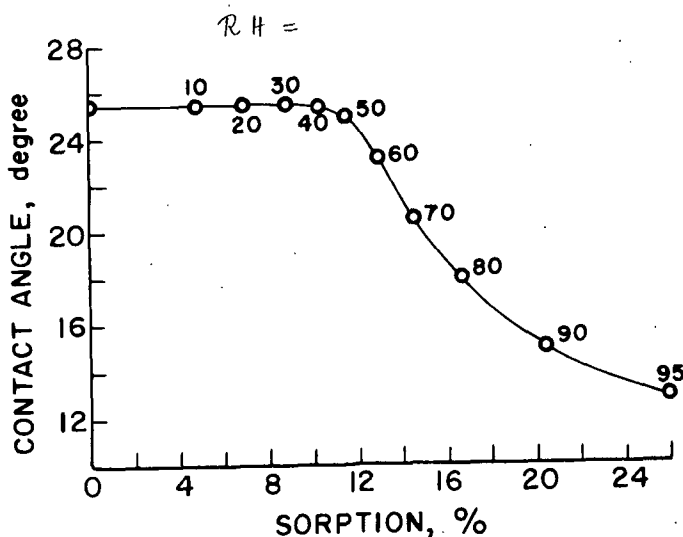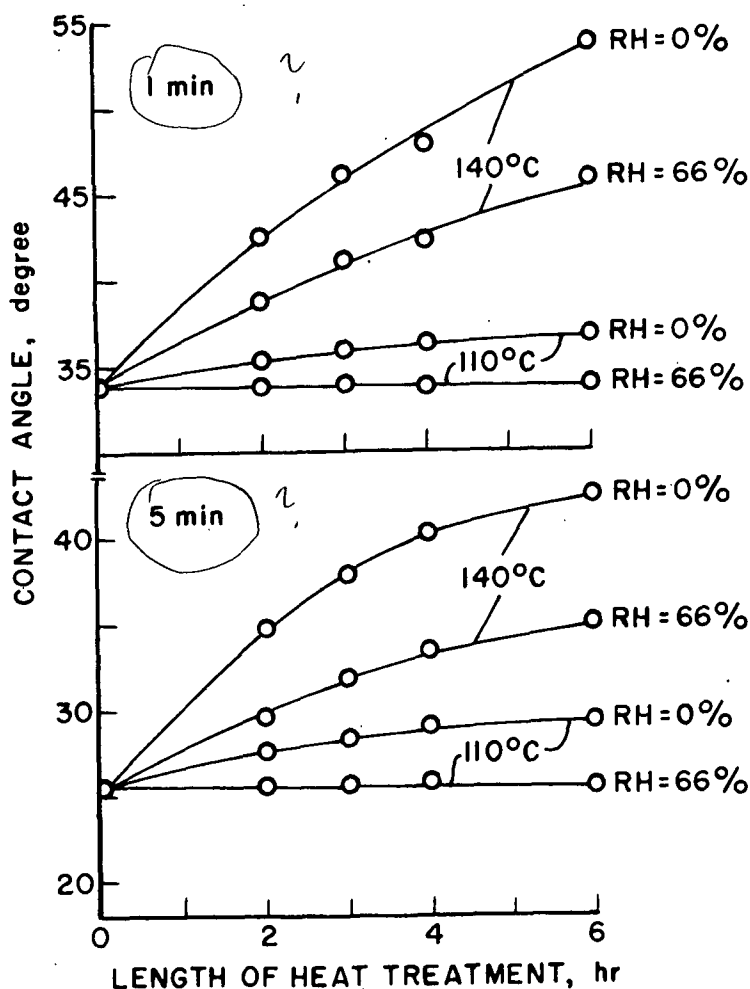
Luner and Sandell ($\underline{13}$) observed a six degree decrease in the initial water contact angle measured first at RH = 2% and then at RH = 32% on a regenerated cellulose film. They also found that the source of cellulose, the method of film preparation, and consequently the physical state of the cellulose surface influenced the wettability of cellulose films.

PRESENTATION OF THE PROBLEM AND THESIS OBJECTIVES

In a study of vapor phase pitch transfer in paper, Swanson and Cordingly
(11) established that stearic acid vapor can be transferred from the crystalline
state in the temperature range 25-105°C. The rate of vapor phase adsorption of
stearic acid in paper was highly temperature dependent. This was believed to
be due at least partially to the higher acid concentration in the vapor at the
higher temperature. While the vapor phase adsorption of stearic acid produced
considerable sizing, the exposure of paper to the vapors of methyl esters of
fatty acids did not produce sizing. This indicates the importance of anchorage
of the carboxyl group in order to obtain water repellency.

In a related paper Swanson (84) reported that the sizing development of ✗ ωωρωll · !
paper using stearic acid is strongly affected by temperature. A seemingly
surprising development occurred when the stearic acid-treated sheets were ex-
tracted with boiling benzene. Following this benzene extraction the quantity
of acid in the sheet dropped to the equivalent of 6% of a monolayer and the
sheet became totally repellent to water. When these totally repellent sheets
were dipped into dilute caustic, extracted with boiling benzene and dried,
they became fully absorbent. This behavior was interpreted as a removal of
the physisorbed stearic acid molecules with the initial benzene extraction while
the mild caustic treatment saponified the cellulose stearate chemical bond.
These experiments indicated that very small amounts (6% of a monolayer) of
properly distributed and anchored sizing compounds are sufficient to produce
a water repellent sheet.

Ferris (78) verified these findings in an investigation concerning vapor
phase adsorption of stearic acid onto cellulose film. The relatively smooth
cellulose film permits accurate measurement of contact angles and thus the

subsequent calculation of surface energy parameters. He found that adsorption of stearic acid from the vapor phase onto cellulose film decreases the wettability of that film in a predictable manner, and that chemically bonded molecules are primarily responsible for the contact angle increase.

Swanson ($\underline{84}$) also observed that the longer chain fatty acids appear to develop sizing more efficiently under the conditions studied. The order of efficiency of size production was: behenic (C_{22}) > arachidic (C_{20}) > stearic (C_{18}) > palmitic (C_{16}). These results indicated that relatively small differences in the molecular structure of the sizing molecule can be quite important when sizing is developed in a sheet of paper with a small fraction of a monolayer of sizing material. In conjunction with this are several statements in the scientific literature similar to the following: "One aspect of surface chemistry which has not received adequate attention is the way in which fractional surface coverage affects the contact angle" ($\underline{101}$).

The primary objectives of this work are to determine an understanding and the conceptual foundations of the following relationships:

1. How does fractional surface coverage of vapor phase chemisorbed fatty acids affect the wettability of cellulose film?

2. What effect do variations in the molecular chain length and branching of the chemisorbed fatty acids have on the wettability of the cellulose film?

EXPERIMENTAL APPROACH TO THE PROBLEM

The substrate chosen for this surface chemical study was hand-cast cellulose film. Cellulose films can be prepared with a characteristic smoothness and purity which make them far superior to paper for surface studies. Since cellulose is a relatively low-energy solid surface (less than 100 ergs/cm^2), contamination resulting from extraneous adsorption should be at a minimum.

The two major measurements required in this study are wettability and amount of adsorption. Wettability is best monitored using contact angle measurements, and only radioactive methods are sensitive enough to determine the quantity of molecules present in fractional monolayer concentration.

Fatty acids exhibit the desirable properties of a sizing agent, that is, they have a high-energy polar end and an extended low-energy nonpolar tail. The fatty acids were carefully selected in order to allow both an understanding of the influence of molecular structure of fatty acids present in fractional monolayer concentrations on the wettability of cellulose film and the development of concepts to explain the observed behavior. Stearic acid (straight chain, 18 carbon atoms) was chosen as the standard adsorbate because it is the most widely studied fatty acid. Behenic acid (straight chain, 22 carbon atoms) was used to investigate differences due to chain length, and isostearic acid (isopropyl group at the hydrophobic end, 18 carbon atoms) to investigate variations due to carbon chain branching. The three acids have similar vapor pressures, thus the same adsorption conditions could be used to study all three adsorbates. In addition the three acids are similar enough to chemical composition and molecular chain length that the chemisorbed molecules should all present the same types of atoms to a contact angle liquid and have similar molecular orientations.

The experimental approach consisted of adsorbing a radioactive fatty acid onto the surface of a smooth cellulose film, measuring the quantity adsorbed, and then determining the concurrent change in wettability by measuring the water contact angle. The particular adsorption appratus and conditions are dependent upon the type of data desired. Since the scope of this study did not include the kinetics and thermodynamics of adsorption, a simple infinite reservoir system was chosen. The variables in the adsorption process are limited to time and temperature at saturation.

The influence of chemisorption on the surface energy parameter was followed by measuring contact angles with two liquids, water and methylene iodide, which differ in surface tension and polarity.

EXPERIMENTAL

MATERIALS

REAGENT PURIFICATION

General

All chemicals used throughout this work were reagent grade and commercially available unless otherwise noted.

Water

The water used in every experimental process was deionized and triply distilled. The first step was deionization through a mixed-bed ion-exchange resin column followed by distillation using a Corning AG1 glass still. Then, following the procedure of Bauer and Lewin (85), distillation took place from a solution of 0.02% potassium permanganate and 0.05% sodium hydroxide, followed by another distillation into clean containers. This procedure removed residual organic matter, especially the nitrogenous material arising from the ion-exchange resins (86,87). The final stage avoided the addition of acid in order to minimize inorganic contamination. The last two distillations were performed using an Ace glass still. The conductivity was monitored and only water having a specific conductivity less than 1.1×10^{-6} mho/cm was accepted. Approximately 30 liters of this water could be produced per day.

Surface tension measurement of the resultant triply distilled water using a Cenco-duNuoy Interfacial Tensiometer Model 10403 gave a surface tension of 72.81 dynes/cm at 21°C. The literature value is 72.80 dynes/cm (14).

Methanol (88)

Methanol (1000 ml) was added slowly to a mixture of iodine (0.5 g) and magnesium turnings (5 g) in a 2000 ml round-bottom flask immersed in an ice

bath. After the reaction subsided, the mixture was refluxed with the exclusion of moisture for 3 hours. The methanol was then fractionally distilled (40 cm Vigreaux column) into bottles which had been previously cleaned, dried, and rinsed with fresh distillate. The middle 500 ml of the distillate was retained.

This carefully dried methanol was used to prepare sodium methoxide-methanol solutions.

Benzene (89)

Thiophene free benzene (700 ml) and absolute ethanol (350 ml) were mixed together and distilled. The low-boiling benzene-ethanol azeotrope was collected. The low-boiling distillation leaves any nonazeotrope-forming impurities behind. The distillate was separated into three fractions and each fraction was washed three times with triply distilled water (3 x 400 ml). The fractions were combined and dried over anhydrous calcium chloride, refluxed over lithium aluminum anhydride (2 g) overnight, and then distilled from lithium aluminum anhydride. The middle fraction was retained and placed in previously cleaned and dried containers.

This carefully purified benzene was used for preparing radioactively labeled and unlabeled fatty acid solutions.

Methylene Iodide

Eastman diiodomethane was passed through a column of alternating layers of silica gel and activated alumina until colorless, then vacuum distilled using a Nester/Faust Teflon spinning-band distillation column. Following distillation the methylene iodide was stored in a tightly stoppered glass bottle that was covered with aluminum foil to exclude light.

The surface tension measured with the Cenco-duNuoy Interfacial Tensiometer Model 10403 was 50.68 dynes/cm. The literature value is 50.8 dynes/cm (16).

Stearic Acid

Stearic-1-^{14}C acid was purchased by Ferris (78) from Dhom Products, Ltd. The labeled acid has a specific activity of 58 millicuries per millimole (mCi/mM). Gas-liquid chromatography (GLC) compositional analysis indicated 99.90% stearic acid and 0.10% palmitic acid (Appendix I).

Nonradioactive stearic acid purchased by Neuman (90) from the Fluka Company was used for dilution. GLC analysis indicated 99.64% stearic acid and 0.28% palmitic acid (Appendix I).

Behenic Acid

Behenic-1-^{14}C acid was purchased from Dhom Products, Ltd. The specific activity was 58 mCi/mM and GLC compositional analysis indicated 98.35% behenic acid, 0.41% arachidic acid, and 0.73% lignoceric acid (Appendix I).

Nonradioactive behenic acid used for dilution was purchased from the Fluka Company; GLC analysis indicated 99.22% behenic acid and 0.74% lignoceric acid (Appendix I).

Isostearic Acid (16-Methylheptadecanoic Acid)

Isostearic-1-^{14}C acid was purchased from Dhom Products, Ltd. The specific activity was 58 mCi/mM, and GLC compositional analysis indicated 99.76% isostearic acid and 0.24% isopalmitic acid (Appendix I).

Nonradioactive isostearic acid was purchased from Analabs, Inc.; GLC analysis indicated 99.9% isostearic acid (Appendix I).

EQUIPMENT

ADSORPTION APPARATUS

Vapor phase adsorption of the fatty acids onto cellulose film was performed in the adsorption apparatus shown in Fig. 5. Two 4 by 8-inch stainless steel
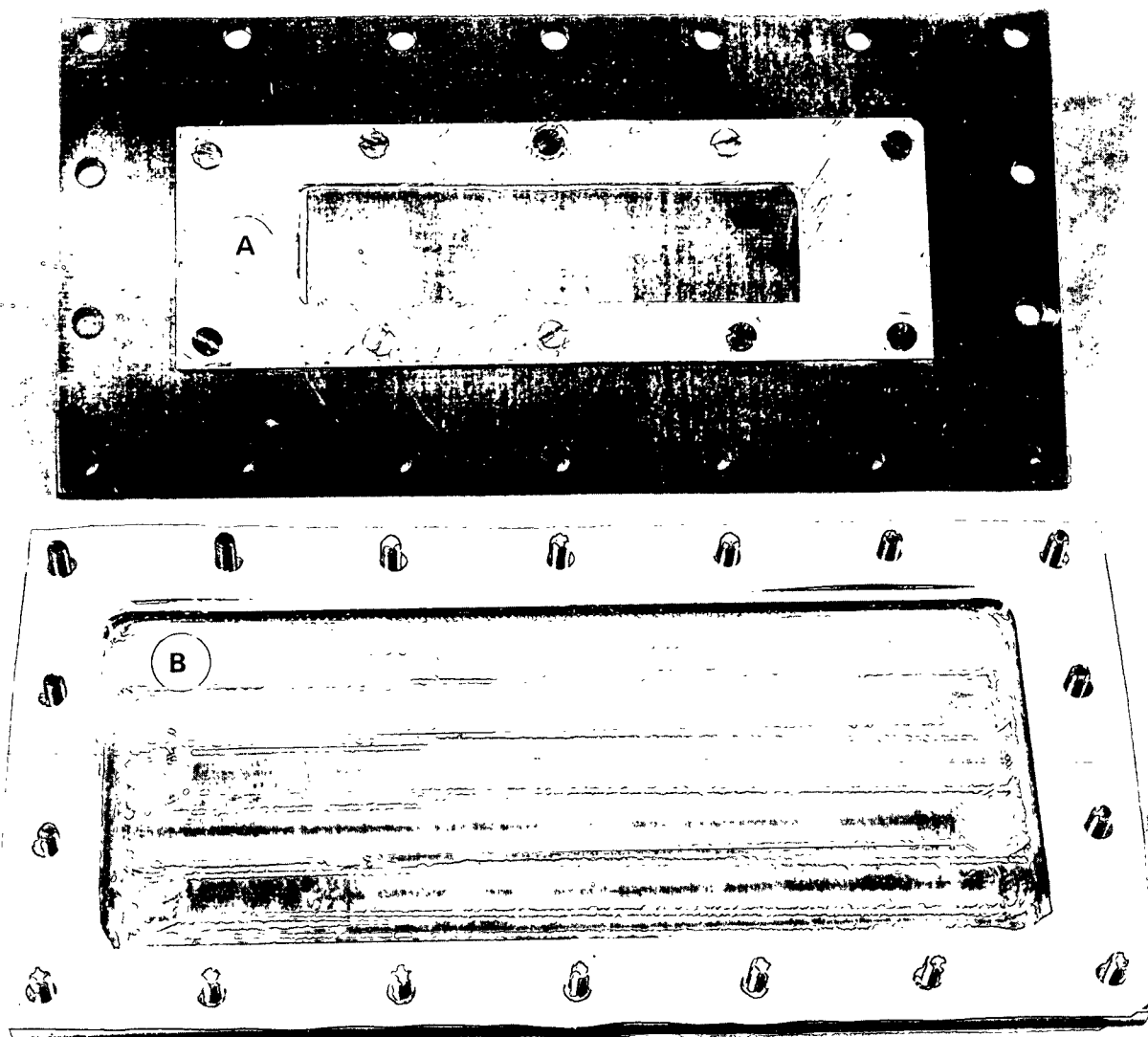
Figure 5. Stainless Steel Adsorption Apparatus; A, Tray Top with Centered
Clamp Holding Film; B, Bottom of Tray with Fatty Acid Bed

plates form the body of the adsorption tray. The bottom 1/4-inch thick plate

was machined to 1/8-inch thickness in the center 3 by 7-inch area. The fatty

acids were placed in this portion of the tray, which served as an infinite

reservoir for the fatty acid in the vapor phase. The top of the tray was 1/8-

inch thick and contained 10 threaded holes which held a 1.5 by 5.0-inch aluminum

clamp and Teflon gasket. The cellulose film was clamped against the top stainless

plate using the aluminum-Teflon assembly. A 1 by 4-inch area of the cellulose film was exposed to the fatty acid vapor. The two halves of the adsorption tray were clamped together using 18 wing nuts and a Teflon seal. The geometry of the adsorption tray allowed the cellulose film to be supported 1/8-inch above the fatty acid bed.

The top and bottom stainless steel required uniform and identical thickness in order to obtain an even distribution of fatty acid on the cellulose film after cooling. Uneven cooling of the adsorption tray has been found to cause the fatty acid either to condense onto or desorb from the cellulose film (78).

RADIOACTIVITY COUNTER

A Nuclear-Chicago Model 182 scaler connected to a Model D-47 gas flow detector was used to count the beta particles. The scaler was operated in the beta proportional mode with the "Micromil" window in place. Proportional "PR-gas" (90% argon + 10% methane) was passed through the chamber at 50 cc/minute. A constant and uniform background count was observed in all work. An operating voltage of 2100 volts was determined (Appendix II). The counting rate obtained in this work was ca. 10% of the maximum which the instrument could detect, thus the range of the counting instrumentation was not exceeded.

The counting efficiencies of the fatty acids on the smooth side of cellulose film, based on quantitative transfer techniques, were determined. The counting efficiency is defined as the ratio of the number of counts the system will detect to the total number of particles emitted from the source. The counting efficiency for stearic acid was 19.2%; behenic acid, 19.4%; and isostearic acid, 18.9% (Appendix III).

CONTACT ANGLE MEASURING APPARATUS

The contact angle measuring system consisted of a basic contact angle goniometer equipped with a variable relative humidity gas purge system (13) and a 35-mm camera. The entire apparatus is shown in Fig. 6.

The wet stream (B), produced by passing prepurified nitrogen through three gas washing bottles containing triply distilled water, is mixed with the dry stream of prepurified nitrogen (C) at the entrance of the contact angle chamber (G). The relative humidity is measured with an Aminco Electric Hygrometer equipped with a remote calibrated probe and is indicated on the meter of the hygrometer (A). A high intensity light bulb and copper sulfate filter (D) provide illumination for the 35-mm Minolta SR-M rapid advancing camera (H). The camera is capable of automatically taking from three frames per second to one per minute and is attached to the goniometer microscope with a 5X magnifying eyepiece. A lab jack (E) smoothly and steadily lowers an ultramicropipet (F) in order to place the contact angle liquid drops.

A more detailed view of the contact angle chamber is presented in Fig. 7. The gas streams enter at (A) and exit through an opening at (D). The hygrometer probe, thermometer, and sample positioning rod extend into the chamber through a rubber stopper at this position. The ultramicropipet (B) passes through a opening at the top of the chamber. A thin rubber seal prevents gas leaks from this opening. Samples mounted on microscope slides are placed on a Lucite platform at (C). The entire chamber can be moved in x, y, and z directions using the corresponding knobs (E).

-43-
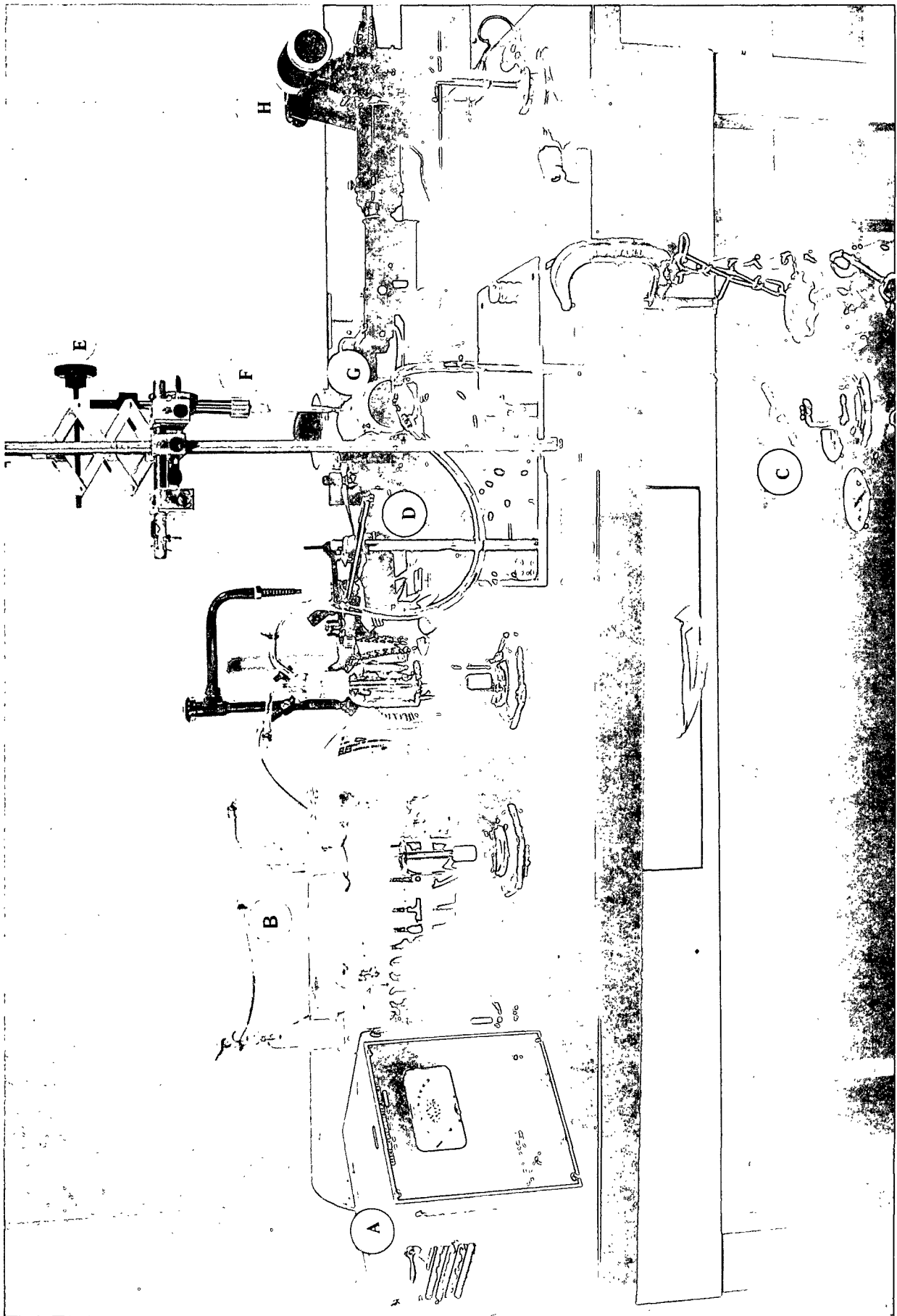
Figure 6. Contact Angle Measuring Apparatus
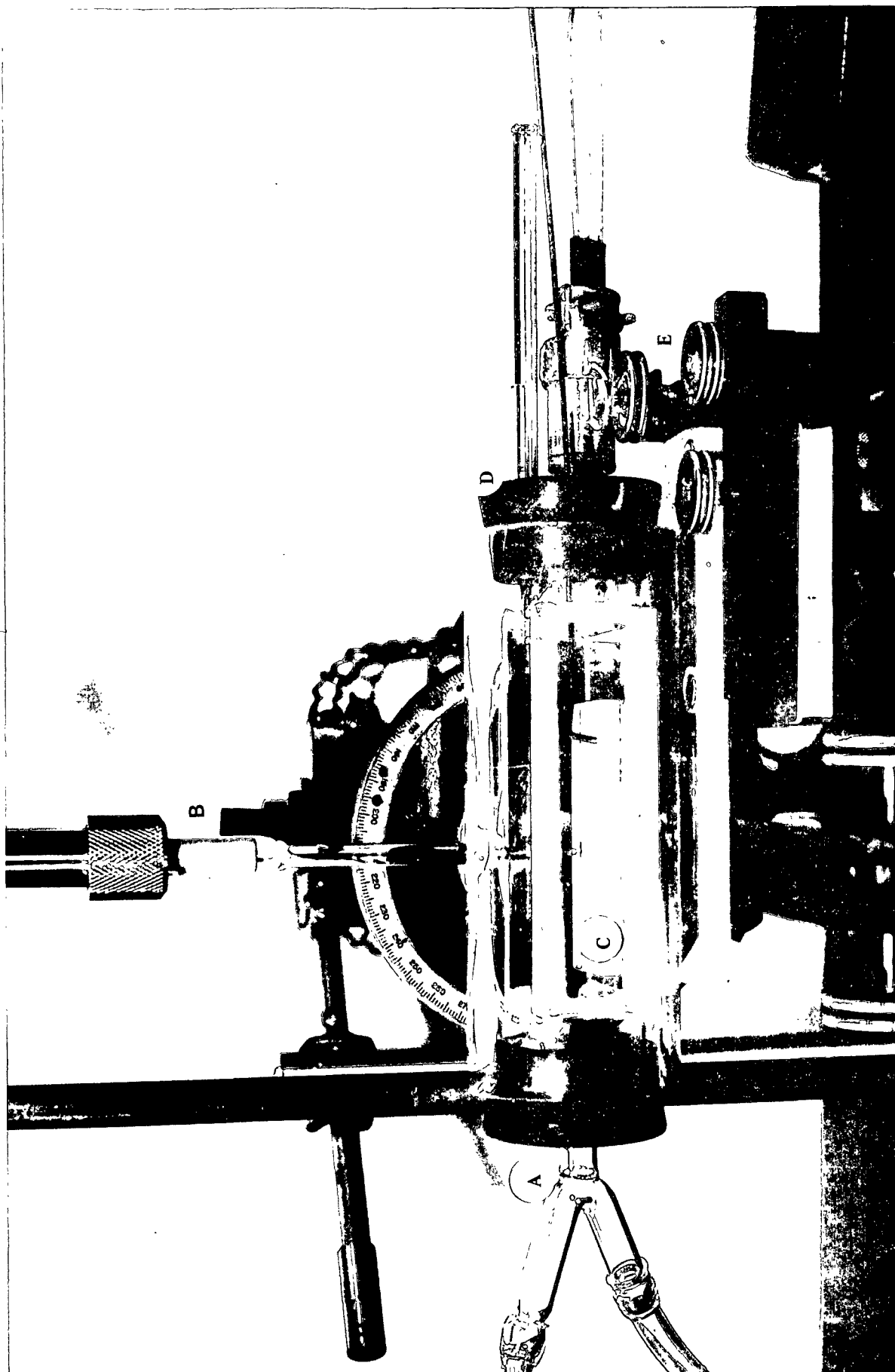
Figure 7. Close-up View of the Contact Angle Chamber

GLASSWARE

All glassware was cleaned with a hot saturated solution of sodium dichromate in concentrated sulfuric acid. This was followed by a thorough rinsing with distilled water and finally with triply distilled water. The glassware was then dried in an oven at 105°C.

MULTIPLE INTERNAL REFLECTION SPECTROSCOPY

Infrared multiple internal reflection (MIR) spectra of the cellulose films were observed using a Perkin-Elmer Model 621 grating spectrophotometer equipped with a Wilk's double beam internal reflection attachment. The attenuated total reflection attachment was designed so that the radiation can be reflected between the plate faces ca. 50 times at a well-defined angle of incidence (91,92). A duplicate set of optics used in the reference beam compensated for atmospheric absorption.

Water present in the ambient atmosphere has been found to reduce the pen response for a given change in transmittance at the absorption frequencies of this material. In order to minimize this problem, the interior of the instrument, including the sample area, was continuously purged with clean dry air.

A 50 by 20 by 1-mm KRS-5 internal reflector plate with a 45° face angle was used. The smooth side of the cellulose film was placed against both sides of the reflection plate and the strong CH bending absorption at 1360 cm^{-1} was adjusted to 80-85% transmittance in all spectra.

ELECTRON MICROSCOPY

Transmission electron microscopy was used to examine the physical structure of the surface of the cellulose films. The cellulose film surface was shadowed

with platinum 10-cm distant at an angle of 30°. Platinum is highly opaque to the electron beam and yields a finer grain when evaporated than do the other heavy metals. Carbon was then vaporized onto the platinum surface to increase the mechanical strength of the system. The cellulose was dissolved with a 72% aqueous solution of sulfuric acid, washed with water, and the replica was placed over a 100-mesh nickel grid. The replicas were examined and photographed using a RCA EMU-3F electron microscope equipped with high-voltage fine focusing.

PROCEDURES

CELLULOSE FILM PREPARATION

Hercules cotton linters served as the source of cellulose. The cellulose was solubilized by converting it into the xanthate derivative according to the method described by Browning (79). The viscose was cast and regenerated according to the two-bath procedure of Luner and Sandell (13).

The cotton linters were continuously extracted in a Soxhlet apparatus for 48 hours with benzene-ethanol (2:1) to remove surface active agents that could produce self-sizing. This was followed with intermittent extractions with triply distilled water over a 12-hour period to remove the benzene-ethanol. Sufficient sodium hydroxide solution was added at room temperature to mercerize the linters for 90 minutes in 18% NaOH at 5% consistency. The mercerized linters were filtered and mechanically pressed until 3.0-3.5 times the original oven dry (o.d.) weight of the linters was obtained. The alkali cellulose was then carefully picked apart and aged for 72 hours at room temperature in a loosely stoppered bottle.

Following the 72-hour aging period, the alkali cellulose was xanthated by adding a quantity of carbon disulfide equal to 75% of the original o.d. fiber weight. Upon addition the container was placed on a rotator for five hours.

After this time the xanthate crumbs were a deep orange-yellow. The product was dissolved by the gradual addition of a caustic solution at room temperature until the mixture contained 7.0% cellulose, 6.0% sodium hydroxide, 5.0-5.5% carbon disulfide, and ca. 82% water. The mixture was rotated until a homogeneous solution was obtained, then the viscose was ripened for 72 hours at 72°F. After the ripening process had proceeded for 24 hours, the solution was ultracentrifuged (Sorval Model RC-1) for 40 minutes at ca. 18,000 g. Following ultracentrifugation the viscose was deaerated and placed in clean containers for the reminder of the ripening period.

Laboratory casting of the viscose into films followed the 72-hour ripening period. The films were cast onto clean dry 3 by 3-inch pyrex glass plates using a 0.012-inch Bird bar. The upper left corner of each film was removed to identify the glass-formed side as the smooth side. The glass plate containing the cast film was placed in a 15% ammonium sulfate solution at room temperature until the film lifted off the plate and decolorized, losing the characteristic orange color of viscose. The film was then transferred with the use of Teflon-tipped forceps to a 12% sulfuric acid bath at room temperature where the cellulose was regenerated. The film, which became opaque white upon contacting the acid, was removed when it had again become transparent. It was then washed in a 1% sodium sulfide-0.25% sodium hydroxide bath at 65°C for ca. 15 minutes. This was followed with a 3-hour soak in 0.25% sodium hydroxide. The films were then repeatedly washed with triply distilled water over a two-day period (ca. 16 washings) and stored in triply distilled water at 4°C. Elemental analysis of the cellulose films can be found in Appendix IV.

CELLULOSE FILM DRYING

A drying procedure was required which minimized contamination of the cellulose film surface. Ferris (78) found that contamination by low molecular weight spreadable (LMWS) material could be a serious problem.

The presence of LMWS material can be detected by passing a piece of the contaminated film perpendicularly through a clean air-water interface onto which was sprinkled ignited talc. The LMWS material spreads on the water, pushing away the talc in an easily observable manner. Ferris (78) found that it was not possible to eliminate this contamination under any circumstances which involved air drying. The LMWS material had to be avoided since this material can spread over the surface of the contact angle liquid, resulting in a lowering of the surface tension of the contact angle liquid and thus a smaller acute contact angle. The following drying procedure resulted in no detectable presence of LMWS material.

A 3 by 8-inch Lucite sheet was cleaned with Alconox in hot water, rinsed in hot water, cleaned with ethanol, and copiously rinsed with triply distilled water. Then, in triply distilled water, a cellulose film was placed smooth side against the cleaned Lucite sheet, and the cellulose film-Lucite was removed from the water. A clean Lucite frame of the same size with a center 1.5 by 4.5-inch rectangle removed was placed over the film and four large Bulldog clips were used to hold the sandwich together. This sandwich was then slowly lowered into a Lucite cylinder (7-inch diameter by 14-inch height) filled with triply distilled water. The cylinder was overflowed with water, flushing away any LMWS material which would have transferred to the water surface. The top of the cylinder was then sealed against an "O" ring and bolted on. Prepurified nitrogen was blown into a port at the top of the cylinder and the water was quickly

removed through the bottom. The film was dried in this chamber for 12 hours with an automatic purging device flowing prepurified nitrogen through the chamber five out of every thirty minutes. The film was then transferred to a 32% RH desiccator ($MgCl_2 \cdot 6H_2O$ saturated salt solution) for 24 hours. The cellulose film was removed from the Lucite by cutting around the edges with a razor blade. The cellulose film snapped off the Lucite and upon inverting the film the clean smooth surface was exposed.

