STUDIES OF ADVANCING AND RECEDING CONTACT ANGLES

BY

BARBARA A. JOHNSON

A thesis submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE
(Pharmacy)

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ACKNOWLEDGMENTS

I sincerely thank Professor George Zografi, who has guided me through this phase of my education. His comments have always steered me in the right direction.

I owe a debt of gratitude to Mr. Arthur F. Swenson, Supervisor of the Physics Instrument Shop for his aid in designing the environmental chamber. I also extend my thanks to the Physics Instrument Shop for building the environmental chamber.

I gratefully acknowledge the financial support provided by The American Foundation for Pharmaceutical Education through the AFPE W. Paul Briggs Memorial Fellowship and The Graduate School of The University of Wisconsin.

Last, but definitely not least, I thank my parents and sister for their emotional support, and in particular I thank my mother for typing my thesis.

STUDIES OF ADVANCING AND RECEDING CONTACT ANGLES

Barbara A. Johnson

Under the supervision of
Professor George Zografi

An apparatus for measuring advancing and receding contact angles was designed to allow four different methods of applying liquid drops to the solid surface. Contact angles were determined directly on sessile drops using a goniometer-telescope. The solids used were paraffin, polymethylmethacrylate (PMMA), and nylon; the liquids used were triple distilled water, ethylene glycol, methylene iodide, and aqueous solutions of sodium di-(2-ethylhexyl) sulfosuccinate (Aerosol OT).

This study showed that there was no statistically significant difference in the contact angle value obtained by the four different methods of delivery. With all solids advancing contact angle values were independent of the sessile drop volume, as expected. Receding contact angle values, however were only independent of volume on paraffin; on PMMA and nylon the values decreased with sessile drop volume. The decrease in the receding angles was accounted for by a stationary three phase line (TPL). It was proposed that forces used to retract the TPL were not sufficient to overcome the physical barrier to movement produced by surface roughness.

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INTRODUCTION

The process by which a liquid, like water coming in contact with a solid, increases its area of contact with the solid by displacing another phase, e.g. air or oil, is known as wetting. A quantitative means of assessing the extent of wetting tendency in a particular system is the measurement of contact angle. Usually designated as $\underline{\theta}$, the contact angle is the angle that is formed by the solid surface and the tangent of the liquid-vapor interface where the three phases meet (Figure 1). This junction will be referred to as the three phase line (TPL). If the liquid forms a spherical cap on the solid surface the TPL is a circle. The contact angle measured in degrees has a range of 0^0 for complete wetting and 180^0 for perfectly non-wetting systems. A finite contact angle ($\underline{\theta}>0^0$) is a common everyday observance, such as is seen for water droplets on a Teflon coated pan or on a plastic container.

Wetting of solids by liquids is important in many pharmaceutical procedures such as: suspension preparation, coating of tablets, pore penetration, and dissolution of dosage forms (1,2). Suspension formulations, for example, can be improved by adding surfactants which will decrease the contact angle and promote wetting of the solid, thereby

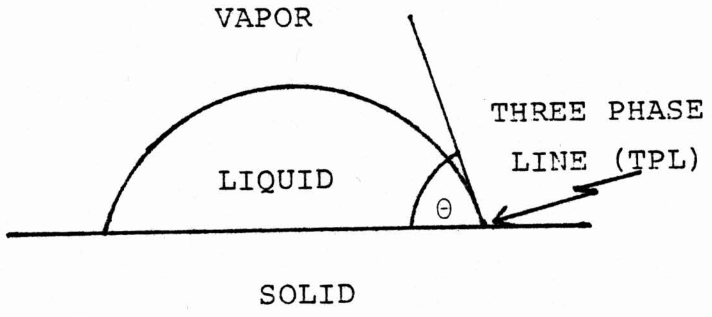


Figure 1. Finite contact angle of a sessile drop on a solid surface.

improving its incorporation into the suspension. Addition of surfactants in the dissolution medium also can increase the dissolution rate of hydrophobic powders if wetting is the rate limiting step. Contact angle, and wetting are also important in nonpharmaceutical processes such as: printing, dyeing, lubrication, and detergency (3).

Equilibrium Contact Angle

A theoretical understanding of the contact angle as a distinct measureable quantity for a specific solid/liquid system is based on the Young Equation (4).

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\Theta_e \qquad \text{(Eq. 1)}$$

The Young equation is a thermodynamic relationship that accounts for the balance of the three interfacial surface free energies (5-7) which produce a particular θ_e at equilibrium. These interfacial energies are: the solid-vapor interfacial free energy, γ_{SV}, the solid-liquid interfacial free energy, γ_{SL}, and the liquid-vapor interfacial free energy, γ_{LV}. The latter, γ_{LV} is the same quantity as the surface tension.

Apparent Contact Angle

The equilibrium contact angle θ_e, obtained from the Young equation is a very restrictive quantity, in that it is experimentally measureable only when the solid surface is smooth, homogeneous, and rigid with no polar impurities in the liquid and vapor phases. If these restrictions are not met, which is usually the case for real systems, contact angles other than an equilibrium contact angle are measured. These angles are referred to as apparent contact angles, and are usually designated as θ' to differentiate them from θ_e. Wenzel (8), assuming the cause of the nonideality to be due to the surface area difference caused by roughness, related θ_e to θ' by a roughness ratio, r, which is the ratio of the true surface area A including the hills and valleys and the apparent surface area A': $(r=A/A')$. This relationship:

$$\cos\Theta' = r \cos\Theta_e \qquad \text{(Eq. 2)}$$

is referred to as the Wenzel equation. Cassie and Baxter (9), assuming that the nonideality was due to a nonhomogenous surface accounted for the apparent contact angle with a composite surface; i.e. a solid surface having air pockets:

$$\cos\Theta' = f_1\cos\Theta_e - f_2 \qquad \text{(Eq. 3)}$$

In this case f_1 and f_2 are the surface area fractions of the solid-liquid interface and the air-liquid interface respectively.