Aluminum pellets were degreased by heating to 500°C, resulting in the formation of an oxide layer on the aluminum. This aluminum shot was used in the desiccators in order to adsorb organic contaminants (93).

OPTIMIZATION OF CELLULOSE FILM SMOOTHNESS

Modification of the film, either chemically or using irradiation, was considered to be detrimental to the goal of producing a smooth pure cellulosic surface. The smoothness was optimized by experimentally determining the smoothest surfaces against which the viscose could be cast and against which the resultant film could be dried. Smoothness of the cellulose films was evaluated by comparing electron micrographs of surface replicas.

The smoothest surface suitable for film casting was hard (pyrex) glass. Electron micrographs indicated that this surface was much smoother than soft (plate) glass. Although a freshly cleaved mica surface was smoother than the pyrex glass surface, films cast onto the mica surface could not subsequently be separated from the mica. Prior to viscose film casting, the hard glass plates were washed with Alconox in hot water, rinsed with triply distilled water, oven dried, and cooled to room temperature.

Drying the film against either hard or soft glass resulted in such strong

adhesion that the film could not be removed from the glass. Drying against

freshly cleaved mica gave the same result. Lucite proved to be the most suit-

able surface against which to dry the films. The Lucite was carefully scrubbed

with Alconox in hot water using a cotton swab, rinsed in hot water, scrubbed with

ethanol using a cotton swab, and thoroughly rinsed with triply distilled water.

Great precautions were taken so that the Lucite surface was not scratched.

An electron micrograph (22,700X) of the dried film surface is shown in

Fig. 8. Also included are electron micrographs at the same magnification of sur-

faces of freshly split mica, whose surface has a roughness value of approxi-

mately 1.0 (94), pyrex glass, and Lucite.
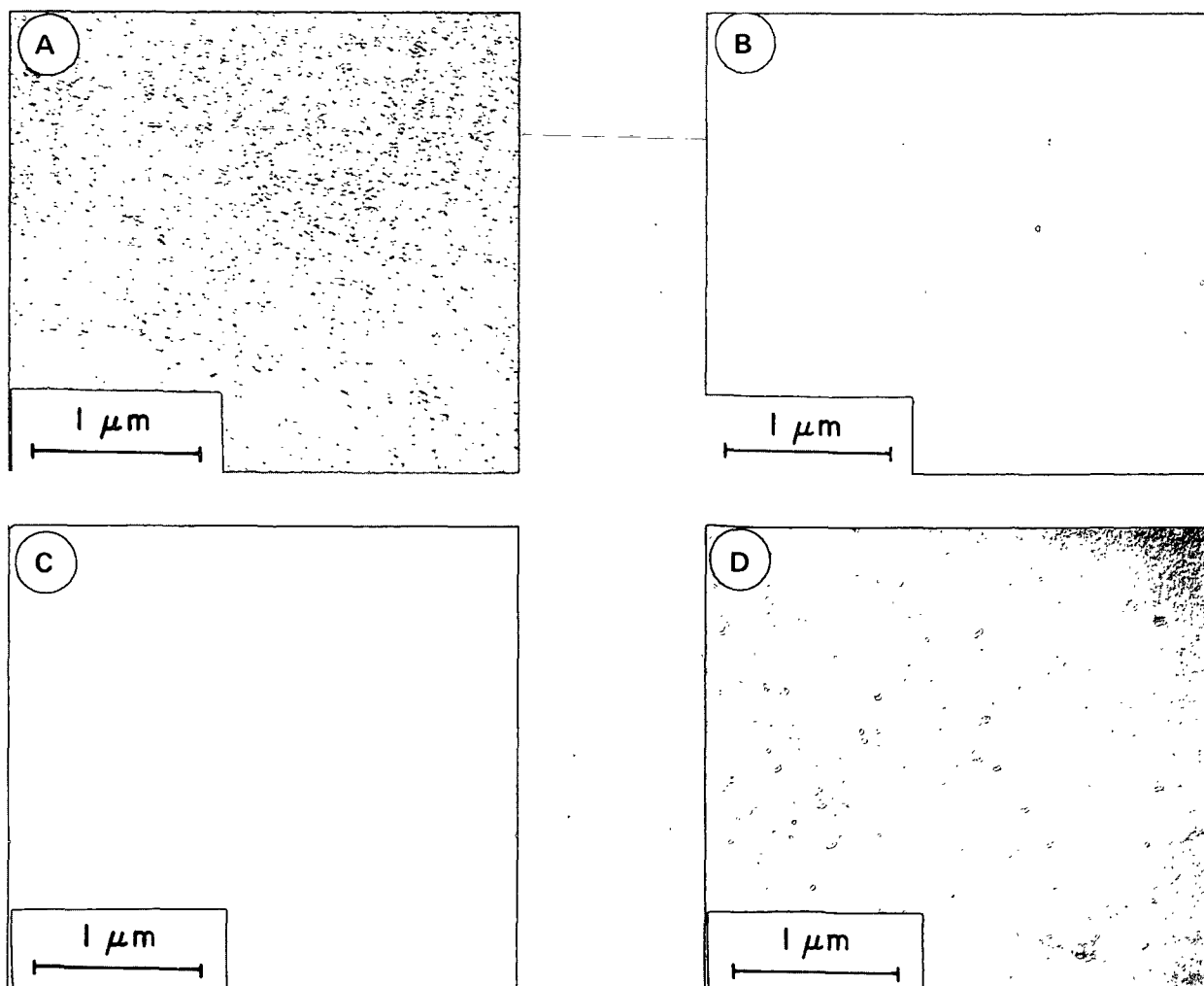
Figure 8. Electron Micrographs of: A, Dried Cellulose Film Surface; B, Freshly
Cleaved Mica; C, Pyrex Glass; D, Lucite; 22,700X

Lowering the degree of polymerization (DP) of the cellulose source resulted in weak films which tore during normal handling. Also no detectable smoothness increase was noted in films made from the lower DP cellulose source.

ROUGHNESS OF THE CELLULOSE FILM

The determination of the roughness factor of the cellulose film surface would be useful in order to convert the geometric percentage monolayer coverage to a real percentage monolayer coverage. However, the existence of two physical characteristics of the system add large uncertainty to the true monolayer calculations and decrease the value of an accurate knowledge of the roughness factor. The first characteristic is the molecular orientation of the adsorbed fatty acids. As the molecules tilt away from the perpendicular orientation, the projected area per molecule continually increases. The projected area directly affects the monolayer coverage. The second complication is due to the fact that the adsorbed molecules will not be uniformly distributed on the surface. Preferential adsorption will occur at the rough areas of the film, meaning that the molecular concentration measured per unit area is only an average value which includes higher concentrations at the surface asperities.

The roughness factor could also be used for the evaluation of real contact angles as opposed to apparent (measured) contact angles. The use of Wenzel's relationship in order to determine a real contact angle for a surface has been avoided in the literature, and Ferris (78) gives an illustrative example supporting that position.

Finally the data obtained in this study are concerned primarily with similarities and differences among the three acid adsorbates. Since a common surface was used throughout the study, the contributions due to roughness are the same for all three adsorbates.

While the determination of an accurately known roughness factor was not necessary, a relative estimate of it can be helpful for the interpretation of the results. The cellulose films were cast against pyrex glass and dried against Lucite. The surface tension forces evolved during drying should cause the roughness of the relatively conformable cellulose film to approach that of the Lucite surface. Electron micrographs of the respective surfaces indicate that the cellulose film is only slightly rougher than pyrex glass or Lucite (see Fig. 8).

The roughness of glass beads is ca. 1.4-1.5 (5). This can be assumed to be the lower limit for the roughness of the cellulose film used in this study.

FILM AREA MEASUREMENT

Since radioactivity is measured as a count per unit time for a given film area, an accurate method for measuring the area of the cellulose film was required. A noncontact method was needed since contact with any foreign material could contaminate the film and thus affect the following contact angle measurement.

A photographic method met these requirements. A picture of each film piece adjacent to an accurately known area standard of similar dimensions was taken. The Minolta SR-M camera was mounted on a stand and each piece of film was placed alongside the area standard. Since the area standard was used in every picture, knowledge of the magnification factor during the photographic process was not required. Duplicate pictures of each film piece were taken. Kodak Panatomic-X black and white film was used at a 1/15-second shutter speed under normal laboratory lighting conditions at f4.0. The film developing procedure is given in Appendix V.

Five digit coordinates for both the area standard and the cellulose film
were determined from the film negative using the digital x-y coordinate compara-
tor and were punched onto computer cards. The cellulose film area was then
calculated using the computer program FARDET (Appendix VIII).

RADIOACTIVITY MEASUREMENT

The measured radioactivity in counts per minute (cpm) is divided by the
film area in order to give a quantity (cpm/in.^{2}) that can easily be converted
to the convention used in this work — % POML. The convention corresponds to
the percentage Planar Oriented MonoLayer. A 100% POML is the number of acid
molecules contained in a monolayer of fatty acid molecules oriented perpendicularly
to a planar surface. Both stearic acid and behenic acid occupy a cross-sectional
area of 20 A^2 per molecule when participating in a monomolecular surface film
(95,96). A planar monomolecular layer of these acids contains 3.22 x 10^{15} mole-
cules per square inch. Isostearic acid has a cross-sectional area of 32 A^2 per
molecule (97,98) and one monolayer on a planar surface contains 2.01 x 10^{15} mole-
cules per square inch.

The actual monolayer coverage is a function of the roughness factor, R,
and molecular orientation. The actual monolayer coverage can be expressed as
follows:

$$\text{Actual Monolayer Coverage} = \frac{\% \text{ POML}}{R} \times \frac{\text{Effective area/molecule}}{\text{Cross-sectional area/molecule}}$$

Each labeled fatty acid was diluted with sufficient nonlabeled acid so that
10,000 cpm/in.^{2} was equivalent to 100% POML on a completely smooth surface. The
cpm/in.^{2} data can be converted to % POML by dividing by 100. The preparation of
these radioactive solutions is outlined in Appendix VI. The adsorption data in
Appendix IX for isostearic acid was divided by 1.6 so that any given adsorption

level (cpm/in.^{2}) would correspond to the same number of molecules for each of the three acid adsorbates. This was done to facilitate comparison of adsorption quantities among the three fatty acids.

Before each day's use the counter was flushed with PR gas for 30 minutes at a 50 cc/min gas flow rate. The background count was then determined, followed by the counting of a standard C-14 source. The standard was used because the efficiency of electronic counting equipment is subject to small daily changes. The standard source corrects for these small daily variations and makes all the data subject to the same counter efficiency.

All radioactivity counting used in obtaining experimental data involved sufficient counts so that the percentage error during counting was less than 1.8% at the 95% confidence level.

VAPOR PHASE ADSORPTION

The bottom portion of the stainless steel adsorption tray was filled with ca. 200 monolayers of fatty acid. This bed of fatty acid acts as an infinite reservoir in attaining equilibrium with the closed chamber. The fatty acid reservoir was replaced prior to each run in order to minimize the presence of oxidized fatty acids. The vapor volume inside the adsorption cassette holds ca. 33% POML/in.^{2} of fatty acid at 105°C; see Appendix VII. Due to the infinite reservoir, the system is always saturated.

A cellulose film is clamped to the top of the adsorption tray using the aluminum-Teflon clamp. The tray is bolted together and placed in the oven. Adsorption time refers to the time that the sample was in the oven.

CONTACT ANGLE MEASUREMENT

The ultramicropipet containing the appropriate contact angle liquid is placed in position and the nitrogen streams are adjusted to yield a 40% RH atmosphere within the contact angle chamber. A film sample mounted on a microscope slide is removed from the 40% RH desiccator [$Zn(NO_3)_2 \cdot 6H_2O$ saturated salt solution] and placed in the contact angle chamber. The pipet tip is aligned with the front edge of the film. This allows the drop and the cellulose film to be in the same focal plane, resulting in a clear image on the photograph. The pipet is lowered until it is very close to the film and a small hemispherical drop (ca. 0.5 µl) is formed on the pipet tip. The pipet is slowly lowered until the drop contacts the surface, then the pipet is quickly raised until the liquid breaks away from the glass pipet tip, forming a drop. The picture is taken immediately. The preceding operation is observed through the viewfinder of the camera.

An initial advancing contact angle is measured. The contact angle calculated from the first frame picture was found to be only ca. 0.15° lower than a contact angle that was back-extrapolated to zero time when three pictures were taken during the first second. Due to both the relative simplicity and the film savings, the first frame method was used in this work.

Kodak High Contrast black and white film at a shutter speed of 1/60 sec X was used. Three contact angle measurements were taken on each slide. The film developing procedure can be found in Appendix V.

Five digit coordinates were punched onto computer cards using the digital x-y coordinate comparator and the film in negative form. The contact angles are calculated by computer (program CONANG; see Appendix VIII) using Equation (21).

$$\tan\theta/2 = 2H/B \tag{21}$$

$\underline{H}$ is the height of the drop whose width at the base is $\underline{B}$, and θ is the calculated contact angle. A derivative of Equation (21) is given by Guide (<u>99</u>).

Methylene iodide and water were used as the two contact angle liquids. In order to calculate the dispersion and polar components of a solid surface according to the method of Owens-Wendt (<u>16</u>) or Wu (<u>17</u>), at least two contact angles involving liquids of different surface tension and polarity are required. Water was chosen as one liquid because of its fundamental importance in this work. The second liquid was required to have a significant contact angle on cellulose while also having the polar component of its surface tension greatly different than water. Methylene iodide satisfied both of these requirements.

Following the calculation of the contact angles, the numerical values were used as data along with program SEPCAL (see Appendix VIII) to calculate the surface energy parameters.

SIGNIFICANCE OF THE INITIAL CONTACT ANGLE

Cellulose is a hydrophilic material and dry cellulose sorbs aqueous liquids rapidly and extensively. As moisture sorption continues, the character of the cellulose surface changes, with more and more of the surface becoming water-like in nature. The water contact angle on dry cellulose is 34° while cellulose conditioned at <u>ca</u>. 100% RH has a water contact angle of 10.8° (<u>80</u>). The cellulose water interaction is extensive and equilibrium will not be attained until the cellulose-water reaction is complete.

Since the surface properties of cellulose are dependent upon the quantity of sorbed water, either the moisture content of the film or the relative humidity at which the cellulose film was conditioned must be specified. Of equal

importance is the time span between the placement of the water contact angle drop and the actual contact angle measurement. As soon as the water contacts the cellulose surface, the cellulose-water reaction commences and the character of the surface begins changing. Also, water vapor at the perimeter of the drop probably impinges upon the adjacent film and adsorbs. The result is a significant and rapid alteration of the film surface.

Since a true equilibrium contact angle can only be obtained when the cellulose film is conditioned at 100% RH (80), contact angle measurements of cellulose films conditioned at other relative humidities must immediately follow the placement of the drop.

The same principles apply in the more complex case present in this study, that of a heterogeneous surface containing an adsorbed third component. The presence of the water contact angle liquid will alter the surface because of direct adsorption of water onto exposed cellulose surfaces, swelling of the cellulose due to either water or water vapor penetrating the adsorbed film, and overturning of physisorbed molecules. All of the preceding will lower the contact angle with time. It is thus felt that an initial contact angle measured immediately after the drop is placed on the surface will be most characteristic of the actual surface free energy of the cellulose film surface containing the adsorbed fatty acids.

AUTORADIOGRAPHY

Autoradiography was used to monitor the uniformity of the labeled fatty acid adsorption onto the cellulose film. Kodak No-Screen X-Ray film was pressed against cellulose film containing adsorbed acid and the assembly was placed in a light-tight box at room temperature. The time required for a good image was a

function of the quantity of acid adsorbed onto the film and ranged from 12-48 hours. The film development procedures are given in Appendix V.

FILM EXTRACTION PROCEDURES

Fatty acids adsorbed onto various metallic surfaces have been separated into physisorbed and chemisorbed components on the basis of a hot benzene extraction (100,101). The portion removed by the hot benzene extraction was considered to be physisorbed while that remaining was chemisorbed. The vapor phase-adsorbed fatty acid-cellulose system is slightly more complex.

An 80°C benzene extraction of cellulose film containing vapor phase-adsorbed fatty acid results in a rapid removal of fatty acid; see Fig. 9. Following this initial rapid removal, complete after ca. 90 seconds, little or no additional acid can be removed. Extraction times up to 20 minutes resulted in no further removal of fatty acid (78). The acid remaining following benzene extraction represents the chemisorbed species along with physisorbed molecules that are trapped within the cellulose film.
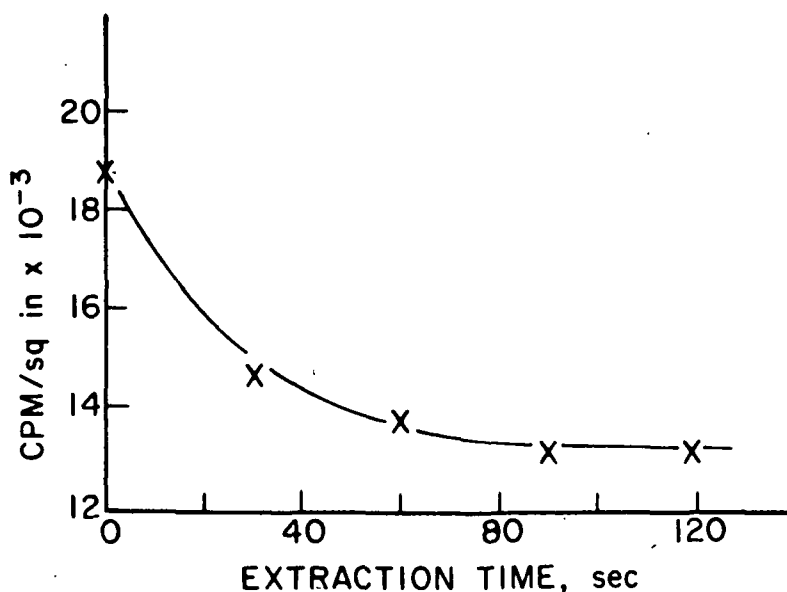
Figure 9. Benzene Extraction of Stearic Acid from Cellulose Film, 80°C

Figure 10 shows the effect of a 21°C water extraction of a cellulose film which had previously been benzene extracted. There is a very fast removal of adsorbed fatty acid, after which no more acid can be extracted. At this temperature water cannot rupture chemical bonds, and therefore the swelling effect of water on cellulose must release molecules trapped beneath the surface. The films in these experiments were water extracted for the prescribed time interval, dipped in ethanol at room temperature for 30 seconds in order to exchange the water for ethanol, and then placed in boiling benzene for two minutes. This resulted in a clear and smooth film which was suitable for radioactivity counting and contact angle measurement.
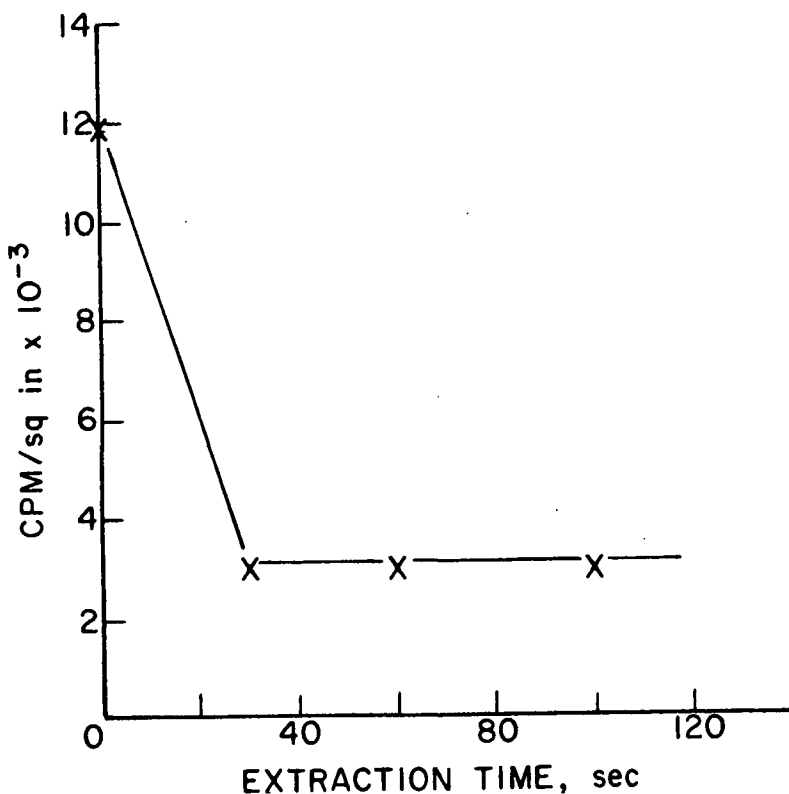
Figure 10. Water Extraction of Stearic Acid from
Cellulose Film, 21°C

The effect of a 0.01M sodium methoxide in methanol (SMM) extraction at 65°C is shown in Fig. 11. The radioactive material is quickly removed, after which no further fatty acid can be extracted. The water contact angle also decreased with

the amount of fatty acid removed. These molecules could not be removed by either a boiling benzene or a water extraction. Also, following the one minute SMM extraction, the water contact angle of the cellulose film was identical to the water contact angle of cellulose film which had never been exposed to fatty acid vapors.
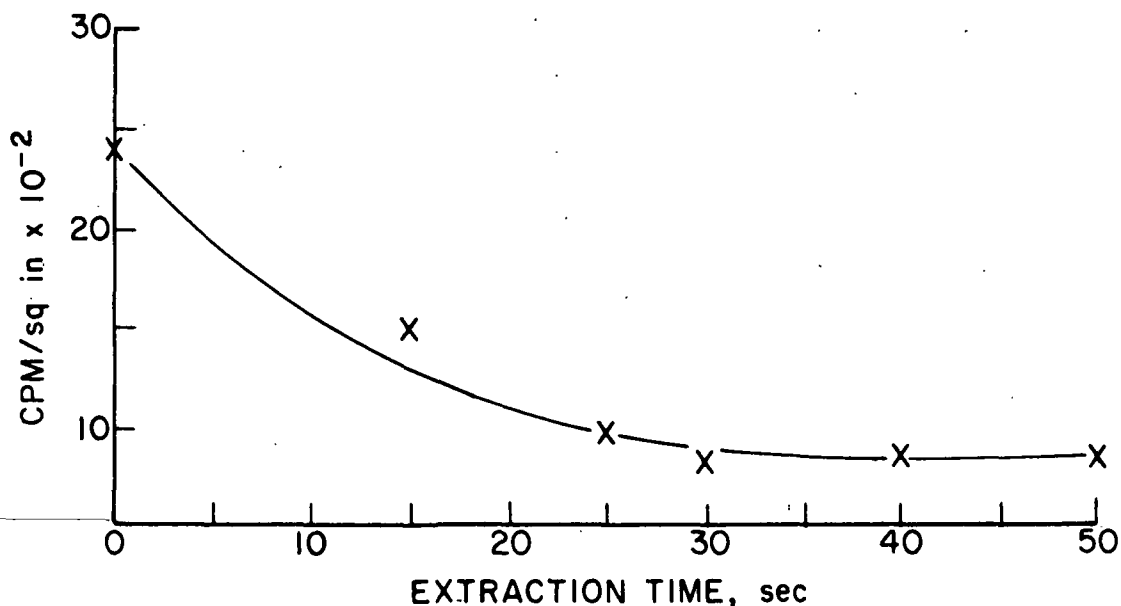
Figure 11. Extraction of Stearic Acid from Cellulose Film
Using 0.01$\underline{M}$ Sodium Methoxide in Methanol, 65°C

As a result of the preceding experiments, the following procedure was used to determine the quantity of physisorbed and chemisorbed fatty acid on the cellulose film.

1. Seven pieces ($\underline{ca}$. 0.45 by 1-inch) of cellulose film which had been subjected to vapor phase adsorption were individually extracted with boiling benzene at 80°C for two minutes and air dried to evaporate the benzene. The radioactivity content of each film was then determined. The difference in cpm/in.^{2} between the initial radioactivity and this value is the amount of fatty acid considered to be physisorbed on the cellulose film surface.

2. The benzene-extracted films were extracted for one minute in
    water at room temperature, transferred to ethanol at room temperature
    for 30 seconds in order to exchange water for ethanol, and then
    placed in benzene at 80°C for two minutes. Following air drying the
    water-extracted counts per minute was determined. The fatty acid
    remaining in the film following this extraction represents that
    which is chemisorbed and that which is trapped within the interior
    of the cellulose film.

3. Three of the films were further extracted in 0.01M SMM at 65°C for
    one minute, followed by a two-minute washing in boiling benzene.
    After the films had air dried, the radioactivity content was deter-
    mined. The difference in radioactivity between the water-extracted
    films and the SMM-extracted ones represented the quantity of chemi-
    sorbed fatty acid on the film surface.

The radioactivity remaining after the SMM extraction represents the quantity
of fatty acid trapped in the film. These molecules could be either physically
trapped in the interior of the film, inaccessible to the swelling action of
water, or chemically adsorbed beneath the surface of the film. The quantity
of fatty acid removed by the water extraction indicates that physisorbed acid
is beneath the surface of the film. The quantity of trapped fatty acid that
either chemically bonds or becomes inaccessible increases with increasing adsorp-
tion time and adsorption temperature. Thus the residual radioactivity remaining
following the SMM extraction increases with increasing adsorption time and
temperature.

Since methanol has only ca. 60% the swelling power of water on cellulose (102),
the trapped chemisorbed fatty acids apparently are not contacted during the SMM
extraction. Also, since the radioactivity level of the film remains constant

after 30 seconds of extraction (see Fig. 11), little or no migration of the trapped molecules from the interior of the film is occurring during this interval.

SNYOPSIS OF EXPERIMENTAL RUN PROCEDURE

The following procedure was used to obtain the data which is contained in Appendix IX.

1. A cellulose film was dried in the Lucite chamber for 12 hours.

2. The film was then conditioned in a 32% RH desiccator at room temperature for 24 hours.

3. The fatty acid was vapor phase adsorbed onto the cellulose film.

4. Upon removal from the oven, the entire adsorption tray was cooled in the laboratory ambient air for one hour.

5. The top of the tray, with the film in place, was placed in a 50% RH desiccator for two hours. This conditioning eliminated curling problems when the film was released from the bracket.

6. The film was cut from the bracket and divided into nine pieces (ca. 0.45 by 1-inch).

7. Duplicate pictures were taken of each film piece along with an area standard. Following film development and card punching, the area of each piece of film was determined using the computer.

8. The initial counts per minute of each film was determined. The count was later converted to counts per minute per square inch, corrected for background and counter efficiency.

9. Two of the film pieces were mounted for unextracted film contact angle measurements. Mounting consisted of placing a 0.5 by 1.0-inch piece of two-sided tape onto the juncture of two microscope slides placed side-by-side. The film was centered on the tape and

the edges were pressed flat with a clean razor blade. The microscope slides were flexed in order to pull the center of the film against the tape. The two slides were slit apart using a clean razor blade, resulting in two contact angle specimens from each piece of film.

10. The seven remaining films were benzene extracted, counted, water-ethanol-benzene extracted, and counted; four of the film pieces were mounted for water-extracted film contact angle measurements.

11. The three remaining pieces were SMM extracted, counted, and mounted.

12. The mounted films were conditioned in a 40% RH desiccator for four hours prior to contact angle measurement.

13. The contact angle measurements were taken. Twelve water contact angles were measured on each of the unextracted, water-extracted, and SMM-extracted films. Twelve methylene iodide contact angles were measured on the water-extracted films. The photographic film was developed; computer cards were punched; and the contact angles were calculated using the computer.

14. Autoradiograms were started on the slides used for contact angle measurements. Once adsorption uniformity was verified, autoradiographs were not taken when the counts per minute data were uniform. The autoradiograms were developed 12-48 hours later.

EXPERIMENTAL RESULTS

SURFACE PROPERTIES OF THE CELLULOSE FILM SUBSTRATE

A cellulose film was dried according to the standard procedure, conditioned in a 32% RH desiccator for 24 hours, mounted smooth-side up onto microscope slides, and conditioned for 4 hours in a 40% RH desiccator. Water and methylene iodide contact angles were measured. The results are in Table II. Surface energy parameters (SEP) were calculated from these contact angle values using the computer program SEPCAL (Appendix VIII), and these results are also in Table II.

TABLE II

CONTACT ANGLES AND SURFACE ENERGY PARAMETER
VALUES OF CELLULOSE FILM

Liquid	Contact Angle ± 95% Conf. Limit, deg.
Water	28.42 ± 0.69
Methylene iodide	34.35 ± 0.59
Component	Owens-Wendt SEP[a], ergs/cm^2
Total	68.2
Dispersion	36.4
Polar	31.8
Fractional polarity	0.47

[a]Surface energy parameter.

The water contact angle value agrees with that obtained by Ferris (78) and is ca. 4-6° lower than that previously reported in the literature (12,13,80). The methylene iodide contact angle is 8° higher than that obtained by Ferris and is near that of 36° reported by Bartell and Ray (12) and by Luner and Sandell (13).

Both authors indicated a confidence interval of ±2° for their value. The Owens-Wendt polarity of 0.47 obtained in this work is identical to the value calculated from Ray's data, and the Owens-Wendt dispersion value of 36.4 is identical to the $\gamma_{\underline{s}}^{\underline{d}}$ value reported for regenerated cellulose (14).

The water contact angle disagreement is difficult to explain. The film surfaces used in this work have been prepared under conditions far more conducive to smoothness than any other films reported in the literature. Contamination resulting from a spreadable material is very unlikely as indicated by the negative talc test. The cellulose used in the other studies may possibly have been slightly derivatized, resulting in the higher contact angles. Only Borgin (80) has reported the use of organic solvents to remove resins and fats before the cellulose is dissolved. Slight differences in the porosities of the films could also be the cause of the contact angle differences.

Both the water and the methylene iodide contact angles measured on the cellulose film used in this study were very uniform and reproducible.

VAPOR PHASE ADSORPTION

ADSORPTION TEMPERATURE AND FILM MOISTURE CONSTRAINTS

Borgin (83) found that the length of heat treatment, the temperature, and the humidity of the air in which the heat treatments were carried out were important in changing the surface properties of cellulose. He reported that a treatment at 140°C resulted in an increased water contact angle on cellulose. Decreases in the wettability of cellulose at lower temperatures resulted only from very low treatment humidities or very long treatment times.

Table III contains the results of conditioning cellulose films at various relative humidities for 24 hours according to the standard film drying procedure.

The films were then subjected to vapor phase adsorption at several time-temperature conditions using stearic acid as the adsorbate. These results are summarized in Table IV.

TABLE III

MOISTURE CONTENT OF CELLULOSE FILM AS A FUNCTION OF
CONDITIONED RELATIVE HUMIDITY

Relative Humidity[a], %	Salt Solution	Moisture Content of Cellulose Film, %
11.1	Lithium chloride	4.7
22.9	Potassium acetate	6.6
32.4	Magnesium chloride	8.9
58.5	Sodium bromide	12.5
64.4	Sodium nitrite	13.8

[a]$23°C$.

TABLE IV

EFFECT OF FILM MOISTURE CONTENT AND ADSORPTION TIME AND
TEMPERATURE ON THE ADSORPTION OF STEARIC ACID AND THE
PHYSICAL STATE OF THE CELLULOSE FILM

Film Moisture, %	Time, hr	Temperature, °C	Result
4.7	72	105	Film cracked severely
6.6	90	105	Film cracked
8.9	120	105	No cracking
8.9	24	125	Film cracked; film quite brittle
12.5	36	105	Increased adsorption; large portion of the acid was not extractable
13.8	60	105	Increased adsorption; large portion of the acid was not extractable

Cracking occurred at low film moisture contents and high adsorption temperatures. The film cracking was caused by "drying" the film at high temperatures while it was under the constraint of the Teflon gasket. This seal was required

in order to avoid adsorption onto the backside of the cellulose film. Higher film moisture contents resulted in increased total adsorption of stearic acid. Furthermore, large quantities of this adsorbed acid could not be extracted with benzene, water, or 0.01M sodium methoxide-methanol. This unextractable portion corresponds to the massive penetration observed by Ferris (78).

While the adsorption constraints have not been rigorously defined, there is a moisture content range as well as an upper adsorption temperature limit at which adsorption can be performed without encountering undue complications. It is apparent that the massive penetration observed by Ferris was due to high film moisture content. It has been shown that increased vapor permeability results from increasing the moisture content of cellophane or from increasing the relative humidity of the atmosphere surrounding the cellophane (103-105). The relation of molecular entrapment to film moisture content is in agreement with the conclusions of Merchant concerning the trapping of hydrocarbon molecules during WAN-drying of cellulose (106).

The workable moisture content range for these cellulose films using the specified adsorption apparatus lies between 6.6% and 12.5% moisture, while the upper limit for adsorption temperature is less than 125°C. Controls run at 105°C for various times up to 150 hours using cellulose film having 8.9% moisture resulted in no change in the cellulose film contact angle. Also, no large-scale penetration or adsorption of unextractable fatty acid was observed using cellulose film conditioned in a 32% RH desiccator at the time-temperature conditions used in this study.

ADSORPTION OF STEARIC, BEHENIC, AND ISOSTEARIC ACIDS

The adsorption isotherms for the three fatty acids on cellulose film are presented in Fig. 12. The adsorption, extraction, contact angle, and surface energy parameter data for each experimental run are presented in Appendix IX.
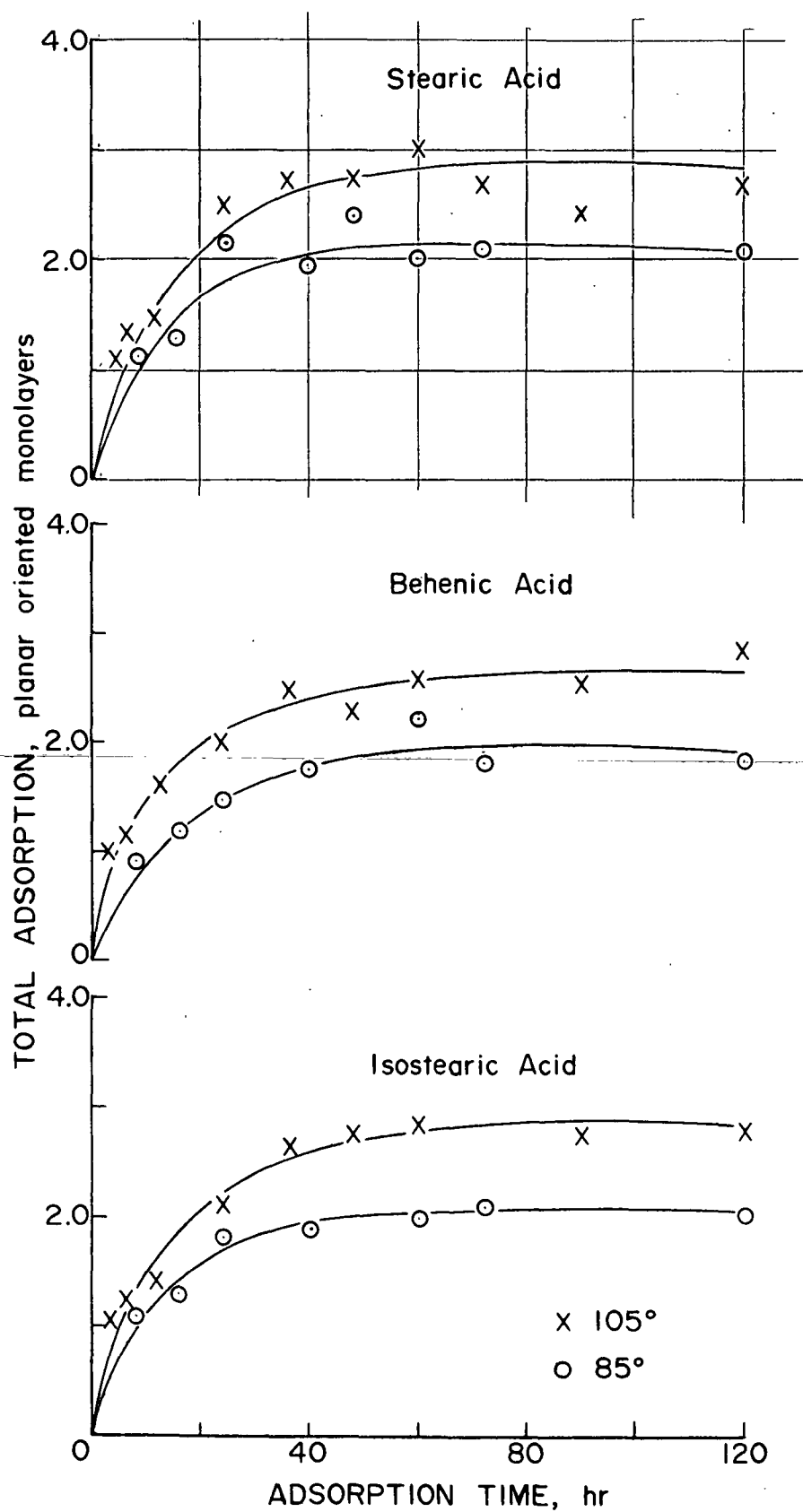
Figure 12. Total Adsorption as a Function of Adsorption Time

The isotherms for the three acids are very similar in shape and can be divided into two portions. Adsorption occurs up to an equilibrium value in the first portion (0-ca. 40 hours), after which no additional acid is adsorbed. Table V contains the equilibrium adsorption levels for the three acid adsorbates at the two adsorption temperatures investigated.

TABLE V

EQUILIBRIUM ADSORPTION LEVELS OF FATTY ACIDS ON CELLULOSE

Adsorbate	Adsorption, 85°C	Temperature, 105°C
Stearic acid, POML	2.05	2.80
Behenic acid, POML	1.90	2.60
Isostearic acid, POML	2.05	2.85

The physical significance of the increased total adsorption at higher temperature is analyzed in detail in the Discussion and Results section.

CHEMISORPTION

The chemisorption isotherms for the three acids are presented in Fig. 13. The rate of chemisorption is temperature dependent, and is independent of the molecular structure of the fatty acid. The three curves are essentially identical for a given adsorption temperature.

While the curves are parabolic in shape, the initial portion (up to ca. 40 hours) can be approximated by a straight line. When this is done, an estimate for the rate of chemisorption may be obtained. The rate of chemical bonding over the initial portion is 0.28% POML per hour at 85°C and 0.70% POML per hour at the 105°C adsorption temperature.

The quantity chemisorbed is less than 10% of the total adsorption in up to 36 hours adsorption time at 105°C, and it is always less than 10% of the total
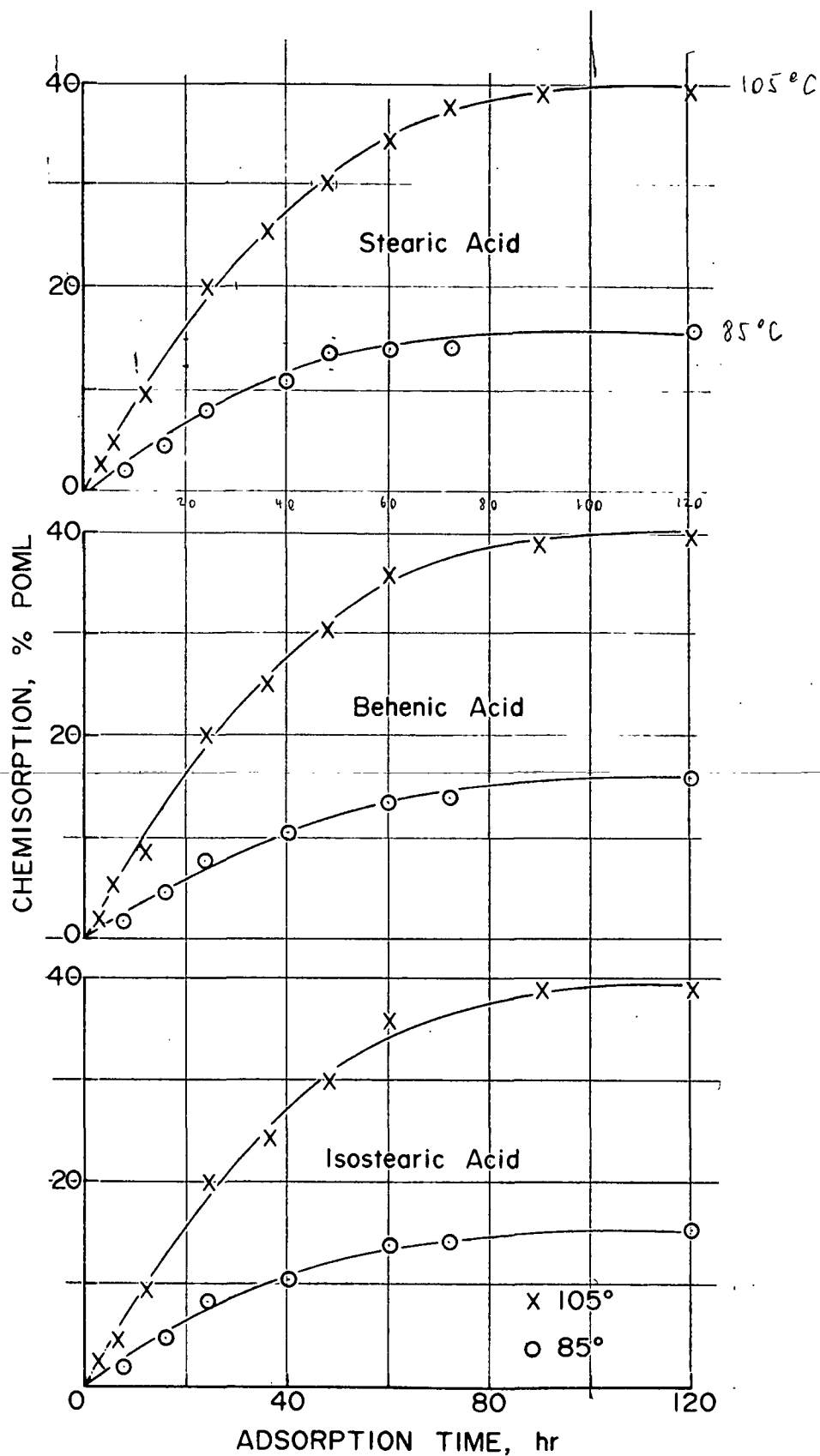
Figure 13. Chemisorption as a Function of Adsorption Time

adsorption at 85°C. The maximum percentage of chemisorbed species is 15% of the total adsorption, and this occurs at the long adsorption times at 105°C. As shown in the Discussion of Results section, this maximum quantity of chemisorbed acid is ca. 40% of the fatty acid present on the cellulose surface. This analysis discriminates between the quantity of fatty acids on the cellulose surface and the total quantity adsorbed.

Chemisorption is very slow compared with physisorption. In many systems the rate of chemisorption is dependent on the mass transport rates in the gas phase (107). However, this is not the case here. The fatty acids are rapidly physisorbed, and then they slowly react chemically with the solid surface.

CONTACT ANGLE DEVELOPMENT

UNEXTRACTED FILMS — WATER CONTACT ANGLE

Figure 14 shows the change in wettability of unextracted films as a function of adsorption time for the three acids. The water contact angle development is temperature dependent, and the curves are characterized by a rapid increase in the water contact angle during the first 30 hours of adsorption. The curves are similarly shaped, with behenic acid exhibiting the greatest wettability decrease and isostearic acid the smallest at both adsorption temperatures. At the long adsorption times at 105°C the contact angle on cellulose film containing vapor phase adsorbed behenic acid and stearic acid is slightly greater than 90°.

WATER EXTRACTED FILMS — WATER CONTACT ANGLE

Following water extraction all the fatty acid remaining on the surface is believed to be chemically bonded to the cellulose. Evidence for this is presented in the Discussion of Results section. The water contact angle of water-extracted film (henceforth designated as extracted film) is greater than that
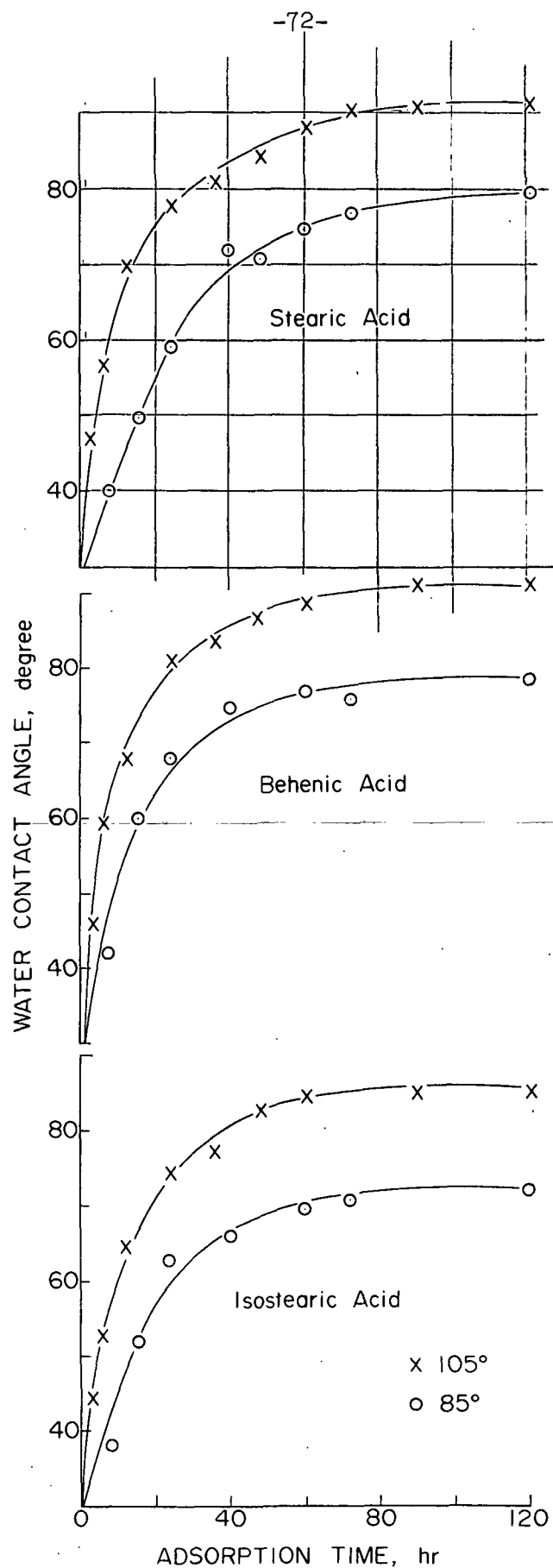
Figure 14. Development of the Water Contact Angle on Unextracted Films as a Function of Adsorption Time

on the unextracted film at small chemisorption levels but is less than that of

the unextracted film at higher levels of chemisorption. This is shown in Fig.

19 (p. 85). Even though this difference exists, the contact angle versus ad-

sorption time curves are very similar to those of the unextracted film for the

three acid adsorbates.

Figure 15 presents the relationship between the quantity of chemisorption

and the contact angle of water on the extracted film. Apparently little or no

difference in the distribution or orientation of the molecules chemisorbed at

the two adsorption temperatures exists since the data fit the same curve so

well for each acid.

The outstanding characteristic of each of these graphs is the large increase

in the water contact angle resulting from the first small quantity of chemi-

sorption. Approximately 60% of the total observed increase in the water contact

angle has occurred after only 5% POML of the particular fatty acid has been

chemisorbed. At the 10% chemisorption level, 75% of the water contact angle

increase has occurred.

Behenic acid decreased the wettability of the cellulose film more efficiently

than either stearic scid or isostearic acid. Stearic acid was only slightly more

efficient than isostearic acid. Also, while the quantity of chemisorbed fatty

acid ranged from 2% to slightly greater than 40% of the total fatty acid on the

cellulose film surface, only relatively minor differences existed between the

water contact angle on unextracted and extracted films.

WATER EXTRACTED FILMS — METHYLENE IODIDE CONTACT ANGLE

The methylene iodide contact angle as a function of the quantity of chemi-

sorbed fatty acid is presented in Fig. 16. Behenic acid produced the largest
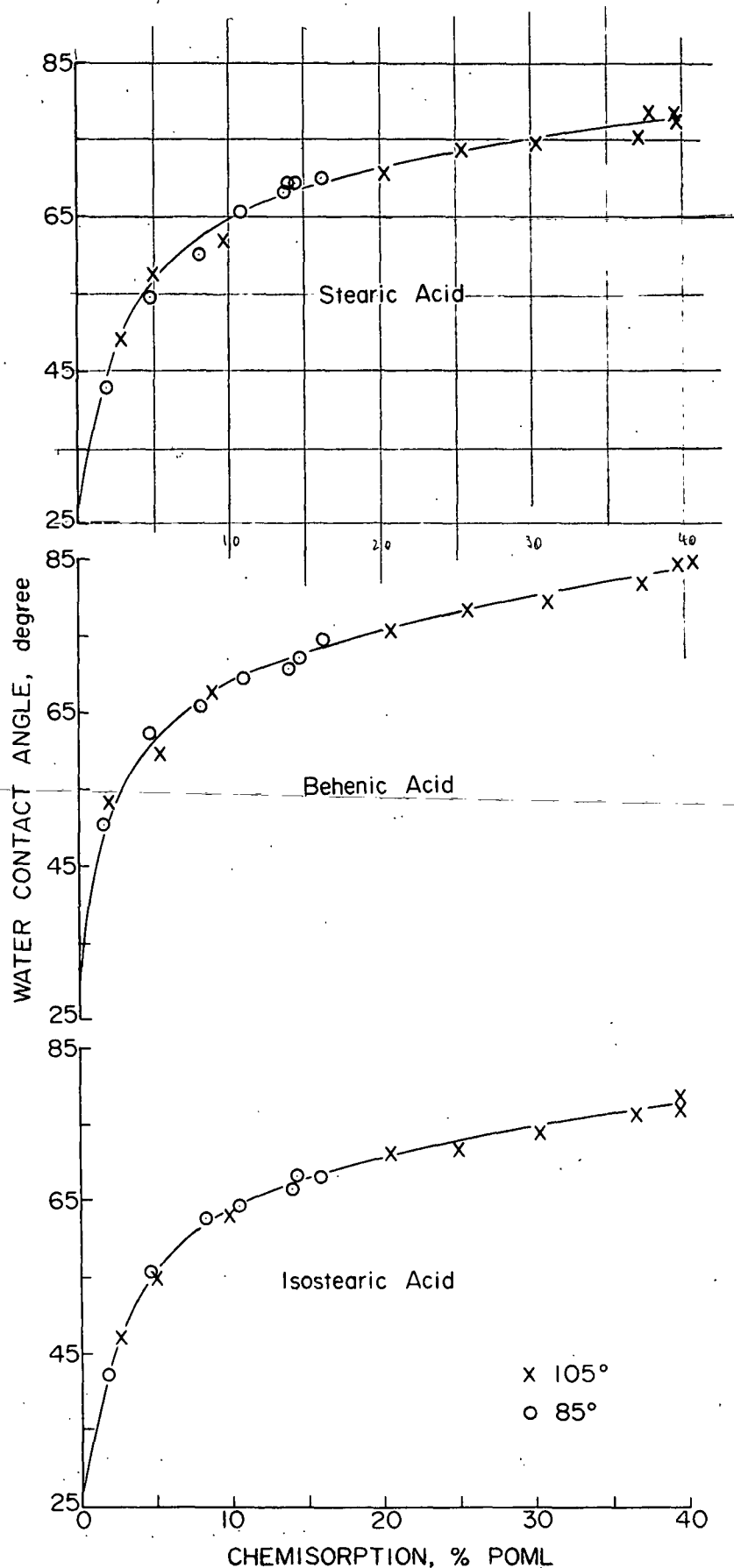
Figure 15. Development of the Water Contact Angle on Water-Extracted Films as a Function of Chemisorption
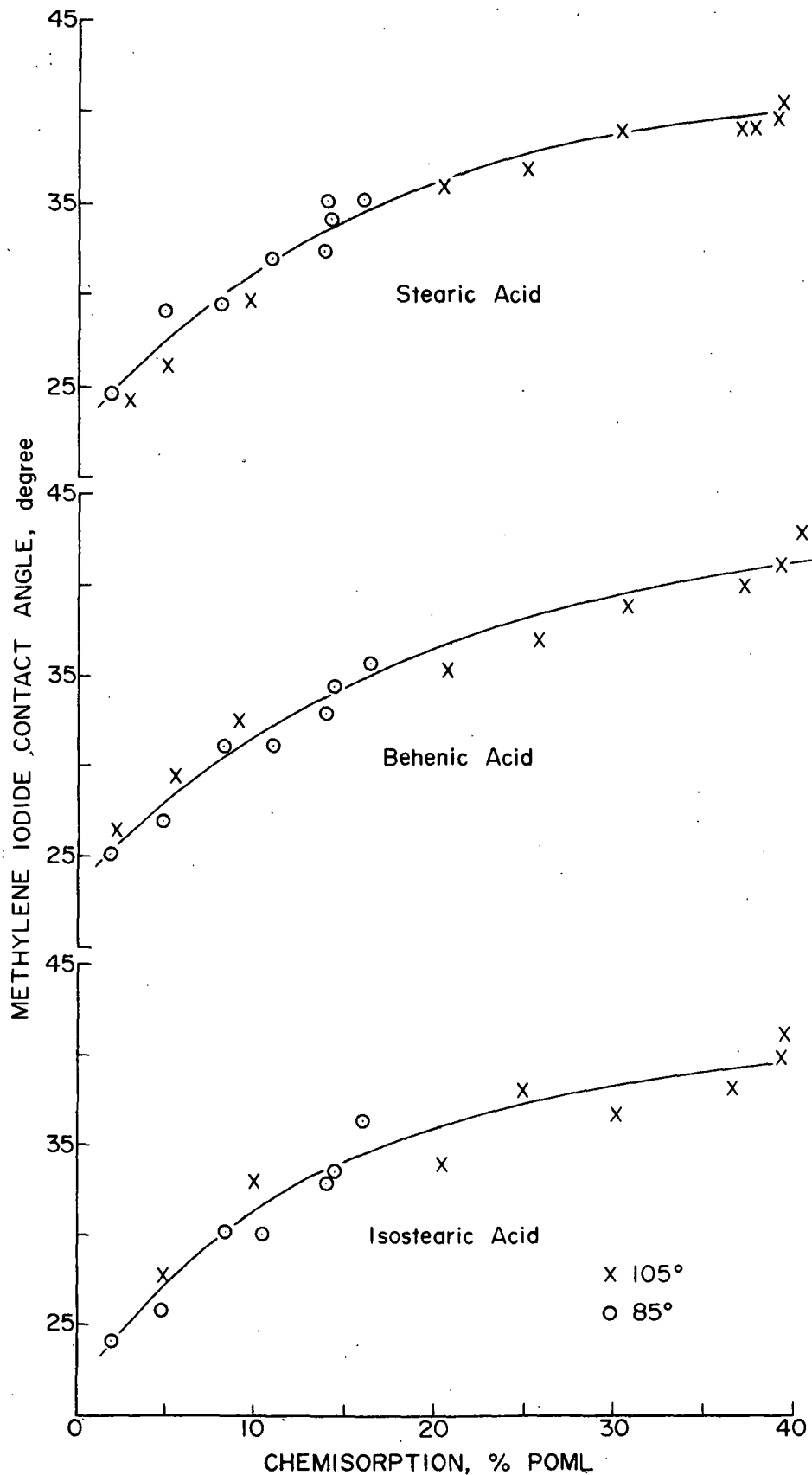
Figure 16. Development of the Methylene Iodide Contact Angle on
Water-Extracted Films as a Function of Chemisorption

methylene iodide contact angle for a given chemisorption level. The methylene iodide contact angle on stearic acid-adsorbed films was only slightly greater than that on films containing isostearic acid. This is consistent with the water contact angle results.

The methylene iodide contact angle appears to be more sensitive or responsive to surface coverage than is the water contact angle since it is still increasing at the higher levels of chemisorption. This is in agreement with theory which predicts that the predominantly nonpolar methylene iodide should exhibit a more slow and steady contact angle increase with chemisorption than would be expected by the more polar water contact angle liquid.

SURFACE ENERGY PARAMETER

The Owens-Wendt surface energy parameter and the polar component of the surface energy parameter are presented in Fig. 17 as a function of chemisorption for the three acid adsorbates. The total surface energy parameter decreases in relation to its polar component while the dispersion component $(\gamma_s - \gamma_s^p)$ remains essentially constant. As expected, the polar component decreases with increasing chemisorption. The surface energy parameter calculated according to the method of Wu shows the same relationship.

The three curves are similarly shaped, with behenic acid producing the greatest decrease in the polar component for a given chemisorption level. Little difference exists between stearic acid and isostearic acid. These curves are characterized by a sharp decrease in the polar component during the first 5-8% POML chemisorbed. Thereafter only a very small decrease in the polar component occurs with increasing chemisorption. This sharp decrease in the polar component mirrors the large increase in the water contact angle observed during the initial chemisorption stages.

$$\gamma_s = \gamma_s^{\,d} + \gamma_s^{\,p}$$
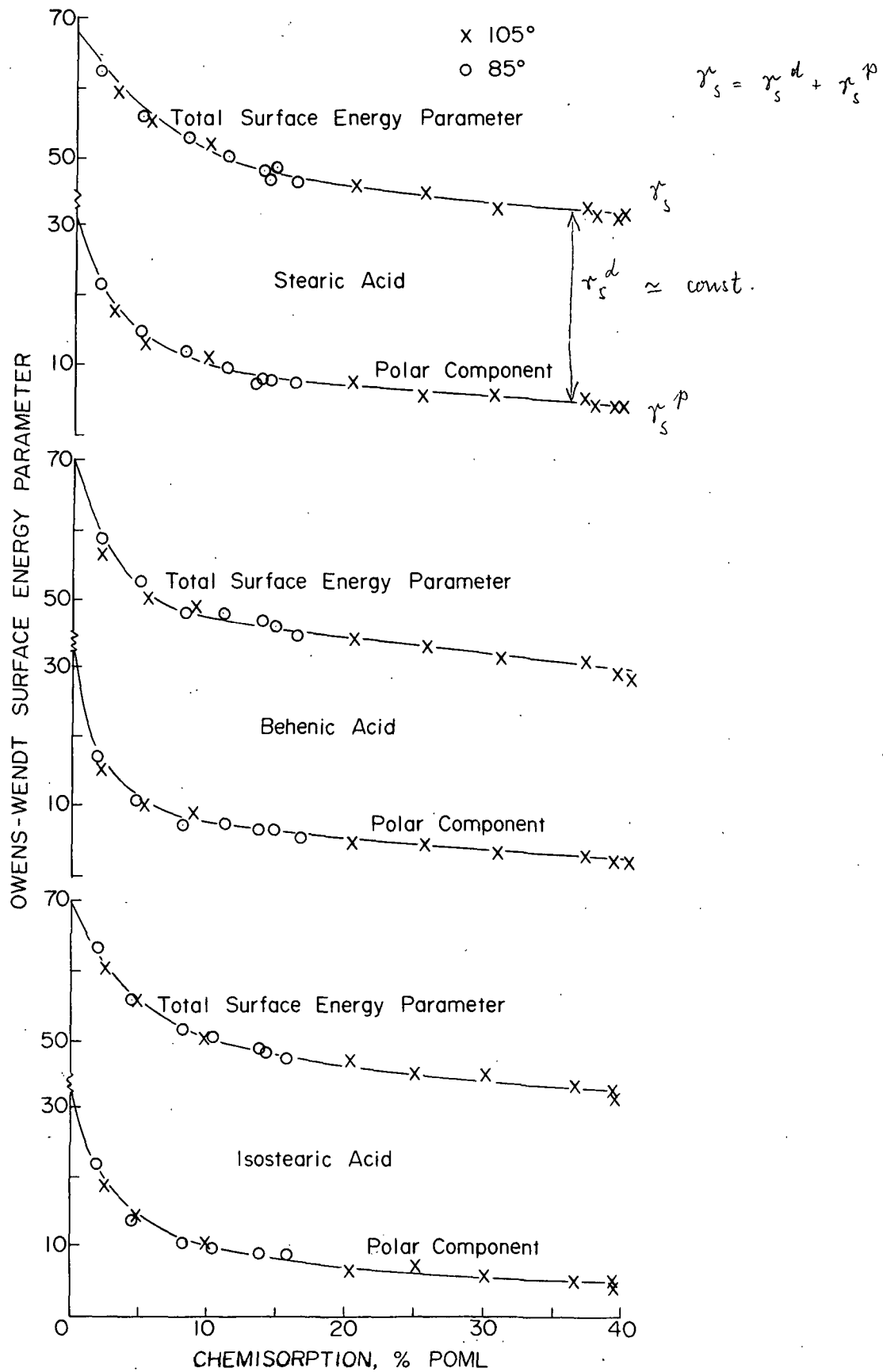
Figure 17.   Changes in the Owens-Wendt Total Surface Energy Parameter
and Polar Component on Water-Extracted Films as a
Function of Chemisorption

DISCUSSION OF RESULTS

The major concern of this study was the changes in surface chemistry which occurred with adsorption of fatty acid molecules. The kinetics and thermodynamics of the adsorption processes were not of primary concern because their determination requires different and more sophisticated equipment, with the result that it would be a study in itself.

STATES OF ADSORBED FATTY ACID ON CELLULOSE FILM

The classical Langmuir-Blodgett deposition of a fatty acid results in a layer of closely packed molecules oriented perpendicularly to the surface. The result is a reproducible system that has been extensively studied. Vapor phase adsorption of a gas onto a solid is a much more complicated system.

In classical vapor phase adsorption the molecules collide with the surface, remain there for some average time, and then desorb back into the gas phase. As the molecular population on the surface increases, interactions between the adsorbed molecules become increasingly important, especially for longer chain length molecules. A further complexity involves chemisorption, in which the adsorbate molecules chemically bond with the surface.

Fatty acid adsorbed from the vapor phase results in an adsorbate-adsorbent system that is very different from the classical Langmuir-Blodgett monolayer. Principles developed from studies of such monolayers in general are not applicable to a vapor deposition system.

The transfer of acid from the infinite reservoir in the adsorption tray across a vapor phase and onto the cellulose film is a complex system resulting in an adsorbed surface layer on the cellulose. Ferris (78) has shown that stearic acid molecules exist primarily in monomeric form in the vapor phase.

The equilibrium constant for the monomer-dimer equilibrium is relatively un-affected by the hydrocarbon chain length of the fatty acids (108). It can be assumed that both behenic and isostearic acids have an equilibrium constant similar to that of stearic acid and thus also exist in the monomeric form in the vapor phase.

The initial adsorption stages can be visualized in the following manner. The molecules first approaching the film collide with the surface, remain on the surface for a finite time, gather energy and then diffuse back into the vapor. As the population on the surface increases, an equilibrium is reached with the vapor in which an equal number of molecules are desorbing from the surface as are adsorbing onto it. This corresponds to the equilibrium region of the adsorption isotherms shown in Fig. 12.

If the surface were perfectly smooth and energetically homogeneous, the result would be a uniform distribution of molecules. Since the cellulose film is neither perfectly smooth nor energetically homogeneous, adsorption will occur preferentially at the higher energy areas. These higher energy areas probably are randomly distributed over the surface on the film; thus the adsorbed acid should approximate a random distribution when considered on a macroscopic scale.

While Fig. 12 indicates that the equilibrium adsorption level is reached after 40 hours adsorption time, an analysis of the quantity of adsorbed acid that can be removed by the benzene and water extractions adds clarity to the picture. These data for isostearic acid are in Table VI; data for the other two acid adsorbates are similar and lead to the same conclusions.

The quantity of acid that is benzene extractable (which corresponds to the amount of acid physisorbed onto the cellulose surface) is nearly constant. The increase in the total adsorption depicted in Fig. 12 results primarily from the

increased quantity of water-extractable acid and to a much lesser extent from the increase in chemisorbed acid and unextractable acid. The fatty acid that is water extractable represents physisorbed acid in pores and crevices, i.e., physi- sorbed acid not at the cellulose surface which forms the interface with the contact angle liquids. This conclusion is supported by separate experiments which showed that the water contact angle on cellulose film containing vapor phase adsorbed fatty acid that was benzene extracted was equivalent to the water contact angle following water extraction of the same film. The increased physisorption into the pores and crevices at the higher adsorption temperature is due to increased mobility of the fatty acid molecules and perhaps also to increased porosity of the cellulose film.

TABLE VI

QUANTITY OF ADSORBED ISOSTEARIC ACID THAT
IS BENZENE AND WATER EXTRACTABLE

Adsorption Time 85°C, hr	Benzene Extractable, cpm/in.^{2}	Water Extractable, cpm/in.^{2}	Adsorption Time 105°C, hr	Benzene Extractable, cpm/in.^{2}	Water Extractable, cpm/in.^{2}
8	9,304	1,609	3	9,380	1,087
16	9,075	3,091	6	9,841	2,036
24	10,196	7,466	12	7,475	4,652
40	6,899	10,682	24	10,586	7,886
60	9,897	8,528	36	11,890	10,388
72	11,025	8,310	48	10,256	13,523
120	10,173	8,343	60	10,161	13,940

The equilibrium quantity of physisorbed acid is present on the cellulose surface at all adsorption times studied. The quantity of chemisorbed and water-extractable fatty acid increases with increasing adsorption time, resulting in the increased total adsorption. Chemisorption occurs rapidly up to ca. 40 hours and then slowly continues throughout the remainder of the adsorption time range

studied while the quantity of water-extractable acid is relatively constant

after ca. 40 hours adsorption time.

The quantity of acid adsorbed onto the film surface (benzene-extractable

acid) is not dependent on the chain length configuration of the acid and shows

little or no dependence on adsorption temperature. These data are included

in Table VII. The major difference in the equilibrium adsorption levels at

the two adsorption temperatures is the acid not present on the cellulose

surface (water-extractable acid).

TABLE VII

EQUILIBRIUM QUANTITY OF BENZENE- AND WATER-EXTRACTABLE ACID

Adsorbate	Adsorption Temp., °C	Benzene Extractable, cpm/in.^{2} ± 95% C.L.	Water Extractable, cpm/in.^{2} ± 95% C.L.
Stearic acid	85	8,889 ± 983	9,678 ± 1,903
Behenic acid	85	8,448 ± 1,441	7,651 ± 1,756
Isostearic acid	85	9,510 ± 1,177	8,666 ± 1,379
Stearic acid	105	10,011 ± 1,040	12,304 ± 1,766
Behenic acid	105	8,939 ± 1,390	11,218 ± 2,012
Isostearic acid	105	10,050 ± 929	11,810 ± 2,291

At each adsorption time and temperature there is a quantity of acid that

is not extractable. As shown in Table VIII for behenic acid, this amount is

dependent upon both adsorption time and adsorption temperature. This unextract-

able acid represents the adsorbed fatty acid which either becomes trapped within

the interior of the film (and is not accessible to the water extraction liquid)

and/or chemisorbs beneath the surface of the film (and is not accessible to the

sodium methoxide-methanol extraction liquid). The water contact angle of the

cellulose film following sodium methoxide-methanol extraction was at all times

equal to the contact angle of untreated cellulose film. This indicated that

the unextractable acid was not present at the liquid interface of the cellulose-

water contact angle.