Angle Hysteresis

A further complication in defining contact angles arises if one compares results obtained from advancing and receding equilibrium contact angles. Advancing contact angles, $\underline{\Theta_a}$, are obtained when the TPL has established an equilibrium position just subsequent to moving over a previously unwetted surface in an environment limiting evaporation. Conversely, receding contact angles, $\underline{\Theta_r}$, are obtained upon equilibration just as the TPL is starting to retract over the already wetted surface. In most cases, the values of $\underline{\Theta_a}$ and $\underline{\Theta_r}$ are consistently different with $\underline{\Theta_a}$ being generally greater than $\underline{\Theta_r}$. The difference between these values is defined as $\underline{H}$, the contact angle hysteresis (10):

$$H \equiv \Theta_a - \Theta_r \qquad \text{(Eq. 4)}$$

There are many different ways of measuring advancing and receding angles (11). One may simply add a sessile drop to a flat surface, measure the advancing contact angle, and then retract the volume of the drop, using a syringe and needle, and measure the receding angle. Another method, using a sessile drop on a flat surface is the tilted plate method (12) in which the flat surface is tilted until the critical tilting angle $\underline{\alpha_{crit}}$, is obtained; $\underline{\alpha_{crit}}$ is the angle at which the drop would begin to slide off the surface. The angles measured at the lowest point and at the highest point of the TPL are the advancing and receding angles respectively. A third approach (11) using a fiber or wire attached to an electrobalance, measures forces on the solid as it is immersed or pulled out of a reservoir of the liquid.

The causes of hysteresis are usually assigned to either surface chemical heterogeneity, surface roughness or both. Hysteresis has been shown to vary with drop size (13). This variation, however, can be removed by using drops larger than about 20 μm.

Surface Chemical Heterogeneity

The effect of surface chemical heterogeneity has been studied theoretically by assuming that liquid encounters alternating strips of substances having different equilibrium contact angles (14, 15). It was shown that advancing angles are a better measure of the low energy portions of a heterogeneous surface (higher θ) and that receding angles are a better measure of the high energy portions (lower θ). Neumann and Good (14) showed that a surface should have domains with lateral dimensions greater than 0.1 µm for hysteresis to occur. It was also shown (16) that metastable states for both θ_a and θ_r within an envelope of maximal θ_a and minimal θ_r may exist depending on the system. Thus the value of H may vary under some apparent equilibrium conditions due in part to surface chemical heterogeneities.

Herzberg et al. (17) noted hysteresis on a Me_3SiCl-treated glass surface and determined the cause to be chemical heterogeneities of the surface due to a less than monolayer coverage. This was confirmed by analyzing the surface after it was treated with tritium labeled Me_3SiCl. They also varied the amount of the surface covered by the trimethysilyl groups and found the advancing angles to be fairly constant after about 20% coverage as predicted by Johnson and Dettre's theory (15).

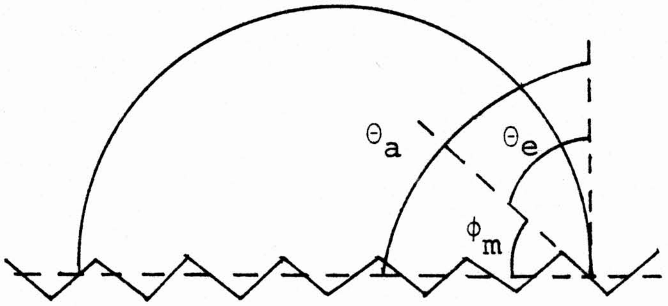
Surface Roughness

Another major factor in producing contact angle hysteresis is the nature and degree of surface roughness. The fact that roughness affects wetting in general was mentioned earlier when discussing the Wenzel equation (Eq. 2). Shuttleworth and Bailey (18), assuming that the equilibrium angle, $\underline{\Theta_e}$, is still the stable angle formed in reference to the solid surface at the microscopic level, but that the observed angle is modified by the slope angle of the rough surface, derived the following equations:

$$\Theta_a = \Theta_e + \phi_m \tag{Eq. 5}$$

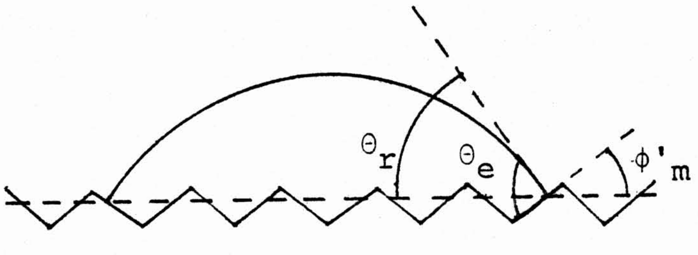
$$\Theta_r = \Theta_e - \phi'_m \tag{Eq. 6}$$

where $\underline{\phi_m}$ and $\underline{\phi'_m}$ are the maximum slope angles of the grooves in the same direction as the advancing and receding TPL, respectively. (See Figure 2). Shepard and Bartel (19) studied the effects of roughness on contact angles using paraffin samples that were cut such that the surface was composed of pyramids of known slope angles and heights. They found that the pyramid height had little effect in comparison to the slope angles on the observed contact angles. From Wenzel's equation, (Eq. 2), one would predict that roughness would increase angles greater than 90^0 and decrease angles lower than 90^0, but Shepard and Bartell noted that roughness caused an increase in the advancing angle and a decrease in the receding angle. They noted that the TPL for stable advancing contact angles was on the pyramid face away from the drop center while for stable



(a) Advancing Sessile Drop:

$$\Theta_a = \Theta_e + \phi_m \qquad \text{(Eq. 5)}$$



(b) Receding Sessile Drop:

$$\Theta_r = \Theta_e - \phi'_m \qquad \text{(Eq. 6)}$$

Figure 2. Effect of Roughness on Contact Angle for both (a) advancing and (b) receding sessile drops.

receding angles the TPL was on the pyramid face towards the drop center. Thus as the liquid recedes down the pyramid face, at some point the next pyramid peak may break through the liquid-vapor interface of the drop causing the TPL to move down the face of this new pyramid leaving liquid behind in the valley.

Johnson and Dettre (20) looked at a model surface of roughness, a surface having concentric grooves, and theoretically determined a series of metastable states for the drop configuration and the energy barriers associated with them. Then knowing the energy of the drop, the roughness ratio, and Θ_e, they could predict values for Θ_a and Θ_r. Their theory showed that increasing roughness increased Θ_a and decreased Θ_r, which was experimentally observed by Shepard and Bartell (19); and that the apparent contact angle predicted by the Wenzel equation (Eq. 2) had the lowest free energy state, but the highest energy barrier between metastable states. Huh and Mason (21) in another theoretical paper, modeled surface roughness by adding to the Wenzel equation (Eq. 2) a surface texture factor Φ such that:

$$\cos\Theta' = \cos\Theta_e \, (\sigma + (\sigma - 1)\,\Phi) \qquad \text{(Eq. 7)}$$

where σ is an area ratio approximately equal to r. This equation has never been tested with experimental data probably due to the difficulty in obtaining Φ and σ for a specific system.

Mason et al. (22, 23) experimentally studied the effect of texture on contact angles by working with materials having different types of roughness and have shown both increasing and decreasing angles relative to smooth surfaces. These included: bead blasted, spiral grooves, hexagonal grooves and radial grooves. The behavior of the advancing contact angle varied with the different surfaces due to the drop shape and movement of the TPL. The TPL moves continuously (no sticking) on surfaces with radial or hexagonal grooves, as the grooves and crevices provided an easy route, acting as wicking channels. In contrast, as a liquid is caused to spread over, or pulled back, spiral grooved and bead-blasted surfaces showed a stick-jump behavior, i.e. the TPL as it is being advanced sticks to edges present on the surface until it finally jumps across the groove to another stable position. These edge effects result in variation of the measured $\underline{\Theta_a}$ and $\underline{\Theta_r}$.

It is clear from this discussion that hysteresis like this must occur on all surfaces exhibiting various degrees of roughness, thus making it important to take into account the possible influence of surface roughness on the interpretations of wetting behavior in more practical situations. It is also important to recognize that roughness and surface chemical heterogeneity are difficult to separate as factors and that roughness in particular is difficult to eliminate. For example Penn and Miller (24) attributed their observations of hysteresis to surface chemical heterogeneity entirely, when they showed by SEM that very shallow grooves existed in their solid sample. Oliver and Mason (22) however, have shown that roughness may play a role in contact angle hysteresis with crystal step heights as low as 0,05 µm.

STATEMENT OF THE PROBLEM

Contact angle hysteresis, as described in the introduction is observed on most solid surfaces. Thus there was a need to design and build an apparatus which could measure both the advancing and receding contact angles on the same sample. Such an apparatus would have to limit evaporation, control the temperature, allow the sample to be leveled, and have the ability to add the liquid from above and below the sample.

The liquid delivery system must be designed so the drop volume would be known while advancing and receding the drop. Systems having a large range of contact angles must be measured and compared with literature values of the same systems to evaluate the performance of the apparatus.

The flexibility of the apparatus must be tested by measuring advancing and receding contact angles on several materials by different methods of liquid delivery. Any parameter which could have an effect on the measured contact angles should be elucidated. These include: liquid polarity, time effects and drop volume effects.

EXPERIMENTAL

Materials

Solids - Three solids were used as substrates in this study, paraffin[1], polymethylmethacrylate[2] (PMMA) and nylon[3]. PMMA and nylon were used in the form of disks having a diameter of about 0.5 inches and a height of about 0.25 inches. Paraffin was used in the form of sheets as received from the manufacturer[1]. Previous studies had shown good agreement in contact angle for block paraffin and the sample used in this study (25).

PMMA and nylon samples were washed using the following procedure. The disks were soaked for at least 4 hours in an Alconox[4] solution. They were gently scrubbed using a new cellulose sponge and rinsed thoroughly using tap, distilled, and tripled distilled water. During the cleaning process the disks were handled with gloved hands, and were placed in a desiccator with phosphorous pentoxide[5]. After a vacuum was drawn the desiccator was placed in an oven at ∿60° C for at least 12 hours. Initially the PMMA disks were dried without heating, but it

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[1] Parafilm M manufactured by the American Can Company.

[2] Glasflex Corporation.

[3] Nylon 11 as used in reference (26).

[4] Alconox Inc.

[5] MCB Manufacturing Chemists, Inc.

was found that the contact angles increased by several degrees when they were heated to 60° C during the drying step.