TABLE VIII

UNEXTRACTABLE ACID AS A FUNCTION OF ADSORPTION
TIME AND TEMPERATURE

Behenic Acid, 85°C adsorption time, hr	Unextractable Acid, cpm/in.^{2}	Behenic Acid, 105°C adsorption time, hr	Unextractable Acid, cpm/in.^{2}
8	139	3	286
16	225	6	305
24	407	12	761
40	512	24	986
60	515	36	807
72	548	48	1094
120	612	90	1416
		120	1381

While the monomeric form of the fatty acid is the predominant species in the vapor phase, the physisorbed acid apparently is primarily dimeric. Ferris (78) inferred extensive dimeric character from the thermodynamically preferable association of monomers into a lower energy state and supported this conclusion with empirical calculations for stearic acid. In the present work, Spectrum C in Fig. 18 provides direct experimental evidence that the physisorbed acids are primarily dimeric. Spectrum C is an infrared MIR spectrum of a cellulose film containing vapor phase adsorbed stearic acid (105°C, 3 hours). Spectrum A is a MIR spectrum of crystalline stearic acid, which is dimeric. The asymmetrical C=O stretching mode of the crystalline stearic acid (1700 cm^{-1}) absorbs in the same region as does the carbonyl group of the physisorbed stearic acid (1695-1700 cm^{-1}). The C=O stretching band of monomers of saturated aliphatic acids absorbs near 1760 cm^{-1}. Thus the spectral evidence indicates that the predominant form of the physisorbed acid is the dimer and not the monomer hydrogen bonded to the cellulose surface.

The chemical evidence indicating the formation of an ester bond between adsorbed fatty acid and cellulose hydroxyl groups is consistent and convincing. The chemisorbed species cannot be extracted with benzene, water, or hydrochloric
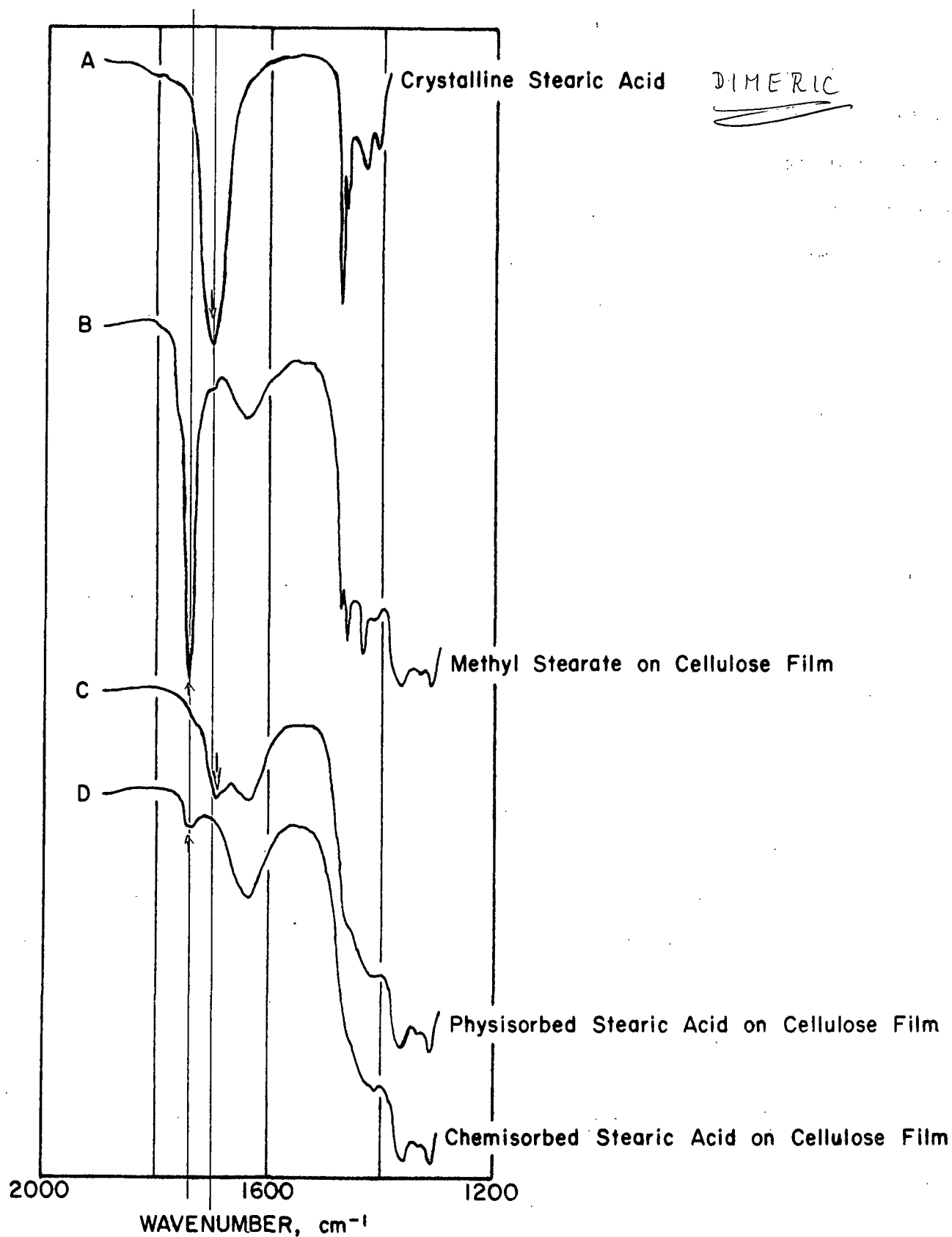
Figure 18. Infrared MIR Spectra of Various Species

acid; it can be removed with sodium hydroxide and sodium methoxide-methanol. Spectrum D in Fig. 18 provides direct physical evidence for the ester bond. This is an infrared MIR spectrum of a cellulose film containing vapor phase adsorbed stearic acid (105°C, 120 hours) that was benzene and water extracted. The carbonyl absorption in Spectrum D (1735-1745 cm^{-1}) compares favorably with the C=O absorption band of methyl stearate (1740 cm^{-1}) presented in Spectrum B. While the absorption in Spectrum D might also be ascribed to a monomer interacting with the surface by means of its carboxyl group, the chemical evidence points to a stronger interaction than that involving only secondary valence forces.

ORIENTATION OF PHYSISORBED MOLECULES

An indication of the orientation of the physisorbed molecules may be obtained from an analysis of the experimental data. The dimer is the predominant physisorbed species, and it may either recline on the cellulose surface or extend outward from the surface.

If physisorbed dimeric molecules are present at the water contact angle liquid-chemisorbed acid interface, the unextracted film water contact angle should be much higher than the water contact angle on water-extracted films. The higher contact angle would be expected because of the increased concentration of methyl and methylene groups at the interface due to the large quantity of physisorbed molecules. The actual data for the three acids are presented in Fig. 19. At the lower chemisorption levels (up to ca. 6-8% POML) the contact angle on the water-extracted film is higher, while at the higher chemisorption levels the reverse is true.

One possible explanation for the behavior depicted in Fig. 19 is that the physisorbed molecules are capable of rapid overturning at the lower levels of
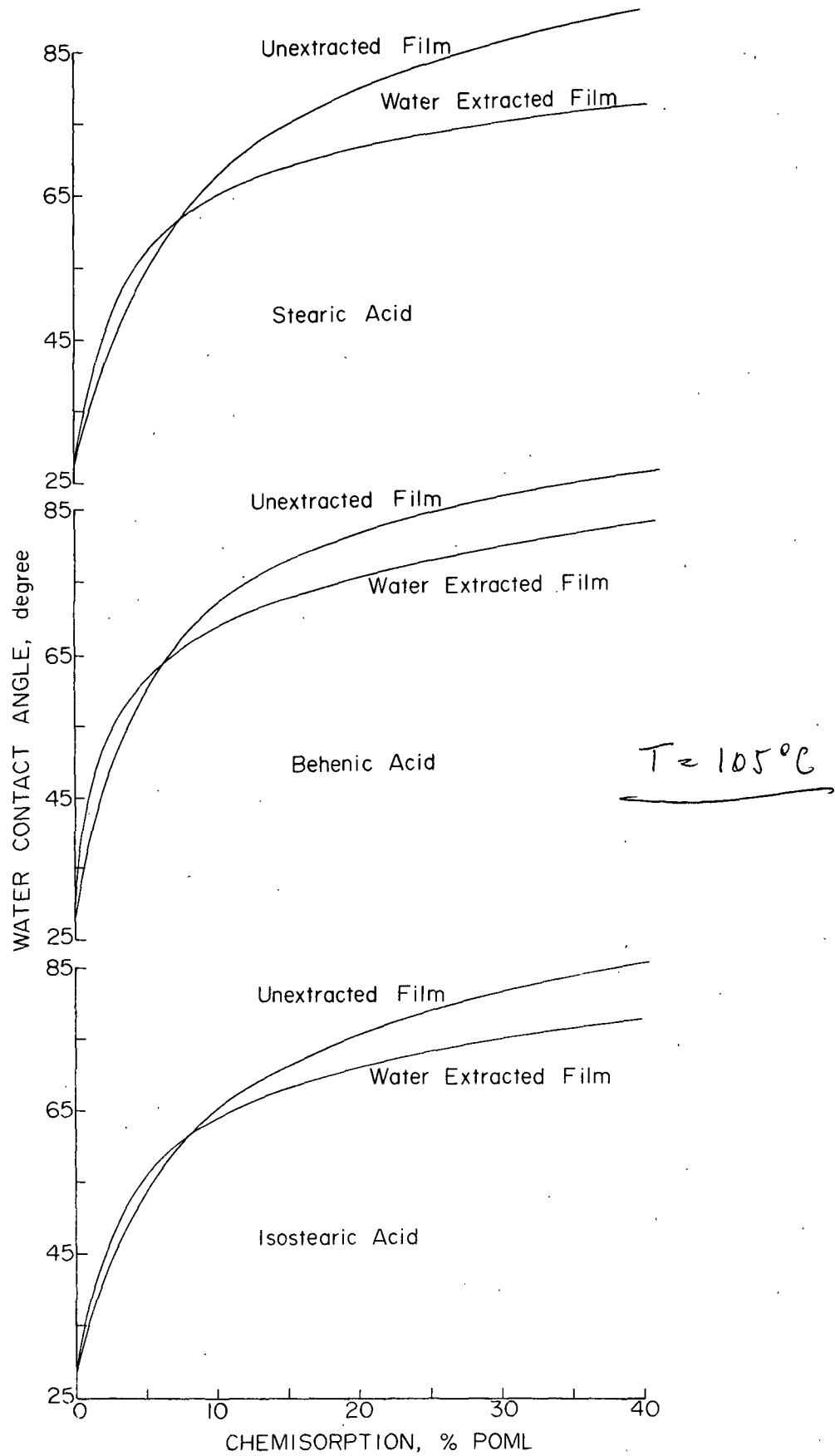
Figure 19. Water Contact Angle on Unextracted and Water-Extracted
Cellulose Films as a Function of Chemisorption

chemisorption. At the higher chemisorption levels the concentration of immobile chemisorbed molecules has increased to such an extent that lateral interactions have become important. These lateral interactions, analogous to those in oriented monolayers, would make molecular overturning occur at a slower rate.

The contact angle data are not totally consistent with this interpretation. At the small chemisorption levels the chemisorbed species account for only 2-7% of the acid on the surface. The contact angle on a surface containing chemisorbed and physisorbed fatty acid would not be expected to be nearly equal to the contact angle of a surface containing only chemisorbed molecules, especially when the physisorbed molecules account for 93-98% of the fatty acid on the surface. This indicates that the physisorbed molecules are not participating at the contact angle liquid-chemisorbed acid interface. If the physisorbed molecules were at this interface, the ratio of overturned molecules to nonoverturned molecules would be the determining factor for the magnitude of the contact angle. Since the physisorbed molecules account for 93 to 98% of the fatty acid on the surface, a fairly constant water contact angle would be expected. However, the water contact angle increases over 20° as the quantity of chemisorbed fatty acid increases from 2 to 6% POML. Furthermore, Yiannos (42) has shown that the time required for molecular overturning is several orders of magnitude greater than the time required to measure an initial contact angle in this study (ca. 1 second).

The contact angle crossover shown in Fig. 19 can be explained by assuming that dimeric physisorbed molecules are in general not present at the chemisorbed acid-water contact angle liquid interface. The smaller contact angle on unextracted films at the low chemisorption levels is due to the presence of polar carboxyl groups underneath, but near to, the sparsely populated surface of methyl and methylene groups. As the concentration of chemisorbed species increases,

the lateral interactions between methylene groups could increase to such an extent that an ordering of some of the physisorbed species by the chemisorbed molecules could become energetically feasible. The result is a surface containing a higher concentration of methyl and methylene groups, which would produce the higher water contact angles that are observed on the unextracted films at the larger chemisorption values. Either physisorbed dimers or newly adsorbed monomers could be ordered by the relatively immobile chemisorbed species.

This analysis results in the conclusion that monomer-cellulose hydrogen bonds are not abundant in this system. The dimer is apparently the energetically preferred state. The contact angle data are also consistent with the conclusion that fatty acid monomers are not present in this system.

CHEMISORPTION

It has been established that the fatty acids are linked to the cellulose by an ester bond. The rate of the reaction is independent of the chain length configuration and is temperature dependent.

The fatty acid monomers diffuse to the cellulose surface, dimerize, dissociate, and then bond. This represents the most likely reaction pathway. However, others may be postulated. The acid monomer could react directly with the surface hydroxyls without intermediate dimerization. Since esterification involves dehydration, the acids could dehydrate to form the anhydride and this species could react directly with the cellulose to form the ester. However, the energy of anhydride formation is very high. Analysis of the experimental data to identify the rate-controlling step, an Arrhenius energy of activation, or a reaction order involves too many assumptions and approximations, with the result that any determination would be tentative at best and quite questionable.

-88-

The chemisorption reaction does slow markedly at longer adsorption times. Because the cellulose surface is heterogeneous, a site energy distribution is involved. The heat of chemisorption on solids usually decreases as the fraction of the surface covered is increased. Besides having the quantity of surface hydroxyl groups decreasing as the reaction progresses, the large chemisorbed fatty acid molecules probably effectively mask adjacent hydroxyl groups. Furthermore, the physisorbed molecules may become partially associated with the nonpolar portions of the chemisorbed molecules and become unavailable for the surface reaction. These effects act in some degree of synergism to produce the diminished reaction at the longer adsorption times.

The difference in the pseudo-equilibrium chemisorption levels depicted in Fig. 13 for the two adsorption temperatures may be due to several factors. There is a higher concentration of fatty acid in the vapor and on the cellulose surface at the higher temperature, and this may be responsible for the observed data. In addition, chemisorption is still occurring at the longest adsorption time studied. At much longer adsorption times the chemisorption levels may begin to merge and attain a true equilibrium.

RELATIONSHIP BETWEEN CONTACT ANGLE AND CHEMISORBED FATTY ACID

The contact angle on organic solid surfaces containing an adsorbed monolayer has been shown to be dependent on the nature and packing of the outermost atoms of the adsorbate, and it is not dependent on the nature and arrangement of atoms in the solid substrate 10 to 20 A below the surface layer. This exemplifies the extreme localization of the attractive fields of force responsible for the adhesion of liquids to organic solids (7).

The contact angle is extremely sensitive to variations in the chemical constitution of the surface, molecular packing of the surface atoms, and the

orientation of foreign atoms or molecules on the surface (109). Zisman studied

the effect of surface constitution on wettability using γ_c and found that γ_c (and

thus the contact angle) was extremely sensitive to both the identity of the atom

substituted for hydrogen and the extent of substitution on a polymer surface

(110). Zisman also showed that γ_c was dependent on the packing of the surface

groups. A fatty acid monolayer had a higher γ_c than did crystalline n-hexatria-

contane (50); this demonstrated the great sensitivity of the contact angle to

subtle changes in the packing of methyl groups comprising the surface. Small

departures from complete adlineation of adsorbed aliphatic molecules caused

changes in γ_c. Bernett and Zisman (4) have also investigated the influence

of terminal branching on γ_c.

The contact angle can be used as an indicator of surface coverage at all

levels of adsorption. At less than monolayer coverage the contact angle is

dependent upon the extent of surface coverage and the molecular orientation.

As the surface coverage approaches a complete monolayer, it has been demon-

strated that the contact angle is sensitive to slight variations in packing,

orientation, and molecular adlineation (4). At all adsorption levels the

contact angle is dependent on the identity of the atoms at the surface.

Water and methylene iodide contact angles measured on cellulose films con-

taining varying quantities of vapor phase adsorbed stearic, behenic, and iso-

stearic acids were observed in this study. For any arbitary level of chemi-

sorption, the contact angle was dependent on the identity of the acid adsorbate.

The preceding brief review of the literature indicated that a contact angle

difference on identical surfaces containing adsorbed molecules must be due to

either one or any combination of the following:

1. the identity of the adsorbate atoms at the surface;
2. the extent of coverage of the adsorbent;
3. differences in orientation of the adsorbate.

The three acid adsorbates used in this study were hydrocarbons containing a polar carboxyl group. The nonpolar chain consisted of methylene groups and a terminal methyl group. Isostearic acid has two terminal groups adjacent to a CH group. Since the three acids are so similar in molecular composition, they should present the same types of atoms (methyl and methylene groups) to the contact angle liquid. The result is that differences in wettability cannot be related to this factor.

The contact angles are compared at constant levels of chemisorption of the three acids. At any given chemisorption level all three acids are present at the same molecular concentration. While this is true, the acids do have different chain lengths and isostearic acid is branched. The result is that each acid could effectively mask an area of the adsorbent that is dependent on the physical dimensions of the particular acid. Thus the variations in contact angle could be due to differences in the effective coverage of the cellulose film.

The three acids have similar chemical compositions and molecular chain lengths. Gross differences in the orientation of the acid adsorbates would not be expected to result from the relatively minor differences in the molecular structure of the three acids. Furthermore, when the thermal motions of molecules around an axis are considered, specific molecular orientations are of little importance.

This analysis has resulted in the conclusion that the measured differences in wettability obtained in this study are due to the ability of the molecules of the three acid adsorbates to mask areas of the cellulose film adsorbent to different extents which are dependent upon the molecular structure of the individual acid adsorbates.

ORIENTATION OF CHEMISORBED MOLECULES

The chemisorbed species are responsible for the observed wettability changes. The water and methylene iodide contact angles increase with increasing chemisorption, not with increasing physisorption.

The conclusion of the preceding section was that the wettability differences among the acid adsorbates were due to the ability of these adsorbates to mask differing areas of the cellulose film. A molecule lying on the surface would effectively mask its projected area on that surface. The projected area of a fatty acid molecule lying flat is given by (111) $A_o = (\underline{m}-2)5.4 + 35.1$, where $\underline{m}$ is the number of carbon atoms and A_o is the projected area in A^2. A chemisorbed molecule lying on the surface would probably have strained bonds.

A molecule perpendicular to the surface would mask an area proportional to the cross-sectional area of that molecule. Monolayers formed according to the classical Langmuir-Blodgett technique contain molecules that are perpendicular to the surface. However, it is very unlikely that vapor-deposited molecules would exist in this ordered orientation.

Another orientation that the chemisorbed molecules could have is one in which they are inclined at some acute angle to the surface, and the molecules have enough kinetic energy so that the hydrocarbon tail can flail about the surface. The simplest case is that the long rigid chains sweep out a conical volume by swinging randomly about the bonding site. This orientation contains a rigid chain and is denoted as the rigid orientation.

Another orientation falling into this category is a flip-flop one in which the projected area of a hemisphere or cone is masked. This orientation includes everything except the rigid chain and is designated as the flip-flop

orientation. It is an averaging orientation that equally weights all possible

orientations. In a Raman spectroscopy study of n-paraffins, Mizushima (112)

concluded that n-paraffins in the solid state have an extended zigzag configur-

ation and those in the liquid state have at most one kink. Thus at any point

in time the chemisorbed fatty acids should be either linear or have only one

kink.

For both the rigid and flip-flop orientations the masked area is propor-

tional to the square of the length of the fatty acid. Some area per molecule

calculations for these orientations are contained in Appendix X.

The effects on the efficiency of wettability decrease produced by chemi-

sorbed molecules exhibiting these four orientations are summarized in Table

IX. Repellency efficiency is defined as the ratio of the masked area per

molecule divided by the masked area per molecule for stearic acid.

TABLE IX

EFFECT OF MOLECULAR ORIENTATION ON REPELLENCY EFFICIENCY

Orientation	Acid	Masked Area per Molecule, A^2	Repellency Efficiency
Lying on the surface, $A_o = (m-2)5.4 + 35.1$	Stearic	122	1.0
	Behenic	143	1.17
	Isostearic	122	1.0
Rigid or flip-flop (see Appendix X)	Stearic	1544	1.0
	Behenic	2221	1.44
	Isostearic	1414	0.92
Perpendicular to the surface	Stearic	20	1.0
	Behenic	20	1.0
	Isostearic	32	1.6

If the chemisorbed molecules are lying flat on the surface, stearic acid

and isostearic acid would decrease the wettability of the cellulose film in

the same manner while behenic acid would be 1.17 times more efficient. Conversely,

if the molecules are perpendicular to the surface, stearic acid and behenic acid would exhibit the same influence while isostearic acid would be 1.6 times more efficient. Finally, if the molecules obey the rigid or flip-flop model, isostearic acid would be slightly less efficient than stearic acid while behenic acid would be 1.44 times more efficient than stearic acid. The ratio of repellency efficiencies for these latter two models is independent of the inclination angle (see Appendix X).

The results obtained in this study are in Fig. 20. In this figure the water contact angle on water-extracted film is compared with the chemisorption levels of the three acids. At a given chemisorption level the number of molecules chemisorbed onto the cellulose film surface is the same for the three acids.

The data calculated from Fig. 20 indicate that behenic acid is 1.45 ± 0.04 times more efficient than stearic acid in increasing the water contact angle. Also, isostearic acid is 0.91 ± 0.02 times as efficient as stearic acid. These computations are given in Appendix XI. These data are consistent with the conclusion that the chemisorbed molecules sweep out the projected area of a cone or hemisphere.

Other data support this conclusion. The rapid increase in contact angle and the rapid decrease in polarity of the cellulose film during the first few percentage POML chemisorbed indicate that the molecules are masking an area far greater than their cross-sectional area. The self-sizing problems associated with absorbent grades are caused by relatively small levels of fatty acid impurities. Swanson (84) has found that as little as 6% of a monolayer film of stearic acid would produce a fully repellent paper. In addition, Swanson reported that longer chain fatty acids develop sizing in handsheets more efficiently than do shorter chain fatty acids.
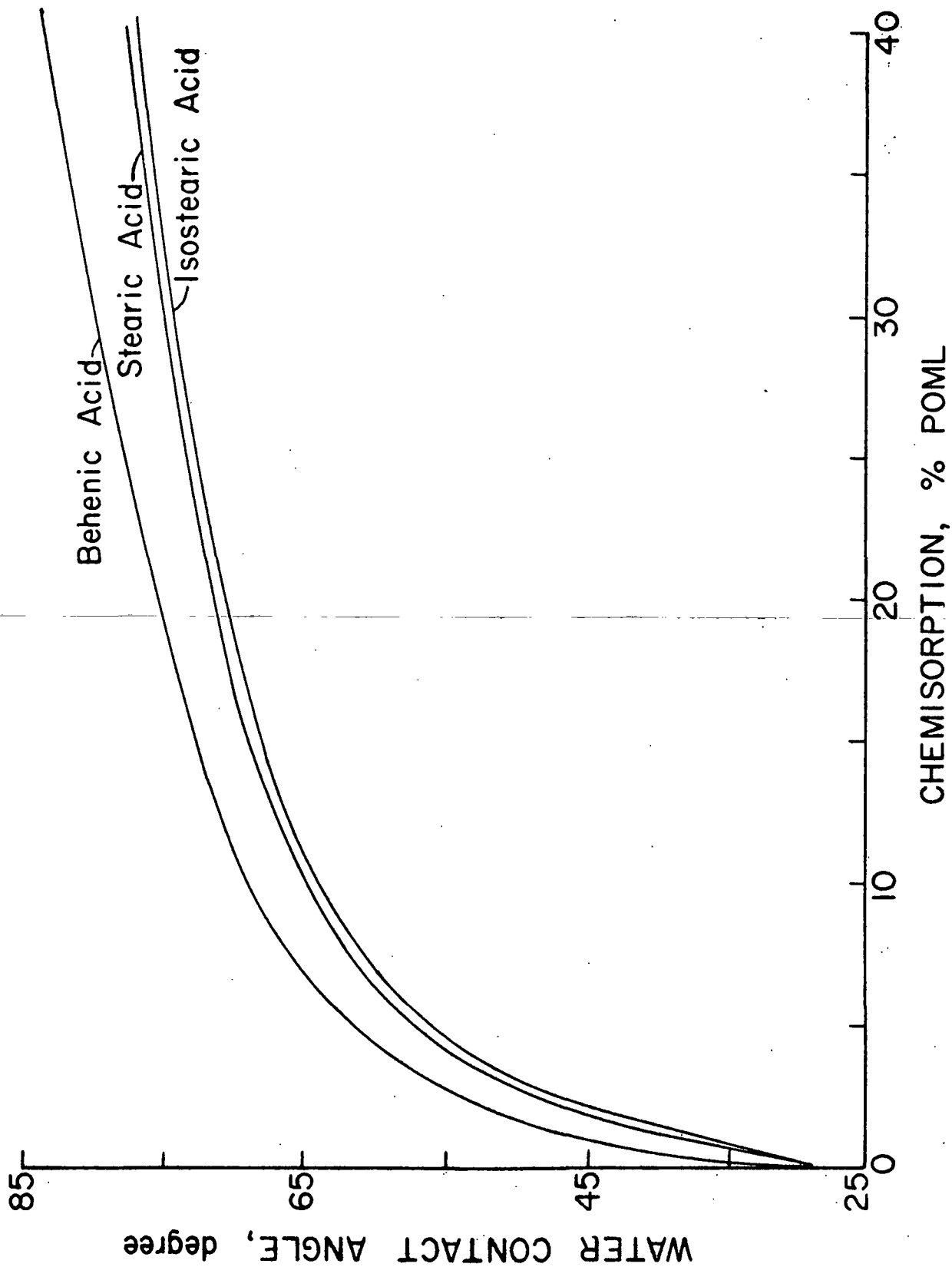
Figure 20. Water Contact Angle on Water-Extracted Film as a Function of Chemisorption

model

A system has been described which explains the experimental facts. The

contact angle data are consistent with the swept-out area concept. Figure 20

on the preceding page presents the experimental data. If the chemisorbed molecules

do sweep out an area, then the swept-out area per molecule should be a function

of the square of the acid chain length. When the abscissa values (chemisorption

expressed as % POML) in Fig. 20 are multiplied by the square of the respective

acid chain length, and these values are plotted versus the water-extracted film

contact angle, all the data points fall on the same parabolic curve. Thus the

rectified data agree with the conceptual model. A plot of the logarithms of

these functions results in a straight line as shown in Fig. 21. The following

equation was obtained from a statistical analysis of these data:

$$\theta = 17.08 \ (1_f^2 \cdot \% \ POML)^{0.15} \tag{22}$$

where θ = the contact angle in degrees

1_f^2 = the square of the molecular chain length in A^2

% POML = the percentage planar oriented monolayer of chemisorbed
fatty acid

Extrapolation beyond the chemisorption limits obtained in this study must

be performed with extreme caution, even though Equation (22) predicts a stearic

acid % POML of 350 for a 108° water contact angle. Since the water contact

angle on an oriented stearic acid monolayer is 108°, this indicates that the

roughness of the cellulose film is 3.5. This is a reasonable value.

While the actual orientation of the chemisorbed molecules cannot be deter-

mined, the flip-flop one masking a hemispherical area appears to be the likely

one at the low levels of chemisorption. This orientation is similar to Pauling's

libration concept (113). Pauling stated that molecules constituting a crystal

lattice undergo an oscillatory or to and fro motion at lower temperatures where

the molecules do not have enough energy to overcome the lattice forces. At
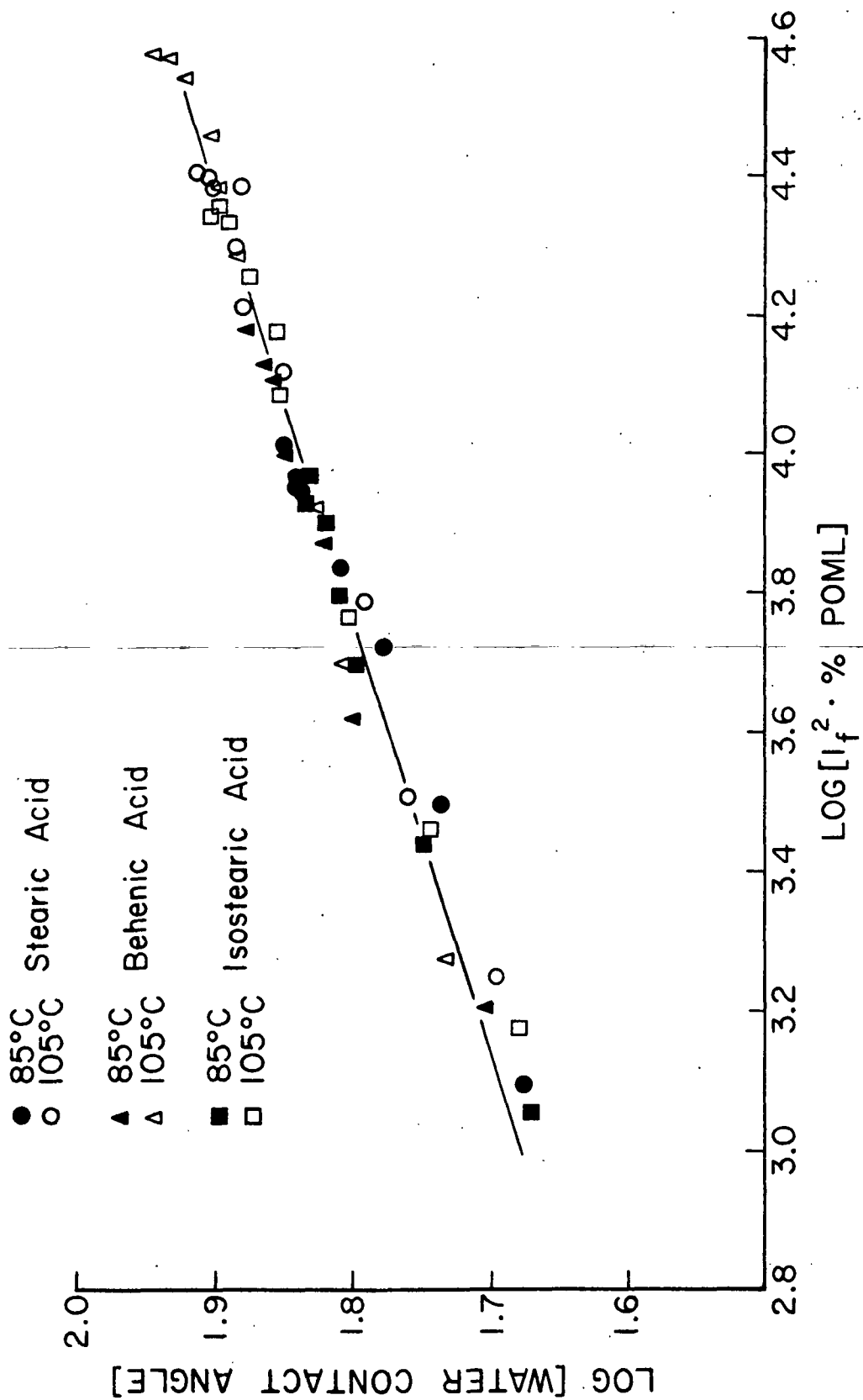
Figure 21. Relationship Between Contact Angle and an Area Function of the Chemisorbed Species

higher temperatures rotation becomes important. The fact that solids have a

vapor pressure is proof that molecular mobility in the solid state exists.

Rideal and Tadayon (114) noted that the "melting point" of a stearic acid

monolayer is lower than the bulk melting point, indicating that such surface

molecules have more energy and mobility than is normally associated with the

solid state.

The flip-flop orientation permits greater entropy, while the rigid orienta-

tion has entropy restrictions. As the hemisphere is swept out, all orientations

are probable. While the linear conformation of the molecule is the most stable

one at the temperatures of interest here, the molecules are kinked part of the

time. However, the major concern is the area masked by the statistically

favored linear molecule.

While the chemisorbed molecules mask a hemispherical area at the lower

chemisorption levels, they mask the projected area of a cone with increasing

chemisorption. As chemisorption continues, the increasing intermolecular im-

pingement between chemisorbed molecules causes the angle between the chemisorbed

fatty acid and a line perpendicular to the surface to become smaller and smaller,

until the molecules constituting a complete monolayer are oriented perpendicu-

larly to the surface.

As chemisorption continues, the water contact angle increases linearly up

to ca. 55° (see Fig. 15). As noted in Appendix XI, this contact angle corre-

sponds to the following chemisorption levels: stearic acid, 4.2 % POML; behenic

acid, 2.9% POML; isostearic acid, 4.7% POML. The actual monolayer coverage can

be expressed as follows:

$$\text{Actual Monolayer Coverage} = \frac{\% \text{ POML}}{R} \times \frac{\text{Effective area/molecule}}{\text{Cross-sectional area/molecule}}$$

If it is assumed that the cellulose surface is completely covered (100% POML) at
the above chemisorption levels, a roughness factor can be calculated when the
area values contained in Appendix X are used for the effective area/molecule
values. When $\theta = 90°$ is used, the calculated R value for the cellulose film
is 4.3. If $\theta = 60°$ is used, the calculated R value is 3.3. Since the effective
chain length of the chemisorbed fatty acids may be slightly shorter than the ex-
tended zigzag chain length due to the presence of kinks or angular restrictions,
this latter calculated value is a good estimate of the minimum roughness value.
Both calculated roughness values fall in the 1.5-6.0 range expected for the cellu-
lose film used in this study.