Liquids - Three liquids, triple distilled water, ethylene glycol[6], and methylene iodide[7] were used for contact angle measurement since they covered a wide range of relative polarities. Aqueous solutions of sodium di-(2-ethylhexyl) sulfosuccinate, Aerosol OT[8] (AOT) were also used as test solutions. The Aerosol OT was purified using a liquid-liquid extraction method with petroleum ether and then dried over phosphorous pentoxide in a desiccator as described previously (26).

The resultant solid AOT was determined to be pure in relation to surface active impurities as there was no minimum in the surface tension vs. logarithm of concentration plot. The critical micelle concentration of AOT in distilled water was experimentally determined as 2.6×10^{-3}M which agrees favorably with 2.5×10^{-3}M from an earlier study (27). The surface tension of all the AOT solutions used in the contact angle experiments was determined at 25° C using the Wilhemy plate technique. The sodium chloride, used in some experiments, was reagent grade[9].

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[6] Ethylene glycol was 99+% from Aldrich Chemical Company,Inc.

[7] Methylene iodide was 99% from Aldrich Chemical Company,Inc.

[8] Fisher Scientific Company.

[9] Amend Drug and Chemical Company.

Apparatus for Measuring Contact Angles

An environmental chamber (Fig. 3) consisting of an air tight plexiglas square box of inner dimensions 6"x6"x6" was built to prevent evaporation of the test liquid. Several beakers (A) filled with test liquid are placed inside the chamber to decrease the evaporation rate from drops used for contact angle measurement. The temperature inside the chamber is regulated by water (which is heated by an external water bath) circulating through copper tubing (B) coiled inside the chamber, and monitored by a thermometer (C) with 0.1^0 C graduations.

The chamber (Fig. 4) was designed so that the test liquid can be delivered to the solid sample either from the top or from the bottom through a hole in the solid sample. The top of the box is removable to gain access inside the chamber. A rubber o-ring (a) seals the chamber when the lid (b) is screwed (c) in place. The solid sample is placed on a flat circular stainless steel surface (d) which has a hole drilled through the center for bottom delivery. This steel sample support can be leveled by the 3 screws (e) in the support base (f). Also the entire chamber can be leveled by its tripod base.

A known volume of test liquid is placed on the solid sample using a micrometer-syringe assembly, (Fig. 5). It consists of a Hamilton gas-tight luer lock 1.0 ml. syringe (A)

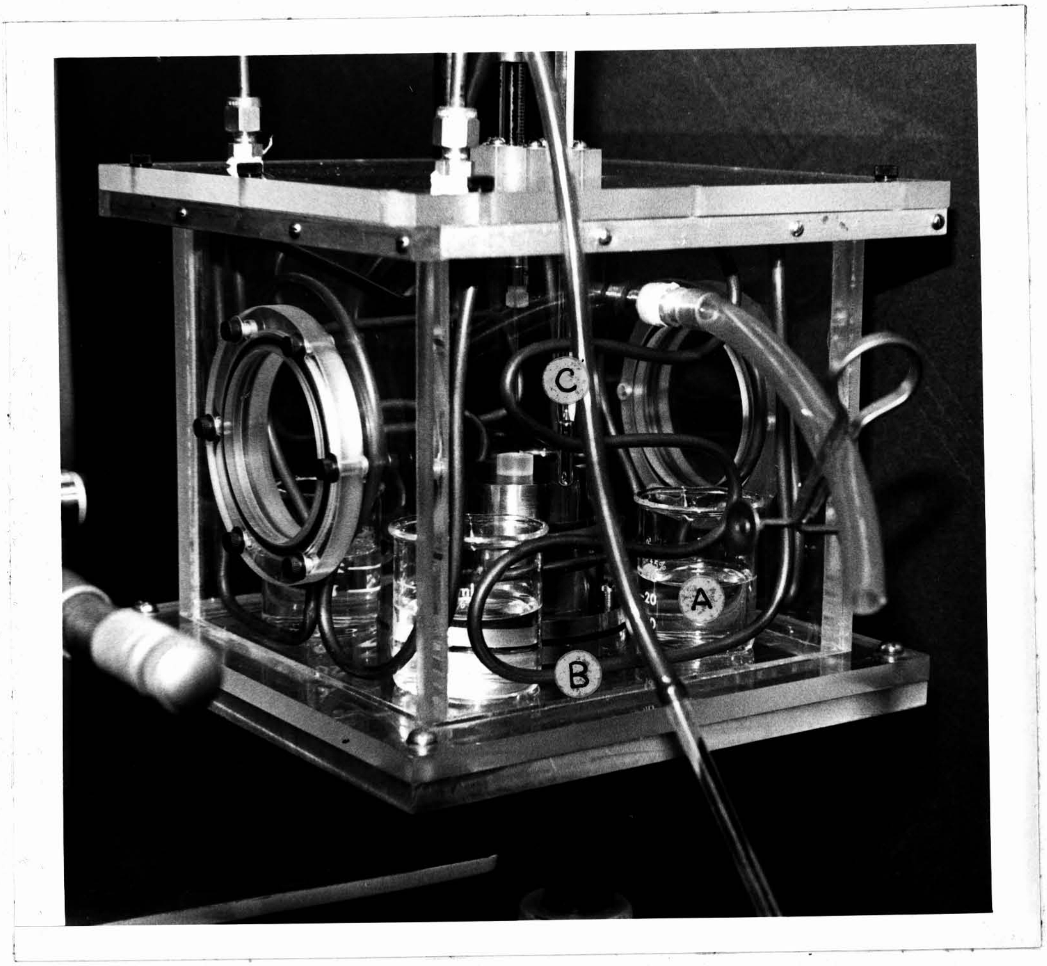

Figure 3. Environmental Chamber:

(A) 50 ml beakers, (B) Copper tubing

(C) Thermometer

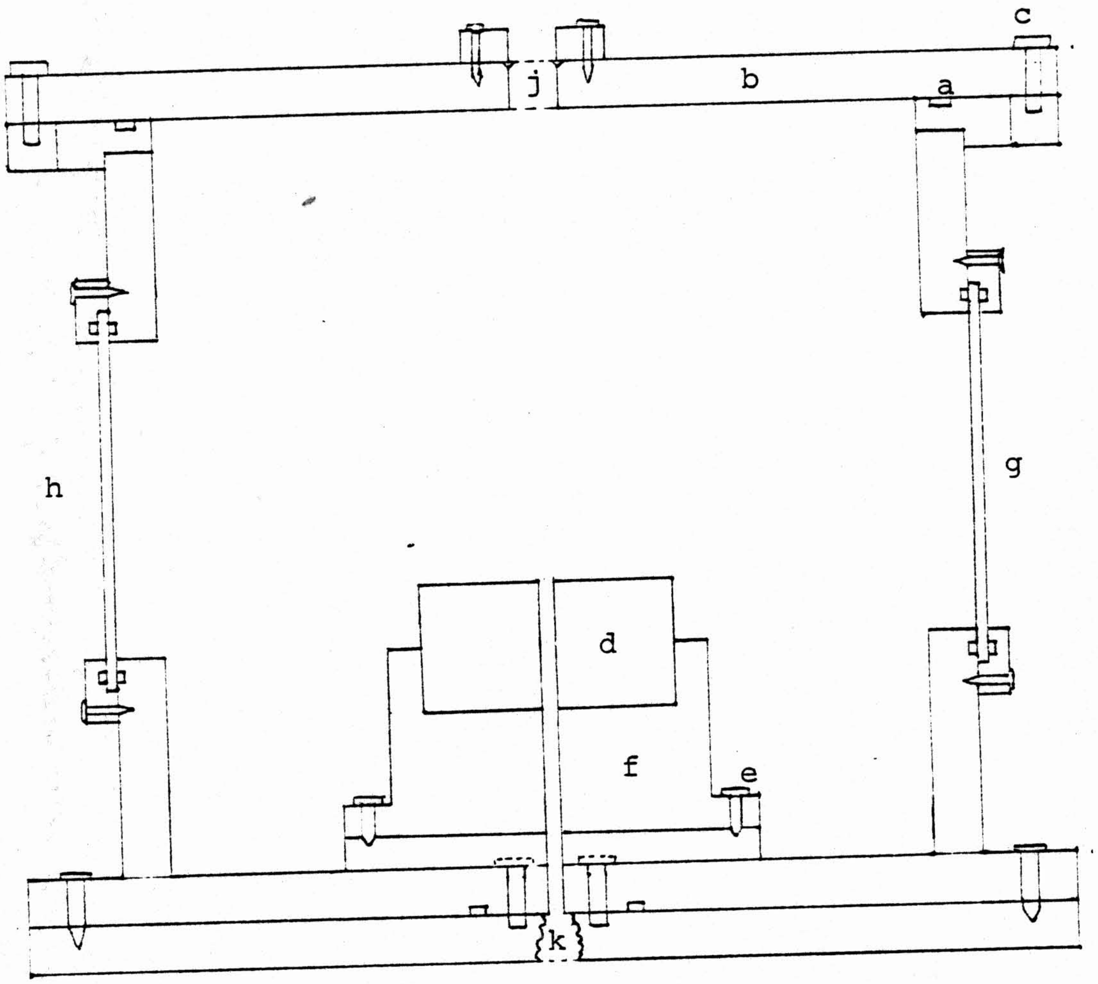

Figure 4. Diagram of Environmental Chamber: (a) lid o-ring, (b) lid, (c) lid screws, (d) sample support, (e) leveling screws, (f) sample support base, (g) front glass window, (h) back glass window, (j) syringe o-ring, (k) Swagelok fitting.