This interpretation suggests that the contact angle increases linearly as
new cellulose surface is being masked. The deviation from linearity above 55°
occurs because additional chemisorption results in increased packing density
instead of masking new surface. Thus each added chemisorbed molecule has less
effect on the water contact angle once the cellulose surface is effectively
covered.

The polar component of the surface energy parameter (see Fig. 17) exhibits
a marked decrease in slope at or near the above chemisorption values for the
three acids. This behavior is consistent since the polarity of the surface
would be expected to decrease rapidly as new areas are being covered, but
would decrease at a much slower rate after the surface is effectively covered
and only the packing density is being increased.

RELEVANCE OF THE SURFACE ENERGY PARAMETER

Methylene iodide contact angles were measured on water-extracted films in
order to enable surface energy parameters to be calculated. The results pre-
sented in Fig. 17 are very consistent and are helpful in visualizing the adsorption

process. The parameter values correspond with the predicted behavior for the adsorption system. While the consistency of the data and agreement with expected results are desirable, sufficient fundamental difficulties are present which limit interpretation. The surface energy parameters were developed for two component systems while the system involved in this study contains a third component present at the interface. Also, the determination of the polar component of the surface energy parameter is based on an empirical approach, as opposed to the theoretical basis for the determination of the dispersion component. These considerations were presented in depth in the Literature Review section. In light of these criticisms, the parameter values are considered important in order to explain differences occurring during adsorption. However the absolute values of the parameter under given adsorption conditions cannot be used for fundamental considerations.

A parabolic curve similar in shape to that obtained for the water contact angle data is obtained when the methylene iodide contact angle is plotted against the product of the square of the acid chain length and the % POML chemisorbed. A plot of the logarithms of these functions is presented in Fig. 22. A statistical analysis of the data resulted in the following equation,

$$\gamma = 7.36 \; [1_f^2 \cdot \% \; POML]^{0.17} \tag{23}$$

in which γ is the methylene iodide contact angle and the other variables are the same as previously defined. Methylene iodide exhibits a 70° contact angle on pure methyl surfaces (101). When this value along with the stearic acid chain length is used with Equation (23) in order to estimate the roughness of the cellulose film, a roughness of 8 is calculated. This is much higher than the 3.5 obtained from the water contact angle data.
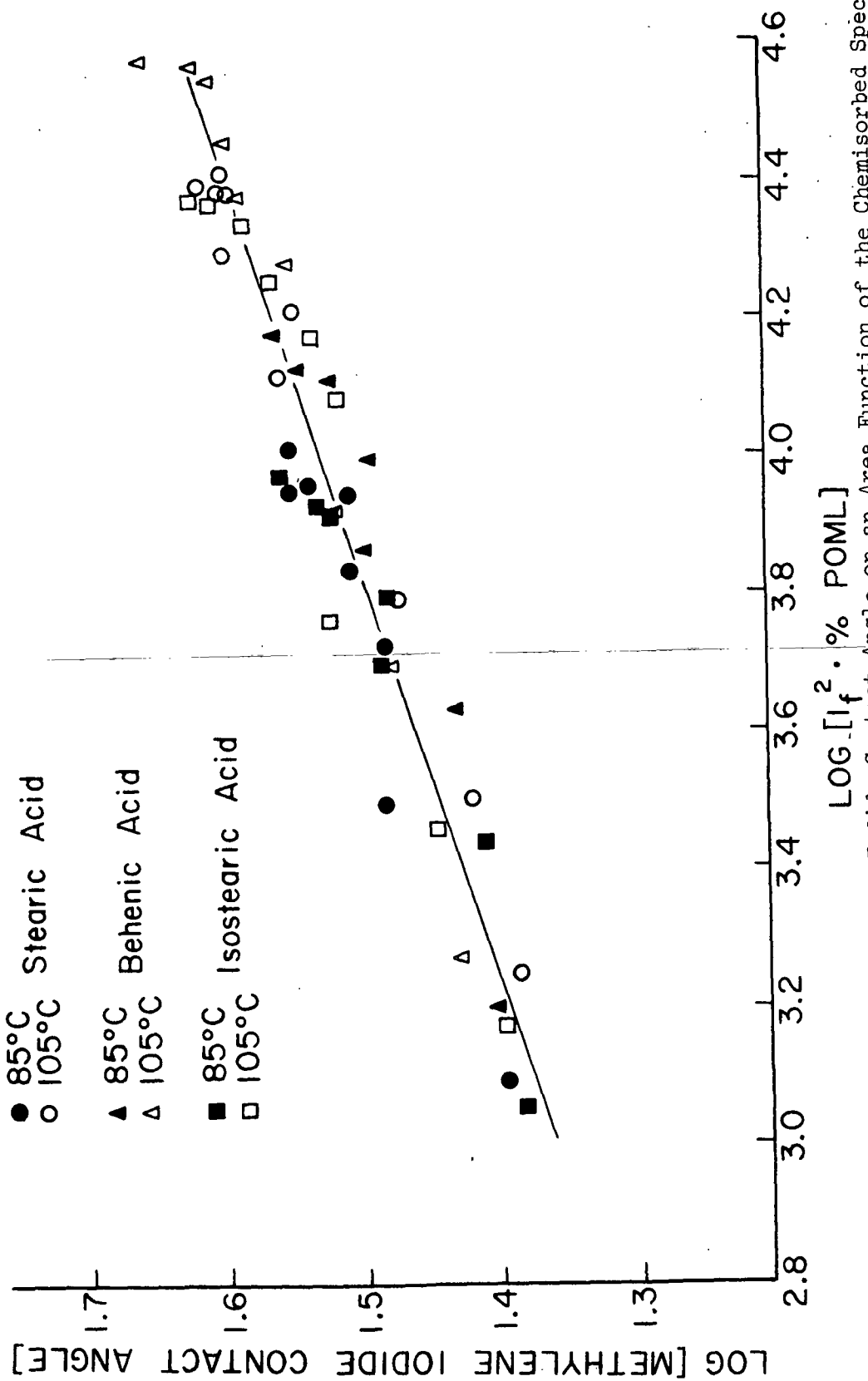
Figure 22. Dependence of the Methylene Iodide Contact Angle on an Area Function of the Chemisorbed Species

This disparity may be due to the fact that the roughness estimate using the methylene iodide data involves an extrapolation over a contact angle range that is 50% larger than that involved in the extrapolation of the water data. While the validity of such an extrapolation can be questioned in either case, the much longer extrapolation involved in the methylene iodide roughness approximation is much more suspect.

In addition it has been hypothesized (78) that the hydrocarbon tails of fatty acids dissolve in the methylene iodide contact angle liquid. If this is the case, the contact angle would also depend on the concentration of the acid at the interface and not only on the masking ability of the hydrocarbon chains. Such an interpretation also makes the surface energy parameter determinations questionable since the two liquids would be forming angles against different surfaces.

Finally, the methylene iodide contact angle data contain more scatter than do the water contact angle data. The result is that less confidence is associated with any analysis based on the methylene iodide data.

SUMMARY OF CONCLUSIONS

The fatty acids transfer through the vapor phase and physically and chemically adsorb onto the cellulose film. The physisorbed molecules are primarily dimeric and the chemisorbed molecules are attached to the cellulose surface by means of an ester bond. Physisorption onto the cellulose surface occurs rapidly, with the equilibrium quantity (ca. 0.93% POML) present at all adsorption conditions studied. Increases in total adsorption with time are due to continuing chemisorption and increasing physisorption into the pores and crevices of the cellulose film. The total quantity adsorbed is temperature dependent because chemisorption and physisorption into the pores and crevices occur more rapidly at the higher adsorption temperature. Chemisorption is very slow compared with physisorption. The rate of chemisorption is temperature dependent and is independent of the molecular structure of the fatty acid adsorbate. The chemisorption reaction slows markedly at the long adsorption times; the maximum quantity chemisorbed was 0.4% POML.

The chemisorbed molecules are responsible for the observed contact angle increases even though they only comprise from 2 to 40% of the fatty acid on the cellulose surface at the various adsorption conditions studied. The physisorbed molecules recline on or near the cellulose surface and are not present at the contact angle liquid interface. The water contact angle increases linearly with respect to chemisorption from the 28° value on cellulose film to 55°, where it is believed that the cellulose surface is effectively masked. The slower rate of contact angle increase above 55° occurs because additional chemisorption results in increased packing density rather than masking new surface. Contact angles slightly greater than 90° were obtained at the longest adsorption times studied at the 105°C adsorption temperature.

Behenic acid was 1.45 times more efficient than stearic acid in increasing the water contact angle. Isostearic acid decreased the wettability 0.91 times as efficiently as stearic acid. The molecular chain length of the fatty acid molecules is the physical parameter responsible for the differences in wettability among the three acids.

It is postulated that the large increases in contact angle produced by such small quantities of chemisorbed molecules are due to the hydrocarbon tails of the chemisorbed molecules sweeping out an area far greater than their cross-sectional area. At low chemisorption levels the chemisorbed molecules mask the projected area of a hemisphere while they assume a flip-flop orientation. As the surface concentration of chemisorbed perpendicular and the chemisorbed fatty acids becomes smaller and smaller due to intermolecular impingement. The result is that once the surface is effectively covered the chemisorbed molecules sweep out a projected area of a cone. The masked area per molecule continually decreases as chemisorption continues because the intermolecular impingement decreases the angular movement of the molecules sweeping out a conical volume.

Relationships between the quantity chemisorbed multiplied by the square of the molecular chain length of the particular chemisorbed acid and the contact angle were developed for both the water and the methylene iodide contact angles. These empirical equations were obtained from the conceptual model of swept-out areas. Unfortunately, there are no other data in the literature with which to test the equations.

Sufficient fundamental complications arise due to the presence of a third component at the interface that the surface energy parameter values calculated according to the Owens-Wendt equations cannot be used as an estimate of the solid surface energy. The parameter values are consistent with the other results

and are helpful for visualizing the surface chemical changes which occur with increasing chemisorption.

SOME APPLICATIONS AND SUGGESTIONS FOR FURTHER RESEARCH

The eventual development of a commercial vapor phase sizing process has been mentioned as the long-range goal. However, the subject of wetting is very important in many industries where water resistant or absorbent products are manufactured. Only applications with reference to the paper industry will be discussed here.

Since these fatty acids mask an area so much larger than their cross-sectional area, the difficulty of avoiding self-sizing in absorbent grades can be appreciated. A very small quantity of fatty acid impurity can significantly increase the contact angle and thus the size time if it is properly anchored to the cellulose surface. Self-sizing has been attributed to amphipathic molecules present in ray cells of most wood species (12). The fatty and resin acids migrate out of the ray cells and adsorb onto the surface of the cellulose fibers.

The results of this study also give an indication concerning why the alkyl ketene dimer (Aquapel) is such a good sizing agent. The alkyl ketene dimer reacts with the cellulosic hydroxyl groups to form a β-keto ester, thus it is well anchored to the surface. Furthermore the two long straight-chain alkyl groups present in each molecule not only effectively mask a large area but also provide a greater packing density.

Rosin size is the most widely used internal sizing agent in the paper industry and abietic acid is the principal rosin acid. Abietic acid is a bulky molecule which contains a hindered carboxyl group. There is little chance that this molecule could undergo a flip-flop orientation similar to that of the fatty acids.

Due to this small potential for movement, the masking ability of abietic acid is restricted to the cross-sectional area of the molecule.

The influence of roughness and porosity on wettability needs to be studied. Knowledge of the roughness factor would allow a quantitative relationship between surface coverage and wettability to be determined. Also, does the wettability of a porous surface decrease more rapidly than a nonporous surface? The difference in wettability between the cellulose films used in this study and the handsheets used by Swanson (84) has been ascribed to differences in porosity; however, this area needs an exhaustive quantitative study.

The influence of surface coverage of various fatty acids on the drop-aging contact angle needs to be studied. This study measured initial contact angles. Water resistance is usually determined by the rate of which wettability occurs rather than by the equilibrium condition. The equilibrium contact angle may be quite low but if the time required to reach the value is long, the product can be considered to be water resistant. The end use of the particular product will dictate whether the kinetics or the equilibrium of the wetting process is the controlling factor. Such a study would allow a comparison in order to see if the same molecular structure which provides the most efficient wettability decrease as measured by the initial water contact angle also is the one which exhibits the smallest contact angle decrease with time.

The fatty acid vapor pressures need to be determined at the temperatures used for adsorption, leading to adsorption isotherms over a partial pressure range. These data are required in order to perform a thorough kinetic study. In conjunction with this an investigation of the reactions occurring at the solid-vapor interface is needed in order to determine an Arrhenius energy of activation. The monomer-dimer equilibrium on the cellulose suface needs to be examined.

The reaction rate must be increased if this technqiue is expected to be commercially feasible. Possibilities include higher adsorption temperatures and an alum pretreatment. Once some of these fundamental concepts have been examined, the door will be open for an in-depth probe of vapor phase sizing of a paper substrate.

NOMENCLATURE

A	Angstrom unit, 10^{-8} cm
C	Celsius
C.L.	confidence limits
cpm	counts per minute
DP	degree of polymerization
dpm	disintegrations per minute
f_1	roughness factor, dimensionless
f_2	porosity factor, dimensionless
F	Fahrenheit
GLC	gas-liquid chromatography
l_f	molecular chain length, A
LMWS	low molecular weight spreadable
M	molar
mCi/mM	millicuries/millimole
MIR	multiple internal reflectance
o.d.	ovendry
POML	planar oriented monolayer
ppm	parts per million
R	roughness factor, dimensionless
RH	relative humidity
SMM	sodium methoxide-methanol
W_A	work of adhesion, ergs/cm^2
W_C	work of cohesion, ergs/cm^2
W_{sl}	reversible work of adhesion at the solid-liquid interface, ergs/cm^2
WAN	water-alcohol-nonpolar

γ_c Zisman's critical surface tension, dynes/cm

γ_i^d dispersion force component of the surface free energy of substance $\underline{i}$, ergs/cm^2

γ_i^p polar component of the surface free energy of substance $\underline{i}$, ergs/cm^2

γ_{lv} liquid-vapor interfacial free energy, ergs/cm^2

$\gamma_s{}^o$ solid-vacuum surface free energy, ergs/cm^2

γ_{sl} solid-liquid interfacial free energy, ergs/cm^2

γ_{sv} solid-vapor interfacial free energy, ergs/cm^2

θ contact angle, degrees

θ_A apparent advancing contact angle, degrees

θ_o real contact angle, degrees

π_e equilibrium film pressure of adsorbed vapor, ergs/cm^2

Φ a constant defined by $4(V_a V_b)/(V_a^{1/3} + V_b^{1/3})^2$, where V_a and V_b are molar volumes, dimensionless

ACKNOWLEDGMENTS

LITERATURE CITED

1. Adam, N. K. The physics and chemistry of surfaces. 3rd ed. p. 169, London, Oxford University Press, 1941.

2. Zettlemoyer, A. C., Am. Scientist 47:216-33(June, 1959).

3. Fox, H. W., and Zisman, W. A., J. Colloid Sci. 5(6):514-31(Dec., 1950).

4. Bernett, M. K., and Zisman, W. A., J. Phys. Chem. 71(7):2075-82(June, 1967).

5. Petke, F. D., and Ray, B. R., J. Colloid Interface Sci. 31(2):216-27(Oct., 1969).

6. Shafrin, E. G., and Zisman, W. A., J. Phys. Chem. 76(22):3259-66(Oct., 1972).

7. Zisman, W. A. Relation of equilibrium contact angle to liquid and solid constitution. In Advances in chemistry, Series No. 43. p. 1-51. American Chemical Society, 1964.

8. Bernett, M. K., and Zisman, W. A., J. Colloid Interface Sci. 28(2):243-49 (Oct., 1968).

9. Swanson, J. W., and Becher, J. J., Tappi 49(5):198-202(May, 1966).

10. Glossman, N., Tappi 50(5):224-6(May, 1967).

11. Swanson, J. W., and Cordingly, S., Tappi 42(10):812-19(Oct., 1959).

12. Bartell, F. E., and Ray, B. R., J. Am. Chem. Soc. 74(3):778-83(Feb. 5, 1952).

13. Luner, P., and Sandell, M. A., J. Polymer Sci., Part C, (28):115-42(1969).

14. Fowkes, F. M., Ind. Eng. Chem. 56(12):40-52(Dec., 1964).

15. Girifalco, L. A., and Good, R. J., J. Phys. Chem. 61(7):904-9(July, 1957).

16. Owens, D. K., and Wendt, R. C., J. Appl. Polymer Sci. 13(8):1741-7(Aug., 1969).

17. Wu, S., J. Polymer Sci., Part C, (34):19-30(1971).

18. Langmuir, I., Met. Chem. Eng. 15:468-70(1916).

19. Langmuir, I. In Holmes' Colloid symposium monograph. Vol. III. p. 49-75. New York, The Chemical Catalogue Company, Inc., 1925.

20. Langmuir, I. Collected works of Irving Langmuir. New York, Pergamon Press, 1960.

21. Young, T., Phil. Trans. Roy. Soc. (London), 95:65(1805).

22. Johnson, R. E., J. Phys. Chem. 63(10):1655-8(Oct., 1959).

23. Lester, G. R., J. Colloid Sci. 16(4):315-26(Aug., 1961).

24. Bangham, D. H., and Razouk, R. I., Trans. Faraday Soc. 33:145-72(1937).

25. Bangham, D. H., Trans. Faraday Soc. 33:805-11(1937).

26. Fowkes, F. M. In Marchessault and Skaar's Surfaces and coatings related to paper and wood. Chap. 5. Syracuse University Press, 1967. 507 p.

27. Dupre, A. Theorie mecanique de la chaleur. p. 368-9. Paris, 1869.

28. Wenzel, R. N., Ind. Eng. Chem. 28(8):988-94(Aug., 1936).

29. Cassie, A. B. D., and Baxter, S., Trans. Faraday Soc. 40:546-51(1944).

30. Cassie, A. B. D., Discussions Faraday Soc. 3:11-16(1948).

31. Bartell, F. E., and Shepard, J. W., J. Phys. Chem. 57(1):211-15(Feb., 1953).

32. Tamai, Y., and Aratani, K. J., J. Phys. Chem. 76(22):3267-71(Oct., 1972).

33. Herzberg, W. J., Marian, J. E., and Vermeulen, T., J. Colloid Interface Sci. 33(1):164-71(May, 1970).

34. Dettre, R. H., and Johnson, R. E. Contact angle hysteresis — study of an idealized rough surface. In Advances in chemistry, Series No. 43. p. 112-35. American Chemical Society, 1964.

35. Dettre, R. H., and Johnson, R. E. Contact angle hysteresis — contact angle measurements on rough surfaces. In Advances in chemistry, Series No. 43. p. 136-44. American Chemical Society, 1964.

36. Dettre, R. H., and Johnson, R. E., J. Phys. Chem. 68(7):1744-50(July, 1964).

37. Dettre, R. H., and Johnson, R. E., J. Phys. Chem. 69(5):1507-15(May, 1965).

38. Ruch, R. J., and Bartell, L. S., J. Phys. Chem. 64(5):513-19(May, 1960).

39. Bartell, L. S., and Ruch, R. J., J. Phys. Chem. 60(9):1231-4(Sept., 1956).

40. Weiser, H. B. Colloid chemistry. 2nd ed. p. 68. New York, John Wiley and Sons, 1948.

41. Timmons, C. O., and Zisman, W. A., J. Colloid Interface Sci. 22(2):165-71 (Aug., 1966).

42. Yiannos, P. N. Molecular reorientation of some fatty acids when in contact with water. Doctor's Dissertation. Appleton, Wisconsin, The Institute of Paper Chemistry, 1960. 115 p.

43. Herzberg, W. J., and Marian, J. E., J. Colloid Interface Sci. 33(1):161-3 (May, 1970).

44. Mack, G. L., J. Phys. Chem. 40(2):159-67(Feb., 1936).

45. Neumann, A. W., Haage, G., and Renzow, D., J. Colloid Interface Sci. 35(3): 379-85(March, 1971).

46. Fowkes, F. M., and Harkins, W. D., J. Am. Chem. Soc. 62:3377-86(Dec., 1940).

47. Adam, N. K., and Elliot, G. E. P., J. Chem. Soc. 1962:2206-9.

48. Johnson, R. E., and Dettre, R. H. Surface and colloid science. Vol. 2. p. 144. E. Matijevic, ed. New York, Wiley-Interscience, 1969.

49. Ellison, A. H., and Zisman, W. A., J. Phys. Chem. 58(3):260-5(March, 1954).

50. Fox, H. W., and Zisman, W. A., J. Colloid Sci. 7(4):428-42(Aug., 1952).

51. Hoernschemeyer, D., J. Phys. Chem. 70(8):2628-33(Aug., 1966).

52. Bernett, M. K., and Zisman, W. A., J. Phys. Chem. 63(8):1241-6(Aug., 1959).

53. Langmuir, I., J. Chem. Phys. 1(11):756-76(Nov., 1933).

54. Bigelow, W. C., and Brockway, L. O., J. Colloid Sci. 11(1):60-8(Feb., 1956).

55. Brockway, L. O., and Jones, R. L. An electron microscopic investigation of the adsorption of long chain fatty acid monolayers on glass. In Advances in chemistry, Series No. 43. p. 275-94. American Chemical Society, 1964.

56. Shafrin, E. G., and Zisman, W. A. Monomolecular layers. p. 129-60. H. Sobotka, ed. Wash., D.C., AAAS Symposium Publication, 1954.

57. Bartell, L. S., and Ruch, R. J., J. Phys. Chem. 63(7):1045-9(July, 1959).

58. Shafrin, E. G., and Zisman, W. A., J. Colloid Sci. 7(2):166-77(April, 1952).

59. Langmuir, I., Science (2266):493-500(June 3, 1938).

60. Rideal, E., and Tadayon, J., Proc. Royal Soc. (London) A225(1162):346-56 (Sept. 14, 1954).

61. Yiannos, P. N., J. Colloid Sci. 17(4):334-47(April, 1962).

62. Young, J. E., Aust. J. Chem. 8(2):173-93(May, 1955).

63. Hasegawa, M., and Low, M. J. D., J. Colloid Interface Sci. 30(3):378-86 (July, 1969).

64. Clint, J. H., J. Chem. Soc., Faraday Trans. I. 68(12):2239-46(Dec., 1972).

65. Girifalco, L. A., and Good, R. J., J. Phys. Chem. 62(11):1418-21(Nov., 1958).

66. Girifalco, L. A., and Good, R. J., J. Phys. Chem. 64(5):561-5(May, 1960).

67. Fowkes, F. M., J. Phys. Chem. 66(2):382(Feb., 1962).

68. Fowkes, F. M., J. Phys. Chem. 67(12):538-41(Dec., 1963).

69. London, F., Trans. Faraday Soc. 33:8-26(1937).

70. Fowkes, F. M. Predicting attractive forces at interfaces. In Chemistry and physics of interfaces. Vol. 2. p. 154-67. American Chemical Society, 1971.

71. Adamson, A. W. Physical chemistry of surfaces. 2nd ed. Chap. 5. New York, Interscience, 1960. 630 p.

72. Good, W. R., J. Colloid Interface Sci. 44(1):63-71(July, 1973).

73. Panzer, J., J. Colloid Interface Sci. 31(2):216-27(Oct., 1969).

74. Gordon, J. L., Encyclopedia of polymer science and technology. Vol. 3. p. 833. New York, Wiley, 1965.

75. Meyer, R. F., and Wagner, R. E., J. Phys. Chem. 70(10):3162-8(Oct., 1966).

76. Jayme, G., and Balser, K., Papier 18(12):746-58(1964).

77. Stone, J. E., Treiber, E., and Abrahamson, B., Tappi 52(1):108-10(Jan., 1969).

78. Ferris, J. L. The wettability of cellulose film as affected by vapor phase adsorption of amphipathic molecules. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1974. 154 p.

79. Browning, B. L. Methods in wood chemistry. Vol. II. p. 494. New York, Interscience, 1967.

80. Borgin, K., Norsk Skogind. 13:81-92(March, 1959).

81. Borgin, K., Norsk Skogind. 13:429-42(Nov., 1959).

82. Borgin, K., Norsk Skogind. 14:485-95(Nov., 1960).

83. Borgin, K., Norsk Skogind. 15:384-91(Sept., 1961).

84. Swanson, J. W. Unpublished work, 1965.

85. Bauer, N., and Lewin, S. Z. In Weissberger's Techniques of organic chemistry. Vol. 1. Part 1. p. 136. New York, Interscience, 1959.

86. Schenkel, J. H., and Kitchener, J. A., Nature 182:131(July 12, 1958).

87. Gaines, G. L., J. Colloid Sci. 15(4):321-39(Aug., 1960).

88. Lund, H., and Bjerrum, J., Ber. 64:210(1931); CA 25:3310(1931).

89. Peebles, L. H., Clark, J. T., and Stockmayer, W. H., J. Am. Chem. Soc. 82: 4780-5(Sept. 20, 1960).

90. Neumann, R. D. The properties, structure, and multilayer deposition of stearic acid-calcium stearate monolayers. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1973. 206 p.

91. Wilks, P. A., Jr., Appl. Spectry. 23(1):63-6(1969).

92. Gilby, A. C., Cassell, J., and Wilks, P. A., Jr., Appl. Spectry. 24(5): 530-43(1970).

93. White, M. L. The detection and control of organic contaminants. In Goldfinger's Clean surfaces. p. 361. New York, Marcel Dekker, 1970.

94. Swanson, J. W. A-235 Colloid chemistry class notes. Chap. I. p. 29. 1972.

95. Goddard, E. D., Smith, S. R., and Kao, O., J. Colloid Interface Sci. 21(3): 320-30(March, 1966).

96. Havinga, E., and deWall, J., Chem. Weekblad 34:694-700(1937).

97. Reis, H. E., Proc. Am. Petrol. Inst., Sect. III, 42:152-62(1962).

98. Reis, H. E., and Cook, R. D., J. Colloid Sci. 9(6):535-46(Dec., 1954).

99. Guide, R. G. A study of the sodium aluminate-abietate size precipitates. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1959. 105 p.

100. Cook, R. D., and Reis, H. E., J. Phys. Chem. 63(2):226-33(Feb., 1959).

101. Timmons, C. O., J. Colloid Interface Sci. 43(1):1-9(April, 1973).

102. Swanson, J. W. A-235 Colloid chemistry class notes. Chap. V. p. 4. 1972.

103. Archer, W. L., and Mason, S. G., Pulp and Paper Research Institute of Canada, Quarterly Report, Oct.-Dec., 1948.

104. Bucher, N., Papier (4):123-30(April, 1960).

105. Kunz, W. B., and Cornwell, R. T. K., Tappi 45(7):583-8(July, 1962).

106. Merchant, M. V., Tappi 40(9):771-81(Sept., 1957).

107. Hayward, D. O., and Trapnell, B. M. W. Chemisorption. 2nd ed. Chap. III. p. 67-140. Washington, D.C., Butterworths, 1964.

108. Allen, G., and Caldrin, E. F., Quart. Rev. 7:255-78(1953).

109. Levine, O., and Zisman, W. A., J. Phys. Chem. 61(8):1068-77(Aug., 1957).

110. Fox, H. W., and Zisman, W. A., J. Colloid Sci. 7(2):109-21(April, 1952).

111. Smith, T., J. Opt. Soc. Am. 58(8):1069-79(Aug., 1968).

112. Mizushima, S. Structure of molecules and internal rotation. New York, Academic Press, 1954. 254 p.

113. Pauling, L., Phys. Res. 36:430-43(Aug. 1, 1930).

114. Rideal, E., and Tadayon, J., Proc. Royal Soc. (London) A225(1162):357-61 (Sept. 14, 1954).

APPENDIX I

ANALYSIS OF THE FATTY ACIDS

A. METHOD OF ANALYSIS — Gas-Liquid Chromatography

B. TESTING CONDITIONS

Column: 8% EGSS-X (Applied Science Lab) on Gas Chrom Q 100/120
         Stainless steel column, 6 feet x 1/8 inch

Temperature: Column   — 210°C
              Injector — 230°C
              Detector — 250°C

Carrier gas: Helium at 30 ml/min
              H_2 flame detector

C. ANALYSIS

	Stearic, %	Margaric, %	Palmitic, %
Radioactive	99.9	0.0	0.1
Nonradioactive	99.64	0.08	0.28

	Behenic, %	Arachidic, %	Lignoceric, %
Radioactive	98.35	0.41	0.73
Nonradioactive	99.22	0.04	0.74

	Isostearic, %	Isopalmitic, %
Radioactive	99.76	0.24
Nonradioactive	99.9+	0.0

APPENDIX II

OPERATING VOLTAGE OF NUCLEAR-CHICAGO COUNTING EQUIPMENT

A. EXPERIMENTAL CONDITIONS

Model D-47 gas flow detector
Micromil window in place
β-Proportional operation
Gas flow: 50 cc/min

B. EXPERIMENTAL DATA

Voltage	CPM		Voltage	CPM
1800	41		2075	613
1900	231		2100	626
1950	349		2125	668
2000	470		2150	723
2025	549		2175	940
2050	564		2200	2226

C. PLOT OF DATA
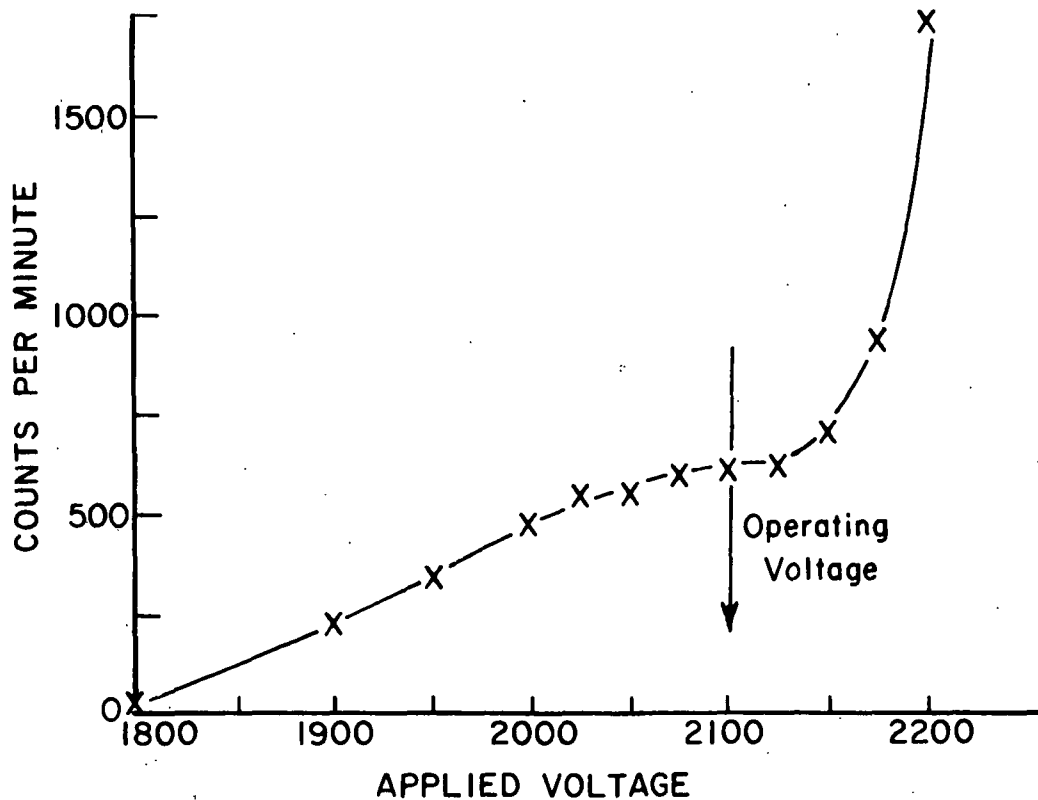
Figure 23. Cpm-applied Voltage Curve

APPENDIX III

C-14 ACID COUNTING EFFICIENCIES

A. EXPERIMENTAL

The counting efficiency of each acid was determined on the smooth side of cellulose film. One milliliter of the standard solution (1 mCi/100 ml benzene) was diluted to 100 ml with benzene. Then 10 µl of this solution was placed on the cellulose film, the benzene was allowed to evaporate, and the film was counted. Sufficient films were counted in order to average the small errors in transferring the labeled acid to the cellulose film.

$$1 \text{ mCi} = 2.22 \times 10^9 \text{ dpm}$$
$$1 \text{ ml diluted solution} = 2.22 \times 10^5 \text{ dpm}$$
$$10 \text{ µl } (0.01 \text{ ml}) = 2.22 \times 10^3 \text{ dpm}$$

B. EXPERIMENTAL DATA

Stearic Acid		Behenic Acid		Isostearic Acid	
Cpm	Efficiency, %	Cpm	Efficiency, %	Cpm	Efficiency, %
417	18.8	436	19.6	431	19.4
426	19.2	408	18.3	424	19.1
510	20.9	423	19.0	413	18.6
445	20.1	456	20.5	422	19.0
396	17.8	390	17.5	404	18.2
409	18.4	401	18.0	418	18.8
432	19.4	475	21.4	433	19.5
447	18.9	438	19.7	420	18.9
473	20.2	448	20.2	422	19.0
422	17.8	441	19.8	411	18.5

Mean is 19.2% ± 0.7%.   Mean is 19.4% ± 0.8%.   Mean is 19.8% ± 0.3%.