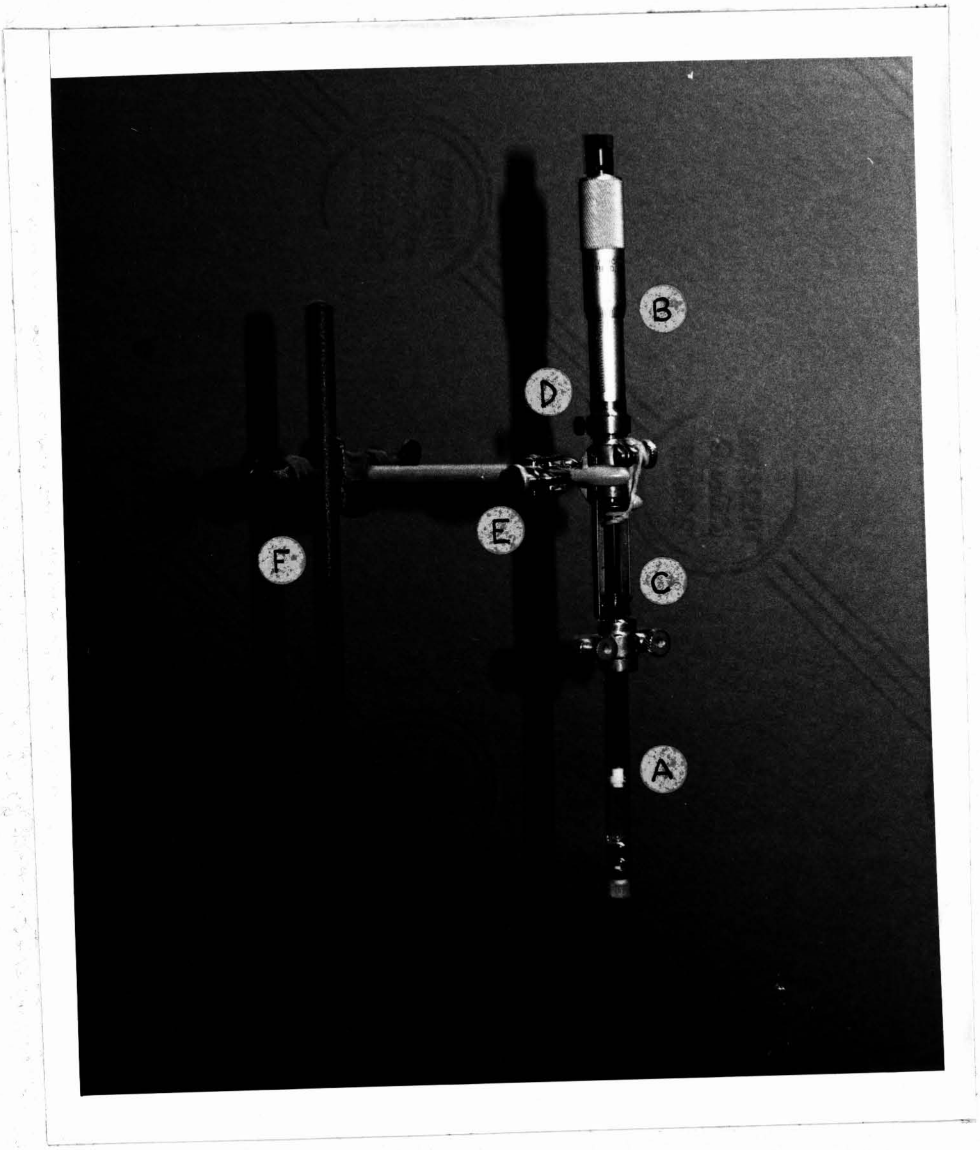

Figure 5. Micrometer-syringe Assembly:

(A) syringe, (B) "Agla" micrometer head,

(C) syringe holder, (D) lock screw,

(E) clamp to secure assembly

(F) ring stand

fitted into an "Alga"[10] micrometer head (B) and holder (C). The micrometer head is calibrated with ethylene glycol such that a micrometer reading of 1.0 units equals 17.0 μl of liquid. Depending on the direction of movement of the micrometer head liquid can be added or removed by the micrometer-syringe assembly in specific volume increments. The syringe plunger can also be secured in place by a lock screw (D) on the micrometer section to prevent changes in liquid volume due to leakage or back suction.

The sessile drop is viewed through a glass window (g in Fig. 4) in the environmental chamber. In order to get a good "two-dimensional" image of the drop, diffuse backlighting through the diametrically opposed back window (h) is used. The contact angles of the sessile drops were measured directly using a goniometer-telescope[11] (See Fig. 6).

Contact Angle Measurement

General Considerations - Using the previously described apparatus for measuring contact angles, there are four possible ways of delivering liquid to the solid sample. They will be referred to as Method I, II, III, and IV. For all of the methods and solid samples the chamber

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[10] Burroughs Wellcome & Company.

[11] Gaertner Scientific Corporation.

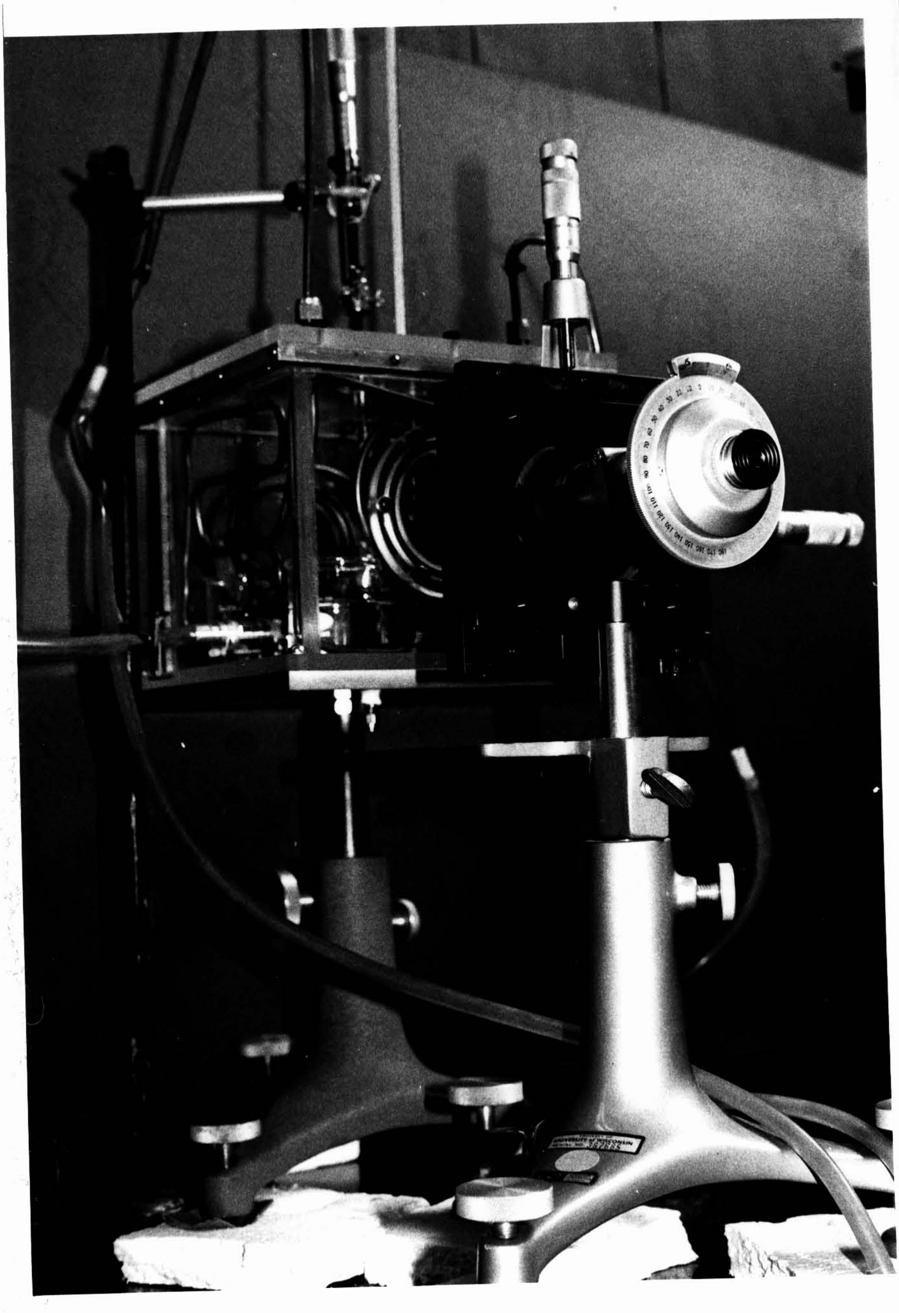

Figure 6. Apparatus for Measuring Contact Angles

was presaturated using beakers filled with the test liquid. For water, presaturation with 4 - 50 ml. beakers was carried out for at least one hour before the drop was introduced. For ethylene glycol, presaturation using 2 - 50 ml. beakers was allowed for at least 15 minutes. The chamber was not presaturated with methylene iodide as it has a low vapor pressure and has a tendency to degrade when exposed to light. For all measurements the temperature inside the chamber was maintained at $25.0^{0} \pm 0.2^{0}$ C.

The contact angles were read directly to the nearest 0.1^{0} from each side of the drop using the goniometer-telescope. At least one minute was sufficient for equilibration of the advancing or receding contact angle when pure liquids were used. Several readings were taken and the values were averaged for each side of the sessile drop. The standard deviations of these average values were usually of the order of 1^{0}. Surfactant solutions were allowed up to about 30 minutes to reach equilibrium, depending on the concentration, since the Aerosol OT molecules require time to adsorb to the liquid-vapor and liquid-solid interfaces of the sessile drop. The reported contact angle values are average values taken at about the 30 minute point which was sufficient for equilibrium in all cases. The sessile drops were generally greater than

20 µl to insure against error due to bulk depletion of the surfactant.

Method I - Liquid was delivered to the solid sample from above using a 2 inch 26 gauge stainless steel needle[12] with a non-beveled tip and a Teflon luer hub affixed to the previously described micrometer-syringe assembly. The assembly was firmly secured by a clamp (E in Fig. 5) attached to a ring stand (F) and sealed into the chamber by an o-ring (j in Fig. 4) in the lid. Method I consisted of adding the liquid dropwise; the needle tip was positioned ∿ 1 inch above the solid sample surface. Two to four drops of liquid were applied initially and sometimes additional drops were used to increase the sessile drop. Only equilibrium advancing angles were obtainable by Method I. This method has the advantage of not having the drop in contact with the needle after coming in contact with the solid but sometimes the liquid, as it was applied, would "bounce" on the solid surface particularly at the higher contact angle values ($\Theta > 90^0$).

Method II - consisted of applying the liquid to the solid sample such that the needle remained in contact with the liquid until the drop settled on the surface.

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[12] Hamilton Company.

Then the needle was carefully removed from the sessile drop. Again, only equilibrium advancing contact angles were obtainable by this method since the needle was no longer in contact with the drop. To assure continued contact between needle and drop during delivery, the needle must be initially positioned very close to the surface, i.e. about 1-2 mm from the solid surface.

Method III - is similar to Method II in that the needle was positioned close to the solid surface, however in this case the needle was not removed but always remained in contact with the liquid. Occasionally contact angles were distorted depending on the position of the needle in the sessile drop, and these values were discarded. In one run it was possible to obtain a series of equilibrium advancing contact angles by increasing the drop in volume increments. Usually, increments of ∿8.5 μl were added until the sessile drop volume was 42.5 to 51.0 μl. Liquid was then removed from the sessile drop in ∿8.5 μl decrements such that a series of equilibrium receding contact angle values were obtained. "Readvancing" equilibrium contact angles could be obtained by again adding more liquid over the same solid surface that had already been covered with the liquid.