APPENDIX IV

ELEMENTAL ANALYSIS OF CELLULOSE FILMS

A. METHOD OF ANALYSIS — Emission Spectroscopy
Ash (500°C), 0.12%

B. RESULTS

Element	Ppm in Ash
Aluminum	8.8
Barium	1.1
Boron	7.0
Calcium	18.0
Chromium	0.32
Copper	6.2
Iron	12.0
Lead	0.48
Magnesium	10.0
Manganese	4.7
Nickel	17.0
Silicon	26.0
Silver	0.087
Sodium	520.0
Titanium	0.87

Total sulfur: 0.014% (total film basis)

APPENDIX V

FILM DEVELOPING PROCEDURES

A. FILM AREA MEASUREMENT

Film: Kodak Panatomic-X

Developer: Kodak HC-110 liquid developer (diluted 1:7)

    1 minute continuous agitation
    3.5 minutes agitation 10 sec out of every 30 sec
    4.5 minutes total

Stop bath: 20 sec rinse in 28% acetic acid

Fixer: Kodak Rapid Photographic Fixer

    0.5 minute continuous agitation
    4.5 minutes no agitation
    5.0 minutes total

Wash: running tap water, 68°F, 10 min
       Kodak Photo-Flo 200, 30 sec

Dry: 10 min in drying cabinet

B. CONTACT ANGLE MEASUREMENT

Film: Kodak High Contrast

Developer: Kodak D-19 liquid developer

    1 minute continuous agitation
    3.5 minutes agitation 10 sec out of every 30 sec
    4.5 minutes total

Fixer: Kodak Rapid Photographic Fixer

    5 min total, no agitation

Wash: running tap water, 68°F, 10 min
       Kodak Photo-Flo 200, 30 sec

Dry: 10 min in drying cabinet

C. AUTORADIOGRAMS

Film: Kodak No-Screen X-Ray Film

Developer: Kodak Liquid X-Ray Developer

    1 minute continuous agitation
    <u>4</u> minutes agitation 15 sec out of every min
    5 minutes total

Stop bath: Kodak X-Ray Indicator and stop bath

    1 minute with continuous agitation
    <u>1</u> minute with agitation last 15 sec
    2 minutes total

Fixer: Kodak Liquid X-Ray Fixer

    2 minutes continuous agitation
    <u>8</u> minutes agitation 15 sec out of every min
    10 minutes total

Wash: running tap water, 68°F, 20 min
      Kodak Photo-Flo 200, 30 sec

Dry: 30 min in drying cabinet

APPENDIX VI

STANDARD C-14 SOLUTIONS OF THE FATTY ACIDS

Desire 10,000 cpm/in.^{2}
Dpm = cpm/counting efficiency

	Stearic	Behenic	Isostearic
Cross-sectional area, A^2/molecule	20	20	32
Counting efficiency, %	19.2	19.4	18.9
Dpm/in.^{2} x 10^4 (for 10,000 cpm/in.^{2})	5.21	5.15	5.29
For 1 POML/in.^{2}:			
molecules/in.^{2} x 10^{15}	3.22	3.22	2.01
mmole/in.^{2} x 10^{-6}	5.35	5.35	3.35
Specific activity (undiluted acid), mCi/mM	58	58	58
Dpm/in.^{2} x 10^5	6.88	6.88	4.31
Dilution factor	13.21	13.55	8.15
Specific activity following dilution, mCi/mM	4.39	4.34	7.12
1 POML equals, cpm/in.^{2}	10010	10001	9999

APPENDIX VII

ACID REQUIRED TO SATURATE VAPOR IN ADSORPTION CHAMBER

Inside measurements of adsorption cassette: 3 in. x 7 in. x 3/16 in. = 64.5 cm^3

Vapor pressure (stearic acid) at 85°C ($\underline{78}$) = $\underline{ca}$. 7.94 x 10^{-5} mm Hg

Vapor pressure (stearic acid) at 105°C ($\underline{78}$) = $\underline{ca}$. 6.31 x 10^{-4} mm Hg

Assume ideal gas law:

$$\underline{n} = \frac{PV}{RT} = \frac{(7.94 \times 10^{-5} \text{ mm Hg}) (64.5 \text{ cm}^3) (10^{-3} \text{ l/cm}^3)}{(62.36 \frac{\text{mm Hg} \cdot \text{l}}{\text{g moles }°K}) (358°K)}$$

$$= 2.29 \times 10^{-7} \text{ mmole at } 85°C$$

$$= 1.73 \times 10^{-6} \text{ mmole at } 105°C$$

Acid required for 1 POML/in.^{2}:

$$\frac{\text{molecule}}{20 \times 10^{-16} \text{ cm}^2} \times \frac{6.45 \text{ cm}^2}{\text{in.}^2} \times \frac{\text{mmole}}{6.023 \times 10^{20} \text{ molecule}} = 5.35 \times 10^{-6} \frac{\text{mmole}}{\text{in.}^2}$$

Thus: $\dfrac{1.73 \times 10^{-6} \text{ mmole}}{5.35 \times 10^{-6} \text{ mmole/in.}^2} = 0.323 \text{ in.}^2$

Therefore $\underline{ca}$. 33% of a planar oriented monolayer of stearic acid is in the vapor at 105°C (basis is one square inch of planar surface).

APPENDIX VIII

COMPUTER PROGRAMS

```
C       PROGRAM FARDET. DETERMINES THE AREA OF CELLULOSE FILMS USING A
C       METAL FILM STANDARD. DATA IS PUNCHED ON THE MICROCOMPARATOR.
C       DATA IS READ IN THE FOLLOWING ORDER   (1) EXPERIMENTAL RUN
C       CODE(15A4), (2) NUMBER(I2) OF FILMS (DO EACH IN DUPLICATE),
C       (3) DATA CARDS - STANDARD  FIRST(FOUR 2F5.0 FIELDS FOLLOWED BY
C       AN A4 CODE ID FOR THE STANDARD), THEN THE FILM(SIX 2F5.0 FIELDS,
C       THEN FOUR 2F5.0 FIELDS FOLLOWED BY AN A4 CODE JD FOR THE FILM).
C       (4) THEN  A CONTINUATION INDEX--- (0)-STOP,(1)-CONTINUE WITH
C       CODE CARD, ETC.
C**********************************************************************
        DIMENSION CODE(15),X(99),Y(99),A(99),B(99),SLENGT(40),SWIDTH(40)
        DIMENSION SAREA(40),FLENGT(40),FWIDTH(40),FAREA(40),ACAREA(40)
      6 READ(5,100)CODE
    100 FORMAT(15A4)
        WRITE(6,101)CODE
    101 FORMAT(1H1,'AREA OF FILMS FOR ',15A4)
        READ(5,102)NUMBER
    102 FORMAT(I2)
        DO 2 J=1,NUMBER
        READ(5,103) (A(I),B(I),I=1,4),ID
C       READ(5,104) (A(I),B(I),I=1,6)
C       READ(5,105) (A(I),B(I),I=7,10),ID
    103 FORMAT(8F5.0,A4)
C       READ(5,103) (X(I),Y(I),I=1,4),JD
        READ(5,104) (X(I),Y(I),I=1,6)
        READ(5,105) (X(I),Y(I),I=7,10),JD
    104 FORMAT(12F5.0)
    105 FORMAT(8F5.0,A4)
        SLENGT(J)=((A(2)-A(1))+(A(3)-A(4)))/2.*12000.
        SWIDTH(J)=((B(3)-B(2))+(B(4)-B(1)))/2.*12000.
C       SLENGT(J)=((A(4)+A(5)+A(6))-(A(1)+A(10)+A(9)))/3.*12000.
C       SWIDTH(J)=((B(9)+B(8)+B(7)+B(6))-(B(1)+B(2)+B(3)+B(4)))/4.*12000.
        SAREA(J)=SLENGT(J)*SWIDTH(J)
C       FLENGT(J)=((X(2)-X(1))+(X(3)-X(4)))/2.*12000.
C       FWIDTH(J)=((Y(3)-Y(2))+(Y(4)-Y(1)))/2.*12000.
        FLENGT(J)=((X(4)+X(5)+X(6))-(X(1)+X(10)+X(9)))/3.*12000.
        FWIDTH(J)=((Y(9)+Y(8)+Y(7)+Y(6))-(Y(1)+Y(2)+Y(3)+Y(4)))/4.*12000.
        FAREA(J)=FLENGT(J)*FWIDTH(J)
C       STANDARD IS STARRETT - AREA IS 0.5065 SQ. IN.
        ACAREA(J)=(FAREA(J)/SAREA(J))*0.5065
        WRITE(6,106)JD,ACAREA(J)
    106 FORMAT(1H0,'AREA OF FILM ',A4,' IS ',F6.4,' SQ. INCHES')
      2 CONTINUE
        WRITE(6,107)ID
    107 FORMAT(1H0,'STANDARD ID IS ',A4)
        READ(5,108)MORE
    108 FORMAT(I1)
        IF(MORE-1)7,8,7
      8 GO TO 6
      7 CALL EXIT
        END
```

APPENDIX VIII (Continued)

```
C      PROGRAM CONANG. CALCULATES CONTACT ANGLES FROM DROP PROFILE INPUT
C      FROM THE MICROCOMPARATOR. DATA CARD CONTAINS THREE 2F5.0 FIELDS
C      (EACH FIELD HAS AN X AND A Y VALUE) FOLLOWED BY AN A4 FIELD FOR TH
C      DROP ID. THE FIRST CARD(CODE) IDENTIFIES THE OPERATION(15A4).
C      SECOND CARD CONTAINS THE NUMBER OF MEASUREMENTS(I2). THIRD, ETC.
C      CONTAIN THE DATA. THEN CARD(I1) WITH THE FOLLOWING  0-GOES TO
C      BEGINNING, BEGINS WITH CODE CARD  1-ANOTHER DATA SET, BEGINS WITH
C      NUMBER OF MEASUREMENTS  2-TERMINATES PROGRAM
       DIMENSION X(40), Y(40), VOLUME(40), ANGLE(40), SUMSQ(40),PCVOL(40)
       DIMENSION CODE(15)
    99 READ(5,102) CODE
       WRITE(6,100)
   100 FORMAT(1H0,'R.E. SWANSON--PROGRAM CONANG')
       WRITE(6,101) CODE
   101 FORMAT(1H1,'CONTACT ANGLE CALCULATIONS FOR ',15A4)
   102 FORMAT(15A4)
    98 WRITE(6,103)
       WRITE(6,104)
   103 FORMAT(1H0,25X,'DROP COORDINATES',19X,'INCHES',3X,'INCHES',1X,
      1'MICROLITERS')
   104 FORMAT(1H ,2X,'DROP',5X,'X(1)',4X,'Y(1)',4X,'X(2)',4X,'Y(2)',4X,
      1'X(3)',4X,'Y(3)',6X,'BASE',4X,'HEIGHT',3X,'VOLUME',3X,'PVOL',5X,
      1'CONTACT ANGLE')
       READ(5,105) NUMBER
   105 FORMAT(I2)
       IA=0.
       DO 10 I=1,NUMBER
       READ(5,106)  (X(J),Y(J), J=1,3), ID
   106 FORMAT(6F5.0,A4)
       BASLIN=(Y(1)+Y(3))/2.
       HAFBAS=(X(3)- X(1))/2.
       BASE=2.*HAFBAS
       HEIGHT=Y(2)-BASLIN
       VOLUME(I)=3.14159*HEIGHT*(3.*HAFBAS**2+HEIGHT**2)*16387.064/6.
       VOLUME(I)=VOLUME(I)/((12000.**3)*(5.51167**3))
       PCVOL(I)=VOLUME(I)/VOLUME(1)*100.
       ANGLE(I)=(ATAN(HEIGHT/HAFBAS))*2.*57.29577
       BASE=BASE/(12000.*5.51167)
       HEIGHT=HEIGHT/(12000.*5.51167)
       WRITE(6,107) ID,X(1),Y(1),X(2),Y(2),X(3),Y(3),BASE,HEIGHT,
      1VOLUME(I),PCVOL(I),ANGLE(I)
   107 FORMAT(1H0,2X,A4,4X,6(F6.0,2X),2(F8.4,1X),F8.4,2X,F6.2,7X,F6.2)
       IA=IA+1
    10 CONTINUE
       IA=NUMBER
       IB=IA-1
       SUMANG=0.
       DO 20 I=1,NUMBER
    20 SUMANG=SUMANG+ANGLE(I)
       AVERAN =SUMANG/IA
       TSUMSQ=0.
       DO 30 I=1,NUMBER
       SUMSQ(I)=(ANGLE(I)-AVERAN)**2
    30 TSUMSQ=TSUMSQ+SUMSQ(I)
       STDEV=SQRT(TSUMSQ/IB)
       ZA=IA
       ERROR=STDEV/SQRT(ZA)
       T=(.856278+IA*(.0703808+1.96*IA))/(.40068466-IA*(1.1734961-IA))
       CONLIM=T*ERROR
       WRITE(6,108) AVERAN
       WRITE(6,110) NUMBER,STDEV
       WRITE(6,120) CONLIM
   108 FORMAT(1H0,2X,'AVERAGE OF THE CONTACT ANGLES  =  'F6.2)
   110 FORMAT(1H0,2X,'STANDARD DEVIATION OF THE' I2  ' CONTACT '
      1'ANGLES  =  'F6.2)
   120 FORMAT(1H0,2X,'95 PER CENT CONFIDENCE LIMITS ARE +/- ' F6.2)
       READ(5,109) MORE
   109 FORMAT(I1)
       IF(MORE-1)40,41,42
    40 GO TO 99
    41 GO TO 98
    42 GO TO 77
    77 CALL EXIT
       END
```

APPENDIX VIII (Continued)

```
C       PROGRAM SEPCAL. THIS PROGRAM IS USED TO CALCULATE THE FOWKES,
C       OWENS-WENDT, AND WU SURFACE ENERGY PARAMETERS FROM CONTACT ANGLE
C       DATA FROM TWO OR THREE LIQUIDS. FIRST DATA CARD CONTAINS A NUMBER
C       (I1) SIGNIFYING THE NUMBER OF LIQUIDS, FOLLOWED BY A CARD(CODE)
C       IDENTIFYING THE OPERATION(10A4), FOLLOWED BY CARDS CONTAINING THE
C       CONTACT ANGLES(F6.2).
C****************************************************************************
        DIMENSION STD(5),STP(5),STT(5),THETA(5),SEPFD(5),ZNUM1(3,3)
        DIMENSION DENOM1(3,3),TERM1(3,3),ZNUM2(3,3),DENOM2(3,3)
        DIMENSION TERM2(3,3),SEPOWD(3,3),            TERM3(3,3),ZNUM4(3,3)
        DIMENSION DENOM4(3,3),TERM4(3,3),SRSEPP(3,3),SEPOWP(3,3)
        DIMENSION TSEPOW(3,3),FPOL(3,3),FACT(5),A(5),B(5),C(5),D(5)
        DIMENSION DENOM3(3,3),SEPWUD(3,3),SEPWUP(3,3),SEPWUT(3,3)
        DIMENSION FPOLWU(3,3),SRSEPO(3,3),CODE(10)
C       THE FOLLOWING INPUTS ARE (1)=WATER  (2)=METHYLENE IODIDE
        READ(5,101)N
101     FORMAT(I1)
        STD(1)=21.8
        STP(1)=51.0
C       STD(2)=49.5
C       STP(2)=1.3
        STD(2)=50.38
        STP(2)=0.38
        DO 10 I=1,N
10      STT(I)=STD(I)+STP(I)
        READ(5,102)CODE
102     FORMAT(10A4)
        DO 20 I=1,N
20      READ(5,103)THETA(I)
103     FORMAT(F6.2)
        WRITE(6,105)
        WRITE(6,104)CODE
        WRITE(6,178)STD(2),STP(2)
178     FORMAT(1H ,'MEI DISPERSION COMPONENT = ',F6.2,' MEI POLAR '
       1'COMPONENT = ',F6.2)
        WRITE(6,177)THETA(1),THETA(2)
105     FORMAT(1H1,'R.E. SWANSON --- PROGRAM SEPCAL ')
104     FORMAT(1H0,'SURFACE ENERGY CALCULATIONS FOR ',10A4)
177     FORMAT(1H0,' WATER = ',F6.2,'    METHYLENE IODIDE = ',F6.2)
        DO 30 I=1,N
30      THETA(I)=THETA(I)/57.29577
C       FOWKES SOLUTION
        DO 40 IX=1,N
40      SEPFD(IX)=(((COS(THETA(IX))+1.)*STT(IX))/(2.*SQRT(STD(IX))))**2.
C       OWENS-WENDT SOLUTION
        IY=1
        IZ=2
41      ZNUM1(IY,IZ)=(STT(IY)*(1.+COS(THETA(IY))))
        DENOM1(IY,IZ)=2.*(SQRT(STD(IY))-(SQRT(STP(IY))*SQRT(STD(IZ))))/
       1SQRT(STP(IZ)))
        TERM1(IY,IZ)=ZNUM1(IY,IZ)/DENOM1(IY,IZ)
        ZNUM2(IY,IZ)=(SQRT(STP(IY))*STT(IZ)*(1.+COS(THETA(IZ))))
        DENOM2(IY,IZ)=2.*((SQRT(STD(IY))*SQRT(STP(IZ)))-(SQRT(STP(IY))*
       1SQRT(STD(IZ))))
        TERM2(IY,IZ)=ZNUM2(IY,IZ)/DENOM2(IY,IZ)
        SRSEPD(IY,IZ)=TERM1(IY,IZ)-TERM2(IY,IZ)
        SEPOWD(IY,IZ)=(SRSEPD(IY,IZ))**2.

        DENOM3(IY,IZ)=2.*SQRT(STP(IY))*(1.-(SQRT(STD(IY))*SQRT(STP(IZ)))/
       1(SQRT(STP(IY))*SQRT(STD(IZ))))
        TERM3(IY,IZ)=ZNUM1(IY,IZ)/DENOM3(IY,IZ)
        ZNUM4(IY,IZ)=(SQRT(STD(IY))*STT(IZ)*(1.+COS(THETA(IZ))))
        DENOM4(IY,IZ)=2.*((SQRT(STP(IY))*SQRT(STD(IZ)))-(SQRT(STD(IY))*
       1SQRT(STP(IZ))))
        TERM4(IY,IZ)=ZNUM4(IY,IZ)/DENOM4(IY,IZ)
        SRSEPP(IY,IZ)=TERM3(IY,IZ)-TERM4(IY,IZ)
        SEPOWP(IY,IZ)=(SRSEPP(IY,IZ))**2.
        TSEPOW(IY,IZ)=SEPOWD(IY,IZ)+SEPOWP(IY,IZ)
        FPOL(IY,IZ)=SEPOWP(IY,IZ)/TSEPOW(IY,IZ)
        NN=N
        NN=NN+1
        IF(NN-4) 50,60,70
60      IY=1
        IZ=3
        GO TO 41
```

APPENDIX VIII (Continued)

```
   70  NN=NN-6
       IY=2
       IZ=3
       GO TO 41
   50  CONTINUE
       WRITE(6,106)(SEPFD(I),I=1,N)
  106  FORMAT(//,'FOWKES SOLUTION ',10X,'WATER-METHYLENE IODIDE',10X,
      1'DISPERSION COMPONENT = ',F4.1)
       WRITE(6,107) TSEPOW(1,2),SEPOWD(1,2),SEPOWP(1,2),FPOL(1,2)
  107  FORMAT(1HO,'OWENS-WENDT SOLUTION ',10X,'WATER-METHYLENE IODIDE',
      1/ 2X,'TOTAL SURFACE ENERGY PARAMETER = ',F4.1,/ 2X,
      2'DISPERSION COMPONENT = ',F4.1,/ 2X,'POLAR COMPONENT = ',F4.1,
      3/ 2X,'FRACTIONAL POLARITY = ',F4.2)
   C   WU SOLUTION
       DO 80 I=1,2
       FACT(I)=STT(I)*(1.+COS(THETA(I)))/4.
       A(I)=STD(I)+STP(I)-FACT(I)
       B(I)=STP(I)*(STD(I)-FACT(I))
       C(I)=STD(I)*(STP(I)-FACT(I))
       D(I)=FACT(I)*STD(I)*STP(I)
   80  CONTINUE
       I=1
       J=2
       KDEX=0
       NDEX=0
       IDEX=0
       GSP=100.
   67  GSD=((A(J)*D(I)-A(I)*D(J))/(A(J)*B(I)-A(I)*B(J)))-((A(J)*C(I)-
      1A(I)*C(J))/(A(J)*B(I)-A(I)*B(J)))*GSP
       SUM=A(I)*GSP*GSD+B(I)*GSD+C(I)*GSP-D(I)
       ABSUM=ABS(SUM)
       IF(KDEX-1)62,61,62
   62  IF(NDEX-1)63,64,63
   63  IF(ABSUM-SUM)64,61,64
   61  KDEX=1
       IF(ABSUM-SUM)27,27,29
   64  NDEX=1
       IF(ABSUM-SUM)29,29,27
   29  IDEX=1
       GO TO 28
   27  IF(IDEX-1)25,26,25
   25  GSP=GSP-1.0
       GO TO 67
   28  GSP=GSP+0.001
       GO TO 67
   26  SEPWUD(I,J)=GSD
       SEPWUP(I,J)=GSP
       SEPWUT(I,J)=GSP+GSD
       FPOLWU(I,J)=SEPWUP(I,J)/SEPWUT(I,J)
       WRITE(6,108)SEPWUT(1,2),SEPWUD(1,2),SEPWUP(1,2),FPOLWU(1,2)
  108  FORMAT(1HO,'WU SOLUTION ',10X,'WATER-METHYLENE IODIDE',/ 2X,
      1'TOTAL SURFACE ENERGY PARAMETER = ',F4.1,/ 2X,
      2'DISPERSION COMPONENT = ',F4.1,/ 2X,'POLAR COMPONENT = ',F4.1,
      3/ 2X,'FRACTIONAL POLARITY = ',F4.2)
       CALL EXIT
       END
```

APPENDIX IX

EXPERIMENTAL DATA

STEARIC ACID

EXPERIMENTAL DATA FOR FILM AD - TEMP 85 - TIME 16 HR   BACKGROUND = 47

ADSORPTION DATA   COUNTING STANDARD = 690

TOTAL ADSORPTION(CPM/SQUARE INCH)
8945. 15164. 9934. 16723. 14209. 9728. 11295.
13724. 12013.
MEAN IS 12415. +/- 2028.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
4315. 5271. 6271. 4959. 5224. 5939. 5922.
MEAN IS 5414. +/- 604.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
644. 621. 646. 566. 585. 605. 603.
MEAN IS 610. +/- 26.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
140. 132. 124.
MEAN IS 132. +/- 15.

QUANTITY BENZENE EXTRACTED   7001. +/- 1923.
QUANTITY WATER EXTRACTED   4804. +/- 464.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED   478. +/- 28.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
48.83 52.46 49.52 47.89 44.41 51.52 47.64
44.45 50.78 52.54 55.48 52.51
MEAN = 49.84 +/- 2.12

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
48.35 54.67 55.13 51.62 55.97 57.21 60.46
52.00 55.97 56.65 49.26 52.90
MEAN = 54.18 +/- 2.62
METHYLENE IODIDE CONTACT ANGLE
33.72 34.02 30.34 28.08 30.41 28.34 27.86
MEAN = 30.39 +/- 2.31

SURFACE ENERGY PARAMETER	OWENS-WENDT	WU
TOTAL ENERGY	55.50	63.20
POLARITY	0.28	0.32

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 26.25 +/- 3.24

STEARIC ACID

EXPERIMENTAL DATA FOR FILM AC - TEMP 85 - TIME 8 HR   BACKGROUND = 45

ADSORPTION DATA   COUNTING STANDARD = 727

TOTAL ADSORPTION(CPM/SQUARE INCH)
10296. 10913. 10380. 10763. 12581. 14282. 14161.
11343. 9970.
MEAN IS 11632. +/- 1244.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
3242. 3215. 3356. 4047. 3954. 3069. 2914.
MEAN IS 3400. +/- 388.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
303. 292. 347. 368. 423. 384. 308.
MEAN IS 346. +/- 43.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
156. 177. 149.
MEAN IS 161. +/- 27.

QUANTITY BENZENE EXTRACTED   8233. +/- 1182.
QUANTITY WATER EXTRACTED   3053. +/- 300.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED   186. +/- 46.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
38.44 41.32 39.34 40.33 40.14 38.56 40.94
40.84 41.58 36.79 39.41 42.88
MEAN = 40.05 +/- 1.04

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
46.39 43.42 42.46 45.56 46.05 43.05 45.29
36.97 41.15 43.46 43.43 36.20
MEAN = 42.78 +/- 2.07
METHYLENE IODIDE CONTACT ANGLE
25.40 22.41 25.10 26.15
MEAN = 24.76 +/- 2.27

SURFACE ENERGY PARAMETER	OWENS-WENDT	WU
TOTAL ENERGY	62.70	70.40
POLARITY	0.34	0.36

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 29.47 +/- 1.62

APPENDIX IX (Continued)

STEARIC ACID

EXPERIMENTAL DATA FOR FILM AK - TEMP 85 - TIME 24 HR

ADSORPTION DATA   COUNTING STANDARD = 649   BACKGROUND = 51

TOTAL ADSORPTION(CPM/SQUARE INCH)
22885. 20978. 21984. 19376. 20192. 22389. 25883.
17806. 22215.
MEAN IS 21523. +/- 1744.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
12210. 10215. 9391. 12337. 10318. 9802. 10833.
MEAN IS 10729. +/- 1024.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
1373. 1318. 1312. 1321. 1334. 1350. 1343.
MEAN IS 1336. +/- 19.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
548. 502. 528.
MEAN IS 526. +/- 42.

QUANTITY BENZENE EXTRACTED   10794. +/- 1758.
QUANTITY WATER EXTRACTED   9394. +/- 786.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED   810. +/- 24.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
57.84 59.15 58.66 60.83 59.76 59.13 59.85
57.17 58.52 60.32 58.46 59.10
MEAN = 59.07 +/- 0.65

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
58.77 60.53 59.96 57.94 58.41 61.44 60.48
61.18 60.32 61.00 58.18 58.35
MEAN = 59.71 +/- 0.81
METHYLENE IODIDE CONTACT ANGLE
27.57 28.39 27.32 29.50 28.33 27.57 30.45
33.00 33.64 29.42
MEAN = 29.52 +/- 1.58

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   53.00   60.70
POLARITY   0.23   0.28

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 26.98 +/- 2.60

STEARIC ACID

EXPERIMENTAL DATA FOR FILM AI - TEMP 85 - TIME 40 HR

ADSORPTION DATA   COUNTING STANDARD = 693   BACKGROUND = 49

TOTAL ADSORPTION(CPM/SQUARE INCH)
21668. 16803. 18303. 16021. 17037. 22606. 17553.
15899. 20044.
MEAN IS 18437. +/- 1849.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
12103. 9196. 9476. 12097. 10580. 9805. 9994.
MEAN IS 10464. +/- 1070.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
1471. 1406. 1477. 1483. 1475. 1582. 1481.
MEAN IS 1482. +/- 46.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
417. 396. 444.
MEAN IS 419. +/- 44.

QUANTITY BENZENE EXTRACTED   7973. +/- 1860.
QUANTITY WATER EXTRACTED   8982. +/- 822.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED   1063. +/- 50.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
74.17 72.01 75.68 72.41 71.15 68.31 69.26
69.65 75.83 74.68 68.14 75.47
MEAN = 72.73 +/- 2.86

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
66.83 64.27 64.44 65.48 64.98 67.61 63.65
65.56 64.79 64.68 66.02 64.30
MEAN = 65.22 +/- 0.72
METHYLENE IODIDE CONTACT ANGLE
31.90 32.10 33.99 30.14 32.35 32.81 30.68
30.43 32.37 33.45
MEAN = 32.02 +/- 0.90

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   49.70   57.30
POLARITY   0.19   0.26

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 27.31 +/- 2.49

APPENDIX IX (Continued)

STEARIC ACID

EXPERIMENTAL DATA FOR FILM AH - TEMP 85 - TIME 48 HR

ADSORPTION DATA   COUNTING STANDARD = 654   BACKGROUND = 49

TOTAL ADSORPTION(CPM/SQUARE INCH)
30057. 22229. 26060. 22208. 22379. 23873. 25583.
21282. 21380.
MEAN IS 23895. +/- 2175.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
18626. 15019. 11858. 16196. 16254. 14168. 14360.
MEAN IS 15212. +/- 1889.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
1931. 1982. 1925. 1816. 1936. 2012. 1838.
MEAN IS 1920. +/- 63.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
589. 583. 550.
MEAN IS 574. +/- 39.

QUANTITY BENZENE EXTRACTED   8683. +/- 2386.
QUANTITY WATER EXTRACTED   13292. +/- 1451.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 1346. +/- 68.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
76.86 69.63 70.88 67.20 72.70 77.49 69.60
67.59 65.08 70.90 70.57 67.35
MEAN = 70.49 +/- 3.07

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
69.20 64.77 67.38 65.16 69.91 70.41 66.67
69.01 71.67 68.70 69.48 68.32
MEAN = 68.39 +/- 1.30

METHYLENE IODIDE CONTACT ANGLE
34.04 31.50 33.42 31.03 31.27 29.97 33.04
31.38 32.85 30.87
MEAN = 31.94 +/- 0.92

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   48.40   55.80
POLARITY   0.16   0.24

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 27.40 +/- 2.12

STEARIC ACID

EXPERIMENTAL DATA FOR FILM AM - TEMP 85 - TIME 60 HR

ADSORPTION DATA   COUNTING STANDARD = 643   BACKGROUND = 52

TOTAL ADSORPTION(CPM/SQUARE INCH)
20813. 22196. 22323. 17645. 18644. 18342. 18956.
19530. 18367.
MEAN IS 19646. +/- 1302.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
10135. 9654. 8291. 11578. 8577. 9130. 9291.
MEAN IS 9522. +/- 981.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
1907. 1924. 1964. 1929. 1965. 1864. 1881.
MEAN IS 1919. +/- 34.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
548. 565. 525.
MEAN IS 546. +/- 37.

QUANTITY BENZENE EXTRACTED   10124. +/- 1377.
QUANTITY WATER EXTRACTED   7603. +/- 754.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 1373. +/- 38.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
73.04 75.12 76.01 76.06 71.41 70.60 71.25
75.74 77.14 79.03 71.62 77.29
MEAN = 74.53 +/- 2.42

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
70.21 68.03 68.96 68.83 69.33 70.53 68.19
66.20 67.09 67.54 73.30 67.78
MEAN = 68.83 +/- 1.19

METHYLENE IODIDE CONTACT ANGLE
35.58 33.84 36.62 35.22 36.63 35.72 35.23
34.95 33.38 35.70
MEAN = 35.29 +/- 0.74

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   47.20   54.50
POLARITY   0.17   0.24

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 27.62 +/- 1.18

APPENDIX IX (Continued)

STEARIC ACID

EXPERIMENTAL DATA FOR FILM AL - TEMP 85 - TIME 72 HR

ADSORPTION DATA   COUNTING STANDARD = 678   BACKGROUND = 50

TOTAL ADSORPTION(CPM/SQUARE INCH)
19629. 21566. 18612. 19682. 21815. 23437. 19879.
20271. 20383.
   MEAN IS 20586. +/- 1095.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
12771. 9901. 9975. 14519. 11381. 11167. 10915.
   MEAN IS 11510. +/- 1456.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
1854. 1859. 1920. 2004. 2053. 1988. 2046.
   MEAN IS 1961. +/- 75.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
547. 555. 566. 18.
   MEAN IS 556. +/- 18.

QUANTITY BENZENE EXTRACTED   9076. +/- 1414.
QUANTITY WATER EXTRACTED   9549. +/- 1119.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 1405. +/- 79.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
77.59 76.18 74.56 73.68 78.46 77.52 76.86
83.41 73.82 76.50 73.64 76.32
   MEAN = 76.54 +/- 3.28

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
67.97 69.10 68.32 69.27 67.33 67.85 72.29
66.71 69.38 71.00 70.31 71.02
   MEAN = 69.21 +/- 1.51
METHYLENE IODIDE CONTACT ANGLE
31.62 33.50 34.66 32.06 37.62 36.10 33.05
36.00 35.20 34.62
   MEAN = 34.44 +/- 1.34

SURFACE ENERGY PARAMETER	OWENS-WENDT	WU
TOTAL ENERGY	46.90	54.10
POLARITY	0.16	0.23

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 27.86 +/- 2.01

STEARIC ACID

EXPERIMENTAL DATA FOR FILM AZA - TEMP 85 - TIME 120 HR   BACKGROUND = 64

ADSORPTION DATA   COUNTING STANDARD = 667

TOTAL ADSORPTION(CPM/SQUARE INCH)
19070. 20356. 21114. 22826. 20640. 19518. 22654.
20632. 20572.
   MEAN IS 20820. +/- 945.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
12637. 11571. 11485. 11728. 10984. 11503. 11232.
   MEAN IS 11591. +/- 466.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
2395. 2368. 2265. 2297. 2330. 2295. 2327.
   MEAN IS 2325. +/- 40.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
768. 749. 719. 745.
   MEAN IS 745. +/- 45.

QUANTITY BENZENE EXTRACTED   9229. +/- 931.
QUANTITY WATER EXTRACTED   9266. +/- 359.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 1580. +/- 44.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
84.85 76.51 75.75 76.69 75.48 76.54 83.29
78.84 80.06 79.90 82.00 79.32
   MEAN = 79.21 +/- 2.17

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
68.18 68.76 69.31 72.95 67.17 68.27 70.93
71.27 67.68 71.82 67.44 68.61
   MEAN = 69.98 +/- 1.63
METHYLENE IODIDE CONTACT ANGLE
34.88 32.36 32.52 37.67 34.59 34.44 36.81
31.62 33.45 38.80 38.86 39.74
   MEAN = 35.41 +/- 1.12

SURFACE ENERGY PARAMETER	OWENS-WENDT	WU
TOTAL ENERGY	46.70	53.90
POLARITY	0.16	0.24

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 27.74 +/- 1.40

APPENDIX IX (Continued)

STEARIC ACID

EXPERIMENTAL DATA FOR FILM AZ - TEMP 105 - TIME 3 HR

ADSORPTION DATA   COUNTING STANDARD = 673   BACKGROUND = 67

TOTAL ADSORPTION(CPM/SQUARE INCH)
10349. 11645. 11176. 11581. 12455. 10193. 11456.
11815. 11130.
    MEAN IS 11311. +/- 533.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
1471. 1766. 1406. 1328. 1547. 1479. 1559.
    MEAN IS 1508. +/- 124.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
533. 477. 458. 478. 510. 483. 484.
    MEAN IS 489. +/- 22.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
218. 202. 235.
    MEAN IS 218. +/- 30.

QUANTITY BENZENE EXTRACTED   9803. +/- 501.
QUANTITY WATER EXTRACTED   1019. +/-   97.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED   271. +/- 25.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
44.42 46.13 45.10 44.94 45.43 44.53 47.14
53.20 49.49 47.23 49.13 48.63
    MEAN = 47.12 +/- 1.65

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
51.16 48.72 48.70 48.48 47.80 49.80 49.61
49.67 50.07 50.83 46.19 47.66
    MEAN = 49.06 +/- 0.89
METHYLENE IODIDE CONTACT ANGLE
23.49 21.83 25.79 25.36 24.80 23.26 22.04
25.37 25.03 25.32
    MEAN = 24.23 +/- 1.03

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
    TOTAL ENERGY   59.60   67.50
    POLARITY   0.30   0.33

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.08 +/- 1.37

STEARIC ACID

EXPERIMENTAL DATA FOR FILM AY - TEMP 105 - TIME 6 HR

ADSORPTION DATA   COUNTING STANDARD = 690   BACKGROUND = 63

TOTAL ADSORPTION(CPM/SQUARE INCH)
12102. 14093. 12460. 14993. 13588. 11238. 14254.
13473. 14093.
    MEAN IS 13366. +/- 904.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
2987. 2916. 2621. 2788. 2759. 2775. 2591.
    MEAN IS 2777. +/- 128.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
770. 723. 799. 770. 732. 736. 796.
    MEAN IS 761. +/- 28.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
291. 266. 261.
    MEAN IS 273. +/- 30.

QUANTITY BENZENE EXTRACTED   10589. +/- 842.
QUANTITY WATER EXTRACTED   2016. +/- 100.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED   488. +/- 30.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
54.55 55.80 58.28 56.39 55.08 57.24 55.96
56.64 57.08 56.41 62.91 56.10
    MEAN = 56.87 +/- 1.35

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
57.33 56.65 51.05 58.61 59.17 59.64 55.25
57.71 60.45 60.44 55.08 59.66
    MEAN = 57.59 +/- 1.74
METHYLENE IODIDE CONTACT ANGLE
26.44 25.97 24.35 25.80 27.01 28.47 24.44
23.86 26.50 25.60 25.68 30.14
    MEAN = 26.19 +/- 1.11

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
    TOTAL ENERGY   54.80   62.80
    POLARITY   0.24   0.29

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.04 +/- 1.35

APPENDIX IX (Continued)

STEARIC ACID

EXPERIMENTAL DATA FOR FILM AP - TEMP 105 - TIME 24 HR

ADSORPTION DATA   COUNTING STANDARD = 641   BACKGROUND = 51

TOTAL ADSORPTION(CPM/SQUARE INCH)
24634. 25053. 27421. 26387. 24826. 24524. 26410.
24866. 27531.
    MEAN IS 25739. +/- 911.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
15028. 13102. 12507. 14603. 13208. 13345. 13437.
    MEAN IS 13604. +/- 794.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
2916. 2814. 2825. 2888. 2871. 2980. 2990.
    MEAN IS 2898. +/- 62.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
903. 883. 875.
    MEAN IS 887. +/- 26.

QUANTITY BENZENE EXTRACTED   12135. +/- 1000.
QUANTITY WATER EXTRACTED   10707. +/- 611.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED   2011. +/- 66.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
74.83 78.30 76.15 75.84 74.88 79.01 75.68
81.73 79.96 78.07 78.36 78.82
    MEAN = 77.64 +/- 1.83

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
70.64 70.22 68.64 70.12 71.25 65.05 69.57
71.96 66.50 70.52 70.16 71.59
    MEAN = 70.69 +/- 2.18
METHYLENE IODIDE CONTACT ANGLE
37.95 32.27 35.95 37.04 36.04 38.67 34.69
35.21 34.58 37.16
    MEAN = 35.95 +/- 1.52

SURFACE ENERGY PARAMETER	OWENS-WENDT	WU
TOTAL ENERGY	46.20	53.40
POLARITY	0.16	0.23

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.05 +/- 1.40

STEARIC ACID

EXPERIMENTAL DATA FOR FILM AX - TEMP 105 - TIME 12 HR

ADSORPTION DATA   COUNTING STANDARD = 697   BACKGROUND = 63

TOTAL ADSORPTION(CPM/SQUARE INCH)
13306. 13607. 13050. 14623. 12998. 12752. 14488.
12782. 13452.
    MEAN IS 13451. +/- 519.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
4534. 5353. 5059. 5166. 4509. 5050. 4578.
    MEAN IS 4893. +/- 308.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
1628. 1629. 1650. 1570. 1622. 1665. 1615.
    MEAN IS 1626. +/- 27.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
684. 666. 675.
    MEAN IS 675. +/- 17.

QUANTITY BENZENE EXTRACTED   8558. +/- 524.
QUANTITY WATER EXTRACTED   3267. +/- 237.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED   951. +/- 29.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
71.57 71.09 64.81 70.41 67.13 68.29 69.44
73.70 72.33 71.96 70.81 68.20
    MEAN = 69.98 +/- 2.14

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
62.68 63.67 65.81 62.75 62.05 61.06 63.10
57.46 61.30 57.86 59.33 62.02
    MEAN = 61.59 +/- 1.52
METHYLENE IODIDE CONTACT ANGLE
28.04 29.45 28.92 31.24 29.02 30.71 28.08
29.77 28.71 28.29 30.81 30.72
    MEAN = 29.48 +/- 0.72

SURFACE ENERGY PARAMETER	OWENS-WENDT	WU
TOTAL ENERGY	52.10	59.80
POLARITY	0.21	0.27

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.94 +/- 1.63

APPENDIX IX (Continued)

STEARIC ACID

EXPERIMENTAL DATA FOR FILM AU - TEMP 105 - TIME 36 HR

ADSORPTION DATA   COUNTING STANDARD = 727   BACKGROUND = 61

TOTAL ADSORPTION(CPM/SQUARE INCH)
26659. 27906. 27568. 27625. 27259. 26884. 26520.
30189. 28541.
MEAN IS 27683. +/- 856.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
19064. 16632. 18587. 18894. 15477. 18864. 15827.
MEAN IS 17621. +/- 1412.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
3965. 3835. 3864. 3928. 4020. 3928. 3995.
MEAN IS 3934. +/- 60.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
1441. 1427. 1400.
MEAN IS 1423. +/- 38.

QUANTITY BENZENE EXTRACTED   10063. +/- 1241.
QUANTITY WATER EXTRACTED   13687. +/- 1084.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 2511. +/- 64.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
79.94 81.01 80.87 80.55 78.98 83.47 79.92
81.72 81.26 77.20 81.28 87.37
MEAN = 81.13 +/- 1.57

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
73.38 69.97 73.70 73.74 72.78 75.83 75.93
75.52 72.77 74.30 73.41 72.68
MEAN = 73.67 +/- 1.04
METHYLENE IODIDE CONTACT ANGLE
30.81 32.40 34.40 37.45 37.46 34.97 32.58
38.60 36.92 33.13 33.54 37.45
MEAN = 34.98 +/- 1.88

SURFACE ENERGY PARAMETER	OWENS-WENDT	WU
TOTAL ENERGY	45.50	52.40
POLARITY	0.13	0.21

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.94 +/- 1.63

STEARIC ACID

EXPERIMENTAL DATA FOR FILM AV - TEMP 105 - TIME 48 HR

ADSORPTION DATA   COUNTING STANDARD = 678   BACKGROUND = 62

TOTAL ADSORPTION(CPM/SQUARE INCH)
27524. 27292. 27928. 29012. 28854. 26955. 28360.
28000. 26843.
MEAN IS 27863. +/- 589.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
19728. 18699. 18326. 18040. 17874. 18528. 17005.
MEAN IS 18314. +/- 746.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
3950. 3949. 3871. 3992. 4059. 4038. 4019.
MEAN IS 3983. +/- 58.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
960. 947. 939.
MEAN IS 949. +/- 19.

QUANTITY BENZENE EXTRACTED   9549. +/- 743.
QUANTITY WATER EXTRACTED   14332. +/- 574.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 3034. +/- 61.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
86.91 86.93 86.48 84.44 85.26 83.03 81.62
83.77 87.44 83.41 85.30 82.19
MEAN = 85.56 +/- 1.88

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
75.09 75.44 75.09 71.65 71.67 70.03 75.53
75.85 75.66 73.65 74.39 76.38
MEAN = 74.20 +/- 2.48
METHYLENE IODIDE CONTACT ANGLE
41.33 36.43 39.69 38.14 37.98 37.98 39.56
38.89 41.10 40.93 39.91 39.51
MEAN = 39.29 +/- 0.93

SURFACE ENERGY PARAMETER	OWENS-WENDT	WU
TOTAL ENERGY	43.70	50.60
POLARITY	0.14	0.22

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.47 +/- 1.74

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APPENDIX IX (Continued)

STEARIC ACID

EXPERIMENTAL DATA FOR FILM AR - TEMP 105 - TIME 60 HR   BACKGROUND = 57

ADSORPTION DATA   COUNTING STANDARD = 717

TOTAL ADSORPTION(CPM/SQUARE INCH)
30608. 31735. 28480. 29324. 32353. 30108. 29954.
31752. 31087.
MEAN IS 30600. +/- 950.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
19923. 18251. 19871. 21676. 18963. 20070. 20199.
MEAN IS 19850. +/- 955.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
5130. 5168. 5194. 5149. 5104. 5292. 5216.
MEAN IS 5179. +/- 56.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
1500. 1506. 1475.
MEAN IS 1494. +/- 30.

QUANTITY BENZENE EXTRACTED   10750. +/- 1092.
QUANTITY WATER EXTRACTED   14671. +/- 734.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 3685. +/- 59.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
87.13 88.83 88.35 88.73 90.08 90.58 88.63
87.99 89.10 85.24 85.00 88.80
MEAN = 88.20 +/- 2.84

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
75.06 71.70 72.56 70.63 75.05 75.66 79.61
74.88 76.07 71.22 75.31 82.67
MEAN = 75.04 +/- 3.03
METHYLENE IODIDE CONTACT ANGLE
34.23 38.10 42.77 42.01 39.70 41.71 34.21
34.70 36.17 40.45 42.18 41.35
MEAN = 38.96 +/- 2.94

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   43.50   50.40
POLARITY   0.13   0.21

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.21 +/- 2.05

STEARIC ACID

EXPERIMENTAL DATA FOR FILM AAZ - TEMP 105 - TIME 72 HR   BACKGROUND = 66

ADSORPTION DATA   COUNTING STANDARD = 664

TOTAL ADSORPTION(CPM/SQUARE INCH)
26609. 25034. 24657. 27663. 25850. 28208. 24621.
25538. 26203.
MEAN IS 26043. +/- 958.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
15673. 15505. 16126. 17214. 15834. 16364. 16361.
MEAN IS 16154. +/- 512.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
4848. 4818. 4828. 4819. 4818. 4820. 5067.
MEAN IS 4860. +/- 82.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
1146. 1130. 1095.
MEAN IS 1124. +/- 48.

QUANTITY BENZENE EXTRACTED   9889. +/- 952.
QUANTITY WATER EXTRACTED   11294. +/- 398.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 3736. +/- 88.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
90.00 91.75 90.88 89.69 87.64 90.86 92.44
85.02 91.09 90.93 91.61 93.94
MEAN = 90.49 +/- 1.45

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
74.44 74.23 72.65 70.45 75.84 76.03 84.57
78.46 82.91 84.77 83.48 87.09
MEAN = 78.74 +/- 3.43
METHYLENE IODIDE CONTACT ANGLE
44.56 36.40 35.38 43.77 36.74 41.51 34.85
43.74 38.74 40.27 37.47 38.61
MEAN = 39.34 +/- 2.14

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   42.20   48.60
POLARITY   0.10   0.19

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.14 +/- 1.37

APPENDIX IX (Continued)

STEARIC ACID

EXPERIMENTAL DATA FOR FILM AM1 - TEMP 105 - TIME 90 HR

ADSORPTION DATA   COUNTING STANDARD = 677   BACKGROUND = 65

TOTAL ADSORPTION(CPM/SQUARE INCH)
23108. 24717. 23566. 24447. 23330. 22592. 23071.
25612. 24970.
MEAN IS 23935. +/- 777.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
16731. 16870. 17067. 17252. 16017. 17839. 16509.
MEAN IS 16898. +/- 515.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
4969. 4999. 4955. 4847. 4862. 4792. 4955.
MEAN IS 4911. +/- 69.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
1097. 1125. 1075.
MEAN IS 1099. +/- 46.

QUANTITY BENZENE EXTRACTED   7037. +/- 800.
QUANTITY WATER EXTRACTED   11987. +/- 399.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED   3812. +/- 74.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
88.80 93.04 91.86 90.87 92.06 93.20 92.58
89.19 92.17 92.60 91.69 91.30
MEAN = 91.61 +/- 0.88

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
79.68 77.00 72.14 79.72 74.62 84.50 74.40
75.15 77.08 84.00 84.59 84.77
MEAN = 78.97 +/- 2.88
METHYLENE IODIDE CONTACT ANGLE
41.87 43.86 33.91 39.98 43.06 43.65 46.53
35.70 43.28 39.98 38.46 42.79
MEAN = 41.09 +/- 2.29

SURFACE ENERGY PARAMETER	OWENS-WENDT	WU
TOTAL ENERGY	41.40	47.90
POLARITY	0.11	0.19

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.24 +/- 1.23

STEARIC ACID

EXPERIMENTAL DATA FOR FILM AB2 - TEMP 105 - TIME 120 HR

ADSORPTION DATA   COUNTING STANDARD = 682   BACKGROUND = 65

TOTAL ADSORPTION(CPM/SQUARE INCH)
26007. 25149. 26654. 26074. 28685. 25417. 28807.
25899. 25067.
MEAN IS 26418. +/- 1063.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
15362. 14473. 15075. 14063. 14406. 15234. 14128.
MEAN IS 14677. +/- 480.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
5223. 5263. 5259. 5280. 5192. 5150. 5203.
MEAN IS 5224. +/- 41.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
1284. 1294. 1320.
MEAN IS 1299. +/- 34.

QUANTITY BENZENE EXTRACTED   11740. +/- 1037.
QUANTITY WATER EXTRACTED   9453. +/- 370.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED   3925. +/- 45.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
93.33 89.71 90.36 87.35 89.02 90.48 92.00
87.89 91.15 86.56 90.85 92.37
MEAN = 90.47 +/- 2.61

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
82.76 78.76 80.27 75.49 74.52 79.97 75.96
74.18 78.19 74.98 82.40 82.28
MEAN = 78.81 +/- 2.67
METHYLENE IODIDE CONTACT ANGLE
39.07 42.59 36.22 41.91 37.92 38.08 40.22
39.54 38.95 37.85 36.65 42.49
MEAN = 39.29 +/- 1.96

SURFACE ENERGY PARAMETER	OWENS-WENDT	WU
TOTAL ENERGY	42.10	48.60
POLARITY	0.10	0.19

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 27.94 +/- 1.39

APPENDIX IX (Continued)

BEHENIC ACID

EXPERIMENTAL DATA FOR FILM BP - TEMP 85 - TIME 8 HR

ADSORPTION DATA   COUNTING STANDARD = 651   BACKGROUND = 70

TOTAL ADSORPTION(CPM/SQUARE INCH)
8749. 9132. 10276. 9875. 11403. 9467. 8476.
10043. 10321.
MEAN IS 9749. +/- 681.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
3765. 3428. 3940. 3624. 3183. 3324. 3416.
MEAN IS 3526. +/- 236.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
319. 296. 282. 317. 304. 338. 291.
MEAN IS 307. +/- 17.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
134. 146. 138.
MEAN IS 139. +/- 11.

QUANTITY BENZENE EXTRACTED   6223. +/- 651.
QUANTITY WATER EXTRACTED   3219. +/- 182.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED   167. +/- 18.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
41.46 41.44 39.64 41.76 41.73 44.41 42.56
41.36 42.69 43.01 41.90 42.72
MEAN = 42.03 +/- 0.72

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
48.73 50.53 51.03 50.78 52.01 52.08 50.63
49.90 52.28 50.14 48.76 52.20
MEAN = 50.76 +/- 0.78
METHYLENE IODIDE CONTACT ANGLE
28.10 25.89 23.11 22.19 19.36 24.25 25.55
24.51 22.20 24.64 30.33 31.75
MEAN = 25.16 +/- 2.21

SURFACE ENERGY PARAMETER	OWENS-WENDT	WU
TOTAL ENERGY	58.50	66.40
POLARITY	0.29	0.32

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.97 +/- 1.52

BEHENIC ACID

EXPERIMENTAL DATA FOR FILM BM - TEMP 85 - TIME 16 HR

ADSORPTION DATA   COUNTING STANDARD = 618   BACKGROUND = 70

TOTAL ADSORPTION(CPM/SQUARE INCH)
12344. 12866. 12464. 12268. 12073. 12655. 12722.
11839. 12060.
MEAN IS 12366. +/- 258.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
5931. 5856. 5601. 5920. 6137. 5622. 5619.
MEAN IS 5812. +/- 183.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
673. 724. 693. 716. 666. 651. 692.
MEAN IS 688. +/- 24.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
240. 228. 207.
MEAN IS 225. +/- 31.

QUANTITY BENZENE EXTRACTED   6553. +/- 269.
QUANTITY WATER EXTRACTED   5124. +/- 142.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED   463. +/- 26.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
60.65 60.58 61.80 61.95 60.87 59.18 60.09
56.63 59.47 59.50 58.89 59.39
MEAN = 59.92 +/- 0.90

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
63.51 61.60 59.82 58.88 62.54 62.70 63.96
61.72 63.54 66.18 63.71 64.53
MEAN = 62.72 +/- 1.27
METHYLENE IODIDE CONTACT ANGLE
26.75 26.95 26.97 26.05 25.92 27.38 27.94
26.28 25.81 26.08 25.61 30.34
MEAN = 26.84 +/- 0.82

SURFACE ENERGY PARAMETER	OWENS-WENDT	WU
TOTAL ENERGY	52.30	60.10
POLARITY	0.19	0.26

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.46 +/- 1.48

APPENDIX IX (Continued)

BEHENIC ACID

EXPERIMENTAL DATA FOR FILM BT - TEMP 85 - TIME 24 HR

ADSORPTION DATA   COUNTING STANDARD = 686   BACKGROUND = 69

TOTAL ADSORPTION(CPM/SQUARE INCH)
16467. 15321. 15864. 14256. 15018. 13745. 14640.
15576. 14879.
   MEAN IS 15085. +/- 628.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
6186. 4746. 6381. 5125. 5648. 6230. 6350.
   MEAN IS 5809. +/- 584.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
1253. 1165. 1226. 1187. 1208. 1164. 1166.
   MEAN IS 1196. +/- 31.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
404. 396. 421.
   MEAN IS 407. +/- 23.

QUANTITY BENZENE EXTRACTED   9276. +/- 703.
QUANTITY WATER EXTRACTED   4614. +/- 449.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED   789. +/- 33.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
68.41 67.27 67.28 69.16 67.05 68.42 69.43
68.62 66.71 69.70 67.90 69.27
   MEAN = 68.27 +/- 0.64

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
64.60 65.78 67.87 67.80 64.84 64.43 65.37
67.88 64.99 65.19 67.30 65.11
   MEAN = 65.93 +/- 0.86
METHYLENE IODIDE CONTACT ANGLE
29.55 32.81 30.51 31.59 30.01 31.63 30.01
31.73 32.45 32.50 31.05 29.90
   MEAN = 31.14 +/- 0.71

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   49.70   57.20
POLARITY   0.18   0.25

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 29.15 +/- 1.37

BEHENIC ACID

EXPERIMENTAL DATA FOR FILM BN - TEMP 85 - TIME 40 HR

ADSORPTION DATA   COUNTING STANDARD = 653   BACKGROUND = 70

TOTAL ADSORPTION(CPM/SQUARE INCH)
17541. 18626. 19217. 18423. 16982. 17834. 20221.
17542. 17049.
   MEAN IS 18159. +/- 806.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
11916. 10206. 9185. 9327. 10784. 9847. 9926.
   MEAN IS 10170. +/- 838.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
1630. 1553. 1578. 1589. 1621. 1573. 1549.
   MEAN IS 1585. +/- 28.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
526. 497. 512.
   MEAN IS 512. +/- 27.

QUANTITY BENZENE EXTRACTED   7989. +/- 938.
QUANTITY WATER EXTRACTED   8585. +/- 643.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED   1073. +/- 30.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
75.56 77.49 75.65 73.41 74.43 73.51 74.89
76.69 76.52 76.15 77.23 73.10
   MEAN = 75.39 +/- 0.95

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
69.87 71.03 67.47 72.25 69.01 69.55 68.68
68.57 69.37 70.23 71.48 71.22
   MEAN = 69.89 +/- 0.88
METHYLENE IODIDE CONTACT ANGLE
30.16 29.24 30.35 30.35 31.23 30.45 31.63
31.59 33.19 31.60 30.59 30.78
   MEAN = 30.93 +/- 0.63

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   48.20   55.50
POLARITY   0.15   0.22

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 27.98 +/- 1.47

APPENDIX IX (Continued)

BEHENIC ACID

EXPERIMENTAL DATA FOR FILM BL - TEMP 85 - TIME 60 HR

ADSORPTION DATA   COUNTING STANDARD = 659   BACKGROUND = 70

TOTAL ADSORPTION(CPM/SQUARE INCH)
20308. 22333. 23144. 20996. 19236. 21597. 20174.
21832. 20182.
MEAN IS 21089. +/- 935.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
10733. 11149. 9969. 10992. 10063. 9863. 10973.
MEAN IS 10535. +/- 491.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
1911. 1915. 1895. 1790. 1845. 1974. 1935.
MEAN IS 1895. +/- 54.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
498. 544. 503.
MEAN IS 515. +/- 46.

QUANTITY BENZENE EXTRACTED   10555. +/- 927.
QUANTITY WATER EXTRACTED   8640. +/- 379.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 1380. +/- 59.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
78.67 78.32 77.45 76.79 79.24 78.90 79.30
77.48 75.25 78.39 78.58 77.39
MEAN = 77.98 +/- 0.74

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
69.05 73.36 68.10 66.87 74.23 70.21 68.53
73.56 67.31 71.79 74.55 74.17
MEAN = 70.98 +/- 1.85
METHYLENE IODIDE CONTACT ANGLE
33.86 34.43 33.63 28.71 32.97 33.63 31.18
29.27 32.63 38.02 31.78 35.76
MEAN = 32.99 +/- 1.63

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   47.10   54.30
POLARITY   0.14   0.22

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 29.41 +/- 1.67

BEHENIC ACID

EXPERIMENTAL DATA FOR FILM BR - TEMP 85 - TIME 72 HR

ADSORPTION DATA   COUNTING STANDARD = 682   BACKGROUND = 68

TOTAL ADSORPTION(CPM/SQUARE INCH)
16879. 17673. 15624. 17842. 19469. 16596. 19676.
17243. 17692.
MEAN IS 17633. +/- 977.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
6192. 7354. 8850. 7495. 8678. 8226. 8747.
MEAN IS 7935. +/- 871.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
1978. 2016. 1957. 1974. 1996. 1958. 2037.
MEAN IS 1988. +/- 27.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
553. 562. 528.
MEAN IS 548. +/- 32.

QUANTITY BENZENE EXTRACTED   9698. +/- 1080.
QUANTITY WATER EXTRACTED   5947. +/- 669.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 1440. +/- 30.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
75.56 75.25 75.85 77.17 72.47 72.45 74.35
71.31 77.12 79.20 80.93 79.99
MEAN = 75.97 +/- 1.93

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
67.59 71.82 73.86 73.48 74.21 73.35 72.79
72.65 72.92 69.42 72.17 73.21
MEAN = 72.29 +/- 1.21
METHYLENE IODIDE CONTACT ANGLE
33.61 36.29 36.60 31.81 35.87 28.56 34.69
34.22 39.32 30.36 36.54 36.11
MEAN = 34.50 +/- 1.90

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   46.10   53.20
POLARITY   0.14   0.22

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 29.41 +/- 1.68

APPENDIX IX (Continued)

BEHENIC ACID

EXPERIMENTAL DATA FOR FILM BO - TEMP 85 - TIME 120 HR

ADSORPTION DATA   COUNTING STANDARD = 626   BACKGROUND = 67

TOTAL ADSORPTION(CPM/SQUARE INCH)
18974. 19236. 17218. 18289. 16647. 18576. 19047.
20173. 18263.
      MEAN IS 18491. +/- 802.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
10274. 8793. 9428. 9864. 11213. 8760. 9238.
      MEAN IS 9653. +/- 785.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
2248. 2206. 2235. 2189. 2242. 2267. 2174.
      MEAN IS 2223. +/- 30.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
589. 642. 604.
      MEAN IS 612. +/- 50.

QUANTITY BENZENE EXTRACTED   8839. +/- 913.
QUANTITY WATER EXTRACTED   7430. +/- 603.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 1611. +/- 35.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
80.49 77.61 76.28 80.69 74.81 80.66 70.72
79.57 80.72 80.12 79.52 79.51
      MEAN = 78.39 +/- 1.93

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
71.28 75.30 74.60 73.26 72.09 74.26 73.07
76.99 83.00 73.30 73.24 74.34
      MEAN = 74.56 +/- 1.91
METHYLENE IODIDE CONTACT ANGLE
37.13 38.46 35.46 32.81 30.88 33.97 35.06
34.26 38.42 40.00 37.11 40.90
      MEAN = 36.21 +/- 1.88

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
  TOTAL ENERGY   44.70   51.50
  POLARITY   0.12   0.21

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 27.98 +/- 1.47

BEHENIC ACID

EXPERIMENTAL DATA FOR FILM BE - TEMP 105 - TIME 3 HR

ADSORPTION DATA   COUNTING STANDARD = 682   BACKGROUND = 65

TOTAL ADSORPTION(CPM/SQUARE INCH)
10120. 11603. 9640. 9857. 11314. 11322. 9622.
10583. 10354.
      MEAN IS 10491. +/- 575.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
1513. 1747. 1450. 1526. 1664. 1475. 1656.
      MEAN IS 1576. +/- 101.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
536. 466. 477. 421. 488. 473. 534.
      MEAN IS 485. +/- 36.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
292. 265. 302.
      MEAN IS 286. +/- 35.

QUANTITY BENZENE EXTRACTED   8915. +/- 537.
QUANTITY WATER EXTRACTED   1091. +/- 82.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 199. +/- 39.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
46.03 45.67 45.83 48.58 46.03 45.11 45.54
45.97 47.48 47.05 45.13 44.47
      MEAN = 46.07 +/- 0.71

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
55.70 51.58 52.97 56.72 54.38 54.37 52.82
52.46 54.07 55.53 51.87 52.17
      MEAN = 53.72 +/- 1.05
METHYLENE IODIDE CONTACT ANGLE
25.47 26.46 26.64 26.57 26.48 23.66 25.99
27.83 31.52 27.18 23.94 28.23
      MEAN = 26.66 +/- 1.29

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
  TOTAL ENERGY   56.60   64.50
  POLARITY   0.27   0.31

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.72 +/- 1.45

APPENDIX IX (Continued)

BEHENIC ACID

EXPERIMENTAL DATA FOR FILM BG - TEMP 105 - TIME 6 HR

ADSORPTION DATA   COUNTING STANDARD = 633   BACKGROUND = 67

TOTAL ADSORPTION(CPM/SQUARE INCH)
11152. 11645. 11764. 11530. 11637. 11731. 12982.
11696. 10953.
MEAN IS 11677. +/- 425.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
3968. 3613. 3893. 2863. 4296. 3923. 2861.
MEAN IS 3631. +/- 502.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
827. 834. 829. 760. 863. 861. 860.
MEAN IS 833. +/- 32.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
305. 311. 300.
MEAN IS 305. +/- 10.

QUANTITY BENZENE EXTRACTED   8046. +/- 520.
QUANTITY WATER EXTRACTED   2798. +/- 386.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED   528. +/- 34.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
58.76 60.00 60.35 59.34 61.85 58.41 56.44
60.42 58.76 60.57 59.53 59.07
MEAN = 59.46 +/- 0.86

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
64.92 65.02 64.06 61.32 62.88 64.43 58.65
68.48 62.23 67.70 60.96 62.93
MEAN = 63.83 +/- 1.75
METHYLENE IODIDE CONTACT ANGLE
29.13 29.21 30.15 29.59 25.95 26.73 29.97
32.31 35.33 30.72 29.11 29.22
MEAN = 29.79 +/- 1.51

SURFACE ENERGY PARAMETER	OWENS-WENDT	WU
TOTAL ENERGY	51.10	58.80
POLARITY	0.20	0.26

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.70 +/- 1.70

BEHENIC ACID

EXPERIMENTAL DATA FOR FILM BD - TEMP 105 - TIME 12 HR

ADSORPTION DATA   COUNTING STANDARD = 696   BACKGROUND = 68

TOTAL ADSORPTION(CPM/SQUARE INCH)
14483. 16902. 14392. 14859. 16603. 16519. 16149.
17249. 16667.
MEAN IS 15980. +/- 829.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
6977. 6844. 6927. 6755. 7330. 7760. 6132.
MEAN IS 6961. +/- 450.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
1644. 1682. 1707. 1657. 1624. 1597. 1617.
MEAN IS 1647. +/- 34.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
745. 772. 767.
MEAN IS 761. +/- 26.

QUANTITY BENZENE EXTRACTED   9020. +/- 826.
QUANTITY WATER EXTRACTED   5314. +/- 346.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED   886. +/- 37.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
67.22 69.02 68.82 69.30 69.70 67.90 67.95
68.68 67.73 66.78 67.77 67.24
MEAN = 68.18 +/- 0.58

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
64.01 68.20 64.53 66.35 68.05 68.30 63.74
66.94 64.65 66.89 66.71 66.81
MEAN = 66.26 +/- 1.03
METHYLENE IODIDE CONTACT ANGLE
35.60 33.93 33.54 32.96 31.34 31.42 33.30
35.68 33.03 32.09 29.54 30.10
MEAN = 32.71 +/- 1.21

SURFACE ENERGY PARAMETER	OWENS-WENDT	WU
TOTAL ENERGY	49.50	57.10
POLARITY	0.19	0.26

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.67 +/- 1.48

APPENDIX IX (Continued)

BEHENIC ACID

EXPERIMENTAL DATA FOR FILM BA - TEMP 105 - TIME 24 HR

ADSORPTION DATA   COUNTING STANDARD = 629   BACKGROUND = 57

TOTAL ADSORPTION(CPM/SQUARE INCH)
18203. 22055. 20383. 20931. 20005. 19221. 20793.
20254. 19363.
MEAN IS 20134. +/- 843.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
14633. 14893. 15685. 13924. 15462. 15294. 16687.
MEAN IS 15225. +/- 779.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
2989. 3086. 3041. 3048. 3025. 3089. 2990.
MEAN IS 3038. +/- 36.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
965. 1008. 986.
MEAN IS 986. +/- 39.

QUANTITY BENZENE EXTRACTED   4909. +/- 943.
QUANTITY WATER EXTRACTED   12187. +/- 599.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 2052. +/- 40.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
78.90 81.32 81.93 81.18 79.34 81.23 80.96
80.70 80.65 82.19 81.37 81.14
MEAN = 80.91 +/- 0.60

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
77.52 78.23 76.76 72.68 76.95 76.83 71.38
78.32 71.06 76.57 76.49 77.64
MEAN = 75.87 +/- 1.64
METHYLENE IODIDE CONTACT ANGLE
32.51 31.21 35.98 31.95 36.40 36.36 36.61
35.57 37.48 37.06 34.44 35.10
MEAN = 35.05 +/- 1.32

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   44.70   51.40
POLARITY   0.11   0.19

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.42 +/- 1.28

BEHENIC ACID

EXPERIMENTAL DATA FOR FILM BJ - TEMP 105 - TIME 36 HR

ADSORPTION DATA   COUNTING STANDARD = 662   BACKGROUND = 68

TOTAL ADSORPTION(CPM/SQUARE INCH)
26348. 25218. 24624. 22815. 24723. 24812. 25121.
25067. 24986.
MEAN IS 24857. +/- 692.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
14649. 13064. 15713. 15373. 14196. 13493. 14531.
MEAN IS 14431. +/- 847.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
3353. 3404. 3322. 3342. 3444. 3342. 3396.
MEAN IS 3372. +/- 39.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
797. 841. 783.
MEAN IS 807. +/- 56.

QUANTITY BENZENE EXTRACTED   10426. +/- 860.
QUANTITY WATER EXTRACTED   11059. +/- 651.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 2565. +/- 44.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
86.91 86.93 74.48 84.44 85.26 83.03 81.62
83.77 87.44 83.41 85.30 80.19
MEAN = 83.56 +/- 2.26

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
78.42 78.11 79.73 77.68 79.71 77.85 76.96
75.98 77.57 79.35 77.91 78.12
MEAN = 78.12 +/- 0.69
METHYLENE IODIDE CONTACT ANGLE
41.62 38.49 39.37 38.78 36.94 39.72 39.15
38.30 39.81 36.04 35.89 38.73
MEAN = 38.57 +/- 1.03

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   43.50   49.90
POLARITY   0.10   0.18

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.20 +/- 1.69

APPENDIX IX (Continued)

BEHENIC ACID

EXPERIMENTAL DATA FOR FILM BF - TEMP 105 - TIME 60 HR

ADSORPTION DATA   COUNTING STANDARD = 616   BACKGROUND = 66

TOTAL ADSORPTION(CPM/SQUARE INCH)
25291. 28463. 27187. 28029. 23993. 24881. 26580.
24951. 24449.
MEAN IS 25980. +/- 1228.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
18473. 17023. 16745. 17163. 17972. 18965. 16599.
MEAN IS 17563. +/- 817.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
5098. 5059. 4946. 5022. 5031. 5163. 5098.
MEAN IS 5060. +/- 62.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
1326. 1334. 1302.
MEAN IS 1321. +/- 31.

QUANTITY BENZENE EXTRACTED   8418. +/- 1265.
QUANTITY WATER EXTRACTED   12503. +/- 629.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 3739. +/- 66.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
89.53 90.48 87.87 89.52 89.32 88.77 89.00
89.65 86.99 87.12 89.23 87.56
MEAN = 88.75 +/- 0.70

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
81.27 81.53 81.99 83.40 80.69 81.27 80.64
81.41 82.28 81.60 80.49 82.68
MEAN = 81.61 +/- 0.54
METHYLENE IODIDE CONTACT ANGLE
43.32 38.97 35.57 38.28 42.55 40.52 39.37
40.65 40.12 41.67 42.20 41.11
MEAN = 40.36 +/- 1.33

SURFACE ENERGY PARAMETER	OWENS-WENDT	WU
TOTAL ENERGY	41.10	47.00
POLARITY	0.08	0.17

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.88 +/- 1.63

BEHENIC ACID

EXPERIMENTAL DATA FOR FILM BK - TEMP 105 - TIME 48 HR

ADSORPTION DATA   COUNTING STANDARD = 587   BACKGROUND = 56

TOTAL ADSORPTION(CPM/SQUARE INCH)
21370. 22762. 22560. 21177. 23037. 22964. 21753.
23115. 24168.
MEAN IS 22545. +/- 720.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
10438. 11808. 11662. 10576. 11626. 12546. 11935.
MEAN IS 11513. +/- 673.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
4104. 4158. 4175. 4204. 4186. 4253. 4075.
MEAN IS 4165. +/- 54.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
1078. 1104. 1099.
MEAN IS 1094. +/- 25.

QUANTITY BENZENE EXTRACTED   11032. +/- 808.
QUANTITY WATER EXTRACTED   7348. +/- 518.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 3071. +/- 57.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
84.62 84.41 84.14 86.26 84.54 85.80 86.49
85.51 87.32 83.06 86.26 91.74
MEAN = 85.85 +/- 1.39

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
76.77 80.13 80.25 79.56 84.28 78.86 81.22
74.79 77.63 79.33 78.98 79.94
MEAN = 79.31 +/- 1.47
METHYLENE IODIDE CONTACT ANGLE
35.28 35.18 43.81 44.54 42.43 35.96 34.64
37.26 36.51 41.47 39.02 43.97
MEAN = 39.17 +/- 2.41

SURFACE ENERGY PARAMETER	OWENS-WENDT	WU
TOTAL ENERGY	42.10	48.70
POLARITY	0.10	0.18

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.10 +/- 1.65

APPENDIX IX (Continued)

BEHENIC ACID

EXPERIMENTAL DATA FOR FILM BH - TEMP 105 - TIME 120 HR

ADSORPTION DATA   COUNTING STANDARD = 655   BACKGROUND = 68

TOTAL ADSORPTION(CPM/SQUARE INCH)
28711. 29701. 29878. 28657. 28595. 27958. 29963.
28210. 29518.
MEAN IS 29021. +/- 567.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
23705. 22545. 21434. 21215. 23205. 21553. 22228.
MEAN IS 22269. +/- 843.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
5464. 5423. 5519. 5481. 5335. 5306. 5386.
MEAN IS 5416. +/- 70.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
1399. 1372. 1372.
MEAN IS 1381. +/- 29.

QUANTITY BENZENE EXTRACTED   6752. +/- 776.
QUANTITY WATER EXTRACTED   16853. +/- 649.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 4035. +/- 74.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
88.98 91.33 89.41 90.62 89.58 92.19 92.16
93.49 92.87 90.50 93.07 93.16
MEAN = 91.45 +/- 1.01

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
86.17 88.91 92.43 88.37 90.13 84.80 87.42
85.38 85.74 84.47 85.99 86.63
MEAN = 87.20 +/- 1.49
METHYLENE IODIDE CONTACT ANGLE
45.01 44.91 44.93 44.70 45.06 46.17 46.89
46.41 47.01 45.65 45.75 46.12
MEAN = 45.74 +/- 0.51

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   37.50   42.60
POLARITY   0.06   0.14

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.31 +/- 1.55

BEHENIC ACID

EXPERIMENTAL DATA FOR FILM BI - TEMP 105 - TIME 90 HR

ADSORPTION DATA   COUNTING STANDARD = 598   BACKGROUND = 60

TOTAL ADSORPTION(CPM/SQUARE INCH)
26721. 24692. 25483. 25870. 27487. 24221. 25226.
26187. 24768.
MEAN IS 25628. +/- 791.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
16842. 15461. 17592. 17718. 16724. 15965. 16552.
MEAN IS 16693. +/- 725.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
5406. 5254. 5271. 5358. 5398. 5366. 5306.
MEAN IS 5337. +/- 54.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
1421. 1438. 1388.
MEAN IS 1416. +/- 47.

QUANTITY BENZENE EXTRACTED   8935. +/- 882.
QUANTITY WATER EXTRACTED   11356. +/- 558.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 3921. +/- 59.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
90.97 91.67 91.35 90.19 90.44 90.99 87.03
92.83 87.56 90.46 92.85 92.38
MEAN = 90.73 +/- 1.16

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
85.98 84.43 84.38 85.60 85.29 83.70 83.85
84.84 83.15 86.18 87.17 86.00
MEAN = 85.05 +/- 0.75
METHYLENE IODIDE CONTACT ANGLE
40.20 39.99 40.16 38.71 40.37 42.24 43.67
43.03 43.42 40.71 42.10 43.35
MEAN = 41.41 +/- 1.00

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   39.90   45.20
POLARITY   0.06   0.15

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 29.25 +/- 1.88

APPENDIX IX (Continued)

ISOSTEARIC ACID

EXPERIMENTAL DATA FOR FILM CO - TEMP 85 - TIME 8 HR

ADSORPTION DATA   COUNTING STANDARD = 673   BACKGROUND = 69

TOTAL ADSORPTION(CPM/SQUARE INCH)
10514. 11043. 10865. 11771. 11594. 11246. 11410.
11104. 11529.
MEAN IS 11231. +/- 297.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
1777. 2144. 1633. 2124. 1844. 1854. 2108.
MEAN IS 1926. +/- 179.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
305. 320. 310. 326. 324. 321. 317.
MEAN IS 318. +/- 7.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
131. 119. 121.
MEAN IS 124. +/- 12.

QUANTITY BENZENE EXTRACTED   9304. +/- 301.
QUANTITY WATER EXTRACTED   1609. +/- 137.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED   194. +/- 8.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
38.15 39.24 36.41 36.40 36.59 36.80 39.80
43.06 39.83 41.58 37.79 37.96
MEAN = 38.63 +/- 1.35

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
43.43 42.50 41.33 40.78 41.58 41.76 42.28
43.60 44.13 41.75 40.37 41.47
MEAN = 42.08 +/- 0.72
METHYLENE IODIDE CONTACT ANGLE
24.55 26.17 25.05 22.24 22.04 22.42 25.03
22.21 22.45 26.60 26.46 26.14
MEAN = 24.28 +/- 1.18

SURFACE ENERGY PARAMETER	OWENS-WENDT	WU
TOTAL ENERGY	63.20	70.90
POLARITY	0.35	0.36

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 29.17 +/- 1.81

ISOSTEARIC ACID

EXPERIMENTAL DATA FOR FILM CL - TEMP 85 - TIME 16 HR

ADSORPTION DATA   COUNTING STANDARD = 673   BACKGROUND = 72

TOTAL ADSORPTION(CPM/SQUARE INCH)
13463. 13154. 12253. 12760. 12700. 12971. 12211.
12957. 12474.
MEAN IS 12771. +/- 313.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
3669. 3692. 4014. 3694. 3577. 3667. 3563.
MEAN IS 3697. +/- 134.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
586. 608. 636. 578. 619. 614. 598.
MEAN IS 606. +/- 18.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
154. 143. 133.
MEAN IS 143. +/- 19.

QUANTITY BENZENE EXTRACTED   9075. +/- 303.
QUANTITY WATER EXTRACTED   3091. +/- 104.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED   462. +/- 20.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
52.82 53.53 54.46 52.36 51.16 51.33 50.79
51.07 52.06 50.05 50.55 52.63
MEAN = 51.90 +/- 0.82

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
53.35 57.43 57.46 54.51 57.64 56.73 57.47
56.64 54.91 53.94 56.07 56.15
MEAN = 56.03 +/- 0.94
METHYLENE IODIDE CONTACT ANGLE
25.61 25.10 24.76 27.43 28.05 28.57 26.72
26.91 25.07 27.24 25.90 27.34
MEAN = 26.56 +/- 0.79

SURFACE ENERGY PARAMETER	OWENS-WENDT	WU
TOTAL ENERGY	55.50	63.40
POLARITY	0.25	0.30

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.04 +/- 1.42

APPENDIX IX (Continued)

ISOSTEARIC ACID

EXPERIMENTAL DATA FOR FILM CJ - TEMP 85 - TIME 40 HR   BACKGROUND = 72

ADSORPTION DATA   COUNTING STANDARD = 674

TOTAL ADSORPTION(CPM/SQUARE INCH)
20509. 19437. 17926. 19241. 18516. 18737. 19520.
19006. 18532.
MEAN IS 19047. +/- 563.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
12046. 12348. 11698. 12073. 12587. 12239. 12046.
MEAN IS 12148. +/- 250.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
1419. 1449. 1436. 1481. 1508. 1471. 1496.
MEAN IS 1466. +/- 29.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
421. 435. 426.
MEAN IS 427. +/- 13.

QUANTITY BENZENE EXTRACTED   6899. +/- 548.
QUANTITY WATER EXTRACTED   10682. +/- 193.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED   1038. +/- 31.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
63.24 64.58 69.88 66.09 67.15 67.33 65.89
62.61 65.85 65.63 67.96 65.06
MEAN = 65.94 +/- 1.26

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
67.30 64.29 62.86 63.37 61.01 68.27 64.14
66.07 61.19 61.65 65.21 66.34
MEAN = 64.31 +/- 1.51
METHYLENE IODIDE CONTACT ANGLE
30.48 30.67 30.40 31.00 31.23 29.85 29.64
28.88 29.00 29.63 27.46 28.31
MEAN = 29.71 +/- 0.72

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   50.80   58.50
POLARITY   0.19   0.26

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 29.36 +/- 1.67

ISOSTEARIC ACID

EXPERIMENTAL DATA FOR FILM CP - TEMP 85 - TIME 24 HR   BACKGROUND = 70

ADSORPTION DATA   COUNTING STANDARD = 679

TOTAL ADSORPTION(CPM/SQUARE INCH)
17989. 18413. 18369. 19129. 19721. 18904. 18677.
19306. 19197.
MEAN IS 18856. +/- 410.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
8069. 8395. 9123. 8678. 8950. 8467. 8942.
MEAN IS 8661. +/- 333.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
1167. 1176. 1217. 1203. 1199. 1193. 1205.
MEAN IS 1194. +/- 16.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
368. 356. 366.
MEAN IS 363. +/- 12.

QUANTITY BENZENE EXTRACTED   10196. +/- 441.
QUANTITY WATER EXTRACTED   7466. +/- 256.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED   831. +/- 17.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
63.23 65.32 70.66 61.48 61.26 61.82 62.93
61.09 63.02 61.55 60.96 63.46
MEAN = 63.06 +/- 1.71

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
64.83 63.10 64.43 64.08 64.86 66.97 63.78
63.74 61.74 57.65 57.45 61.00
MEAN = 62.80 +/- 1.81
METHYLENE IODIDE CONTACT ANGLE
30.07 29.87 29.60 32.05 29.02 28.39 28.23
29.10 28.19 32.18 32.67 31.16
MEAN = 30.04 +/- 1.01

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   51.40   59.10
POLARITY   0.21   0.27

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 29.07 +/- 1.93

APPENDIX IX (Continued)

ISOSTEARIC ACID

EXPERIMENTAL DATA FOR FILM CM - TEMP 85 - TIME 60 HR   BACKGROUND = 71

ADSORPTION DATA   COUNTING STANDARD = 679

TOTAL ADSORPTION(CPM/SQUARE INCH)
20857. 19506. 19961. 20219. 20646. 20565. 19856.
20558. 20380.
MEAN IS 20283. +/- 329.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
9659. 10229. 9794. 10382. 11174. 11155. 10307.
MEAN IS 10386. +/- 532.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
1849. 1873. 1808. 1886. 1862. 1863. 1860.
MEAN IS 1857. +/- 22.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
460. 476. 473.
MEAN IS 470. +/- 16.

QUANTITY BENZENE EXTRACTED   9897. +/- 471.
QUANTITY WATER EXTRACTED   8528. +/- 408.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 1388. +/- 24.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
70.02 69.48 69.15 69.38 69.02 70.43 69.66
69.21 70.14 69.23 69.92 69.26
MEAN = 69.57 +/- 0.28

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
67.10 66.83 66.68 67.01 66.16 65.96 65.37
71.51 64.74 65.76 66.14 66.00
MEAN = 66.61 +/- 1.06
METHYLENE IODIDE CONTACT ANGLE
38.45 32.16 33.47 33.22 33.91 32.28 32.63
32.38 33.12 32.44 28.11 33.39
MEAN = 32.96 +/- 1.43

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   48.80   56.30
POLARITY   0.18   0.25

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 29.03 +/- 1.61

ISOSTEARIC ACID

EXPERIMENTAL DATA FOR FILM CK - TEMP 85 - TIME 72 HR   BACKGROUND = 70

ADSORPTION DATA   COUNTING STANDARD = 683

TOTAL ADSORPTION(CPM/SQUARE INCH)
20055. 20914. 21183. 21606. 21203. 21469. 21813.
21309. 21456.
MEAN IS 21223. +/- 384.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
10417. 10684. 10242. 10448. 9946. 9468. 10183.
MEAN IS 10198. +/- 355.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
1900. 1858. 1869. 1896. 1916. 1884. 1897.
MEAN IS 1889. +/- 18.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
460. 469. 481.
MEAN IS 470. +/- 19.

QUANTITY BENZENE EXTRACTED   11025. +/- 429.
QUANTITY WATER EXTRACTED   8310. +/- 273.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 1419. +/- 19.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
67.04 70.84 71.64 69.27 71.06 69.58 71.22
69.53 72.43 71.69 72.91 70.24
MEAN = 70.62 +/- 1.01

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
67.65 70.47 72.40 64.16 65.90 61.74 68.08
69.28 72.76 69.15 64.11 72.52
MEAN = 68.19 +/- 2.28
METHYLENE IODIDE CONTACT ANGLE
28.54 33.04 34.32 32.91 34.81 35.60 35.66
31.32 33.79 34.22 34.79 31.92
MEAN = 33.41 +/- 1.29

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   48.00   55.40
POLARITY   0.17   0.24

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.36 +/- 1.30

APPENDIX IX (Continued)

ISOSTEARIC ACID

EXPERIMENTAL DATA FOR FILM CR - TEMP 85 - TIME 120 HR

ADSORPTION DATA   COUNTING STANDARD = 673   BACKGROUND = 71

TOTAL ADSORPTION(CPM/SQUARE INCH)
21077. 20350. 20436. 19738. 20482. 20768. 21259.
20784. 20384.
MEAN IS 20589. +/- 340.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
10401. 9298. 9949. 11129. 10968. 10757. 10409.
MEAN IS 10416. +/- 565.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
2102. 2056. 2059. 2067. 2093. 2081. 2053.
MEAN IS 2073. +/- 17.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
519. 511. 498.
MEAN IS 509. +/- 19.

QUANTITY BENZENE EXTRACTED   10173. +/- 495.
QUANTITY WATER EXTRACTED   8343. +/- 434.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 1564. +/- 19.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
72.87 70.05 74.29 69.37 73.65 74.84 72.10
69.35 70.07 72.32 70.50 73.66
MEAN = 71.92 +/- 1.25

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
61.93 70.91 66.45 68.97 67.56 69.36 66.07
70.08 63.12 69.01 70.57 69.26
MEAN = 67.78 +/- 1.81
METHYLENE IODIDE CONTACT ANGLE
35.06 33.75 36.45 35.35 35.32 36.47 38.62
38.35 37.28 35.93 37.74 35.83
MEAN = 36.35 +/- 0.91

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   47.20   54.60
POLARITY   0.19   0.25

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.69 +/- 1.72

ISOSTEARIC ACID

EXPERIMENTAL DATA FOR FILM CD - TEMP 105 - TIME 3 HR

ADSORPTION DATA   COUNTING STANDARD = 658   BACKGROUND = 70

TOTAL ADSORPTION(CPM/SQUARE INCH)
11785. 11418. 10340. 10813. 11188. 10484. 10698.
10729. 10704.
MEAN IS 10907. +/- 351.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
1422. 1451. 1498. 1573. 1553. 1599. 1593.
MEAN IS 1527. +/- 63.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
429. 451. 445. 421. 443. 447. 446.
MEAN IS 440. +/- 10.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
180. 188. 202.
MEAN IS 190. +/- 20.

QUANTITY BENZENE EXTRACTED   9380. +/- 328.
QUANTITY WATER EXTRACTED   1087. +/- 49.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 250. +/- 12.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
43.92 44.20 47.87 42.79 45.02 44.57 45.51
44.18 43.88 44.36 44.80 44.64
MEAN = 44.65 +/- 0.73

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
47.95 47.62 47.87 47.96 46.83 48.30 47.67
48.54 45.09 45.68 48.69 46.43
MEAN = 47.39 +/- 0.72
METHYLENE IODIDE CONTACT ANGLE
26.93 25.38 25.79 24.85 24.44 24.16 26.82
25.46 24.80 23.99 22.61 23.49
MEAN = 24.89 +/- 0.80

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   60.30   68.10
POLARITY   0.31   0.34

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.85 +/- 1.67

APPENDIX IX (Continued)

ISOSTEARIC ACID

EXPERIMENTAL DATA FOR FILM CC - TEMP 105 - TIME 6 HR

ADSORPTION DATA   COUNTING STANDARD = 673   BACKGROUND = 70

TOTAL ADSORPTION(CPM/SQUARE INCH)
12342. 12729. 11698. 12381. 12925. 13514. 13190.
12421. 12365.
MEAN IS 12618. +/- 406.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
2773. 2706. 2800. 2826. 2851. 2724. 2760.
MEAN IS 2777. +/- 47.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
722. 731. 766. 753. 761. 704. 753.
MEAN IS 741. +/- 20.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
252. 271. 257.
MEAN IS 260. +/- 18.

QUANTITY BENZENE EXTRACTED   9841. +/- 377.
QUANTITY WATER EXTRACTED   2036. +/- 39.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED   481. +/- 22.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
53.16 52.81 51.85 53.06 53.25 53.10 52.90
54.78 53.43 53.76 51.79 52.41
MEAN = 53.02 +/- 0.51

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
55.02 56.09 55.28 57.04 53.44 55.03 56.10
53.37 55.42 56.19 57.98 52.48
MEAN = 55.29 +/- 1.00
METHYLENE IODIDE CONTACT ANGLE
28.23 25.95 27.66 28.49 27.96 25.65 28.04
29.56 29.53 27.95 27.11 28.53
MEAN = 27.89 +/- 0.76

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   55.60   63.40
POLARITY   0.26   0.30

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.84 +/- 1.58

ISOSTEARIC ACID

EXPERIMENTAL DATA FOR FILM CB - TEMP 105 - TIME 12 HR

ADSORPTION DATA   COUNTING STANDARD = 668   BACKGROUND = 69

TOTAL ADSORPTION(CPM/SQUARE INCH)
13224. 14237. 13427. 14748. 14043. 12969. 13472.
13718. 12605.
MEAN IS 13605. +/- 499.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
5924. 6786. 6460. 6101. 5596. 6113. 5929.
MEAN IS 6130. +/- 348.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
1460. 1508. 1511. 1460. 1443. 1493. 1471.
MEAN IS 1478. +/- 23.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
521. 490. 519.
MEAN IS 510. +/- 32.

QUANTITY BENZENE EXTRACTED   7475. +/- 519.
QUANTITY WATER EXTRACTED   4652. +/- 267.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED   968. +/- 26.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
65.88 65.24 65.54 63.25 62.97 62.46 67.47
70.21 62.54 64.52 61.13 63.48
MEAN = 64.56 +/- 1.58

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
66.75 66.03 61.91 63.94 63.76 59.21 64.08
63.21 62.91 62.69 63.23 62.40
MEAN = 63.34 +/- 1.21
METHYLENE IODIDE CONTACT ANGLE
33.97 33.78 35.80 35.02 32.04 31.99 32.95
31.52 32.39 33.41 33.55 33.62
MEAN = 33.34 +/- 0.79

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   50.20   57.80
POLARITY   0.21   0.27

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.28 +/- 1.66

APPENDIX IX (Continued)

ISOSTEARIC ACID

EXPERIMENTAL DATA FOR FILM CA - TEMP 105 - TIME 24 HR

ADSORPTION DATA   COUNTING STANDARD = 675   BACKGROUND = 68

TOTAL ADSORPTION(CPM/SQUARE INCH)
22484. 21594. 21185. 21287. 20893. 21144. 20597.
21386. 21008.
MEAN IS 21286. +/- 402.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
10076. 10458. 10745. 10538. 10929. 11181. 10979.
MEAN IS 10701. +/- 334.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
2807. 2827. 2816. 2790. 2876. 2817. 2769.
MEAN IS 2815. +/- 30.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
766. 800. 798.
MEAN IS 788. +/- 35.

QUANTITY BENZENE EXTRACTED   10586. +/- 436.
QUANTITY WATER EXTRACTED   7886. +/- 257.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 2027. +/- 33.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
75.01 74.57 74.74 73.40 75.10 73.43 73.66
75.66 74.59 75.36 72.63 74.62
MEAN = 74.40 +/- 0.58

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
69.79 74.07 72.91 70.86 68.50 69.96 73.11
72.77 69.50 72.58 70.83 71.76
MEAN = 71.39 +/- 1.09
METHYLENE IODIDE CONTACT ANGLE
33.02 32.82 32.92 34.77 33.68 28.38 30.80
32.81 32.71 31.43 34.63 32.92
MEAN = 32.57 +/- 1.09

SURFACE ENERGY PARAMETER	OWENS-WENDT	WU
TOTAL ENERGY	47.10	54.20
POLARITY	0.14	0.22

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 29.16 +/- 1.57

ISOSTEARIC ACID

EXPERIMENTAL DATA FOR FILM CI - TEMP 105 - TIME 36 HR

ADSORPTION DATA   COUNTING STANDARD = 690   BACKGROUND = 71

TOTAL ADSORPTION(CPM/SQUARE INCH)
26805. 26462. 26137. 24896. 25488. 25676. 25355.
25959. 24789.
MEAN IS 25730. +/- 512.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
14393. 12880. 13429. 13673. 14269. 14051. 14186.
MEAN IS 13840. +/- 486.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
3521. 3385. 3431. 3424. 3476. 3480. 3451.
MEAN IS 3453. +/- 40.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
988. 948. 953.
MEAN IS 963. +/- 40.

QUANTITY BENZENE EXTRACTED   11890. +/- 577.
QUANTITY WATER EXTRACTED   10388. +/- 374.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 2490. +/- 43.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
78.03 77.29 76.41 77.81 75.33 78.44 76.97
78.10 77.43 76.71 76.95 77.14
MEAN = 77.22 +/- 0.54

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
70.17 67.61 72.59 68.49 69.42 75.43 74.48
73.90 69.07 72.82 73.60 72.55
MEAN = 71.68 +/- 1.64
METHYLENE IODIDE CONTACT ANGLE
36.79 33.14 37.96 41.30 37.20 40.42 39.10
36.12 39.29 38.78 37.72 38.21
MEAN = 38.00 +/- 1.34

SURFACE ENERGY PARAMETER	OWENS-WENDT	WU
TOTAL ENERGY	45.10	52.20
POLARITY	0.16	0.23

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.58 +/- 1.48

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APPENDIX IX (Continued)

ISOSTEARIC ACID

EXPERIMENTAL DATA FOR FILM CH - TEMP 105 - TIME 48 HR

ADSORPTION DATA   COUNTING STANDARD = 669   BACKGROUND = 71

TOTAL ADSORPTION(CPM/SQUARE INCH)
26804. 27672. 27758. 28627. 28746. 28129. 27734.
27623. 27774.
MEAN IS 27874. +/- 437.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
17191. 18816. 17933. 17675. 17323. 17476. 17613.
MEAN IS 17618. +/- 292.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
4050. 4080. 4148. 4110. 4069. 4132. 4078.
MEAN IS 4095. +/- 32.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
1080. 1123. 1084.
MEAN IS 1096. +/- 44.

QUANTITY BENZENE EXTRACTED   10256. +/- 450.
QUANTITY WATER EXTRACTED   13523. +/- 225.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 3000. +/- 36.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
83.23 83.77 83.54 84.11 83.41 82.11 83.03
82.22 83.43 82.55 82.23 81.50
MEAN = 82.93 +/- 0.50

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
73.89 76.76 74.84 76.75 71.08 72.14 75.88
68.49 74.52 71.95 73.80 75.49
MEAN = 73.80 +/- 1.56
METHYLENE IODIDE CONTACT ANGLE
37.45 38.08 37.19 37.42 37.43 36.33 31.29
37.28 35.86 33.58 36.13 37.05
MEAN = 36.26 +/- 1.23

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   45.00   51.90
POLARITY   0.13   0.21

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 29.61 +/- 1.53

ISOSTEARIC ACID

EXPERIMENTAL DATA FOR FILM CF - TEMP 105 - TIME 60 HR

ADSORPTION DATA   COUNTING STANDARD = 687   BACKGROUND = 71

TOTAL ADSORPTION(CPM/SQUARE INCH)
29806. 27963. 28333. 29177. 29209. 29595. 28911.
28463. 27681.
MEAN IS 28793. +/- 550.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
18219. 18574. 19304. 19118. 18561. 18644. 18004.
MEAN IS 18632. +/- 410.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
4723. 4712. 4664. 4744. 4679. 4659. 4664.
MEAN IS 4692. +/- 30.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
1066. 1012. 1045.
MEAN IS 1041. +/- 50.

QUANTITY BENZENE EXTRACTED   10161. +/- 580.
QUANTITY WATER EXTRACTED   13940. +/- 315.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 3651. +/- 35.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
82.79 83.97 83.57 85.01 85.27 86.16 82.74
84.78 84.88 84.54 85.32 85.56
MEAN = 84.55 +/- 0.68

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
75.93 77.54 76.33 75.02 76.07 76.84 73.26
75.88 75.64 75.31 78.12 78.35
MEAN = 76.19 +/- 0.89
METHYLENE IODIDE CONTACT ANGLE
37.96 40.06 39.05 34.89 33.90 39.16 38.65
35.24 38.83 38.65 39.80 39.77
MEAN = 38.00 +/- 1.32

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   43.50   50.20
POLARITY   0.12   0.20

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 29.19 +/- 1.68

APPENDIX IX (Continued)

ISOSTEARIC ACID

EXPERIMENTAL DATA FOR FILM CG - TEMP 105 - TIME 90 HR

ADSORPTION DATA   COUNTING STANDARD = 679   BACKGROUND = 68

TOTAL ADSORPTION(CPM/SQUARE INCH)
26961. 27287. 28886. 28498. 27449. 28223. 27341.
27654. 27762.
MEAN IS 27785. +/- 474.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
18622. 17343. 17539. 18071. 18488. 18589. 17796.
MEAN IS 18064. +/- 466.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
5107. 5121. 5158. 5126. 5152. 5130. 5133.
MEAN IS 5132. +/- 16.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
1199. 1233. 1211.
MEAN IS 1214. +/- 32.

QUANTITY BENZENE EXTRACTED   9721. +/- 541.
QUANTITY WATER EXTRACTED   12932. +/- 358.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 3918. +/- 19.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
86.15 84.44 84.93 83.15 84.53 87.48 86.76
83.28 82.94 85.07 88.64 79.61
MEAN = 85.12 +/- 1.13

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
75.15 79.02 72.95 76.99 78.00 71.29 77.04
77.37 82.71 72.31 81.03 79.61
MEAN = 76.96 +/- 2.21

METHYLENE IODIDE CONTACT ANGLE
39.09 41.21 41.56 41.48 39.05 43.90 41.66
42.51 38.44 38.00 39.86 37.95
MEAN = 40.39 +/- 1.21

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   42.40   49.00
POLARITY   0.12   0.20

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.94 +/- 1.51

ISOSTEARIC ACID

EXPERIMENTAL DATA FOR FILM CE - TEMP 105 - TIME 120 HR

ADSORPTION DATA   COUNTING STANDARD = 680   BACKGROUND = 73

TOTAL ADSORPTION(CPM/SQUARE INCH)
29987. 26404. 27455. 28551. 28789. 29129. 27929.
28559. 29001.
MEAN IS 28423. +/- 787.

CPM/SQ.INCH FOLLOWING BENZENE EXTRACTION
11665. 12107. 12921. 13015. 12399. 11852. 11998.
MEAN IS 12280. +/- 467.

CPM/SQ.INCH FOLLOWING WATER EXTRACTION
5067. 5078. 5061. 5096. 5119. 5080. 5138.
MEAN IS 5091. +/- 25.

CPM/SQ.INCH FOLLOWING SODIUM METHOXIDE-METHANOL EXTRACTION
1151. 1188. 1141.
MEAN IS 1160. +/- 45.

QUANTITY BENZENE EXTRACTED   16143. +/- 794.
QUANTITY WATER EXTRACTED   7188. +/- 359.
QUANTITY SODIUM METHOXIDE-METHANOL EXTRACTED 3931. +/- 30.

UNEXTRACTED FILM CONTACT ANGLES
WATER CONTACT ANGLE
87.80 86.34 83.92 83.21 89.40 85.34 86.82
84.31 87.13 85.34 85.40 78.47
MEAN = 85.29 +/- 1.73

CONTACT ANGLES ON WATER EXTRACTED FILM
WATER CONTACT ANGLE
79.95 79.42 74.25 81.30 79.19 81.40 72.57
78.42 74.92 80.59 82.86 81.49
MEAN = 78.86 +/- 2.05

METHYLENE IODIDE CONTACT ANGLE
39.90 43.46 40.49 41.76 40.62 41.00 39.02
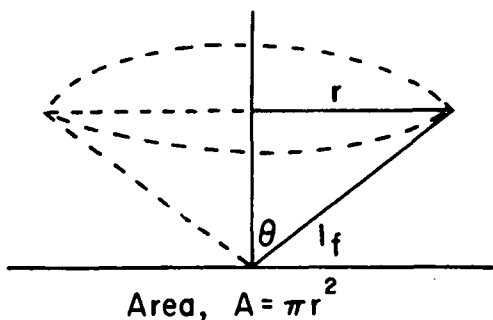41.66 43.46 42.40 41.17 42.64
MEAN = 41.47 +/- 0.86

SURFACE ENERGY PARAMETER   OWENS-WENDT   WU
TOTAL ENERGY   41.30   47.90
POLARITY   0.11   0.19

WATER C.A. ON SODIUM METHOXIDE EXTRACTED FILM = 28.48 +/- 1.45

APPENDIX X

SAMPLE AREA CALCULATIONS FOR THE RIGID AND FLIP-FLOP
MODELS OF MOLECULAR ORIENTATION

Area, $A = \pi r^2$

$\underline{r} = 1_f \sin \theta$,

where 1_f is the length of the fatty acid
(zigzag chain)

1_f (stearic acid) $= 25.6$ A

1_f (behenic acid) $= 30.7$ A

1_f (isostearic acid) $= 24.5$ A

	Stearic	Behenic	Isostearic
Assume $\theta = 30°$			
r,A	12.8	15.4	12.3
Area,A^2	515.0	740.0	471.0
Ratio,stearic = 1.00	1.00	1.44	0.92
Assume $\theta = 45°$			
r,A	18.1	21.7	17.3
Area,A^2	1029.0	1480.0	943.0
Ratio	1.00	1.44	0.92
Assume $\theta = 60°$			
r,A	22.2	26.6	21.2
Area,A^2	1544.0	2221.0	1414.0
Ratio	1.00	1.44	0.92
Assume $\theta = 90°$			
r,A	25.6	30.7	24.5
Area,A^2	2059.0	2961.0	1886.0
Ratio	1.00	1.44	0.92

Since the ratios remain constant, the efficiency of these molecules to
produce decreases in wettability on cellulose film is independent of the
inclination angle θ when these orientation models are assumed.

$$A = \pi r^2 \qquad r = 1_f \sin \theta$$

$$A = \pi 1_f^2 \sin^2 \theta$$

$$A_1 / A_2 = 1_{f_1}^2 / 1_{f_2}^2$$

APPENDIX XI

REPELLENCY EFFICIENCY CALCULATIONS FOR THE THREE ACIDS

Data: Figure 20

Contact Angle, deg.	Chemisorbed, % POML			Ratio*	
	Stearic Acid	Behenic Acid	Isostearic Acid	Stearic/ Behenic	Stearic/ Isostearic
48	2.4	1.5	2.7	1.53	0.89
50	2.8	1.8	3.2	1.55	0.88
53	3.5	2.4	4.0	1.46	0.88
55	4.2	2.9	4.7	1.45	0.89
58	5.4	3.8	6.0	1.42	0.90
60	6.3	4.5	7.1	1.40	0.89
63	8.3	6.0	9.1	1.38	0.91
65	10.0	7.3	10.8	1.37	0.93
68	13.6	9.6	14.4	1.42	0.94
70	17.1	11.7	18.0	1.46	0.95
73	23.5	15.8	25.2	1.49	0.93
75	29.0	19.5	30.8	1.48	0.94

*Ratio, stearic/behenic, mean is 1.45 ± 0.04;
ratio, stearic/isostearic, mean is 0.91 ± 0.02.