Method IV - consisted of delivering the liquid to the solid sample from the bottom. To accomplish this a hole ∿ 1 mm in diameter was punctured into the paraffin samples using an 18 Gauge needle or drilled into the PMMA disks. The liquid was delivered to the solid sample using a 20 Gauge Teflon tube needle with a luer hub affixed to the previously described micrometer-syringe assembly. The assembly was secured by a clamp attached to a ring stand and the Teflon needle was sealed into the environmental chamber by a Swagelok fitting (k in Fig. 4) in the bottom of the chamber. Since the paraffin samples were so thin, the Teflon needle would inevitably stick out ∿ 1 mm above the surface. This was an occasional source of distortion of the contact angle depending on the needle position in the sessile drop. There seemed to be no leakage problem at the paraffin-Teflon needle interface, but leaking did occur at the PMMA-Teflon needle interface. The leakage problem was solved by placing the PMMA disk on a sample of paraffin, puncturing the paraffin with a 22 Gauge needle, inserting the Teflon needle through the paraffin layer, and lodging the Teflon needle firmly in the drilled hole of the PMMA disk. In this case the Teflon needle did not stick up above the PMMA surface thereby eliminating the needle placement as a source of contact angle distortion. As with Method III a series of equilibrium advancing and receding contact angles could be obtained by adding or removing, respectively, incremental volumes of liquid.

RESULTS

Equilibrium Advancing Contact Angles on Paraffin

Water - Advancing contact angles of water on paraffin were measured by the four different methods of delivery using different volumes of sessile drops. The values in Table I were obtained by averaging the individual contact angle values for the left and right side of the sessile drop for each specific volume and method. Within each method there was no statistically significant difference ($p=0.25$) in the contact angle values due to volume differences. The greatest variation in contact angle values seemed to be due to the different solid samples, i.e. different runs. Thus a procedure grouping the different volumes within a run to obtain $\underline{\overline{\Theta}_{Left}}$ and $\underline{\overline{\Theta}_{Right}}$ values for each run was used. These values were then averaged to obtain the average contact angle values listed in the last row of Table I. There was no statistically significant difference ($p=0.05$) between the four methods, using grouped volumes. The average contact angle value for water on paraffin of 106.9^0 was the value obtained by averaging all $\underline{\overline{\Theta}_{Left}}$ and $\underline{\overline{\Theta}_{Right}}$ for each run regardless of the method. This value compares favorably with previously reported data for water on paraffin (Table II).

TABLE I. ADVANCING CONTACT ANGLES OF WATER ON PARAFFIN

	DELIVERY METHOD			
DROP VOLUME	I	II	III	IV
10 μℓ				105.5°
15 μℓ				104.6°
20 μℓ		106.4°	108.4°	104.7°
25 μℓ	104.6°			105.3°
30 μℓ	108.0°	106.4°	108.0°	103.3°
35 μℓ			109.0°	105.2°
40 μℓ			108.2°	105.7°
45 μℓ			108.4°	104.8°
50 μℓ			108.4°	106.4°
Average	106.3°	106.4°	108.4°	105.2°

TABLE II - REPORTED ADVANCING CONTACT ANGLES ON PARAFFIN

WATER

CONTACT ANGLE	REFERENCE
106.9°	This work
103°	Pyter (26)
105°	Elton (28)
106°	Adamson (29), Zografi (30), Panzer (31)
108°	Shafrin (32), Owens (33)
109°	Zografi (25)
108° - 111°	Fox (34)
110°	Dann (35), Shepard (19)
110° - 111°	Krien (36)
111°	Fowkes (37)

ETHYLENE GLYCOL

81.6°	This work
79°	Zografi (30)
81°	Shepard (19)
81.5°	Elton (28)
83°	Dann (35)
86°	Panzer (31)

Ethylene Glycol - Advancing contact angles of ethylene glycol on paraffin were measured using different volumes of sessile drops and three different methods of delivery. There was no statistically significant difference due to volumes (p=0.25) nor was there a statistically significant difference (p=0.025) between the three different methods using grouped volumes (Table III). The average contact angle for ethylene glycol on paraffin of 81.6^{0} compares favorably with previously reported values (Table II).

Aqueous AOT Solutions

Advancing contact angles of six different aqueous AOT solutions of various concentrations were measured on paraffin. Four of the solutions (A,B,C,D) were in 0.1 M sodium chloride while two of the solutions (E,F) contained no sodium chloride. Contact angles of Solution F were studied extensively in reference to different sessile drop volumes and the four different methods of delivery. The values in Table IV (Rows 1 - 6) were obtained by averaging the individual 30 minute equilibrium contact angle values for the left and right side of the sessile drop for each specific volume and method. Within Method III there was no statistically significant difference (p=0.10) due to volumes in the contact angle values. There was no statis-

TABLE III - ADVANCING CONTACT ANGLES OF ETHYLENE GLYCOL ON PARAFFIN

DROP VOLUME	DELIVERY METHOD		
	II	III	IV
20 μℓ		83.0°	
25 μℓ	79.5°	82.0°	81.5°
30 μℓ	80.8°	83.0°	
35 μℓ			80.6°
40 μℓ		84.1°	
45 μℓ			81.0°
50 μℓ		83.5°	
60 μℓ		82.6°	81.4°
Average	80.2°	83.2°	81.2°

TABLE IV - ADVANCING CONTACT ANGLES OF 1 x 10^{-3} M AEROSOL OT IN WATER ON PARAFFIN (SOLUTION F)

DROP VOLUME	DELIVERY METHOD I	II	III	IV
10 μℓ	61.1°			
15 μℓ			68.5°	
25 μℓ	61.8°		66.2°	
30 μℓ		63.6°		
35 μℓ	62.0°	66.0°	64.8°	63.8°
40 μℓ			68.2°	67.0°
Average	61.6°	64.8°	65.3°	65.0°

tically significant difference (p=0.10) between the four different methods using grouped volumes. Table V shows the average contact angle values along with the corresponding concentration and surface tension data for the six different aqueous solutions of AOT.

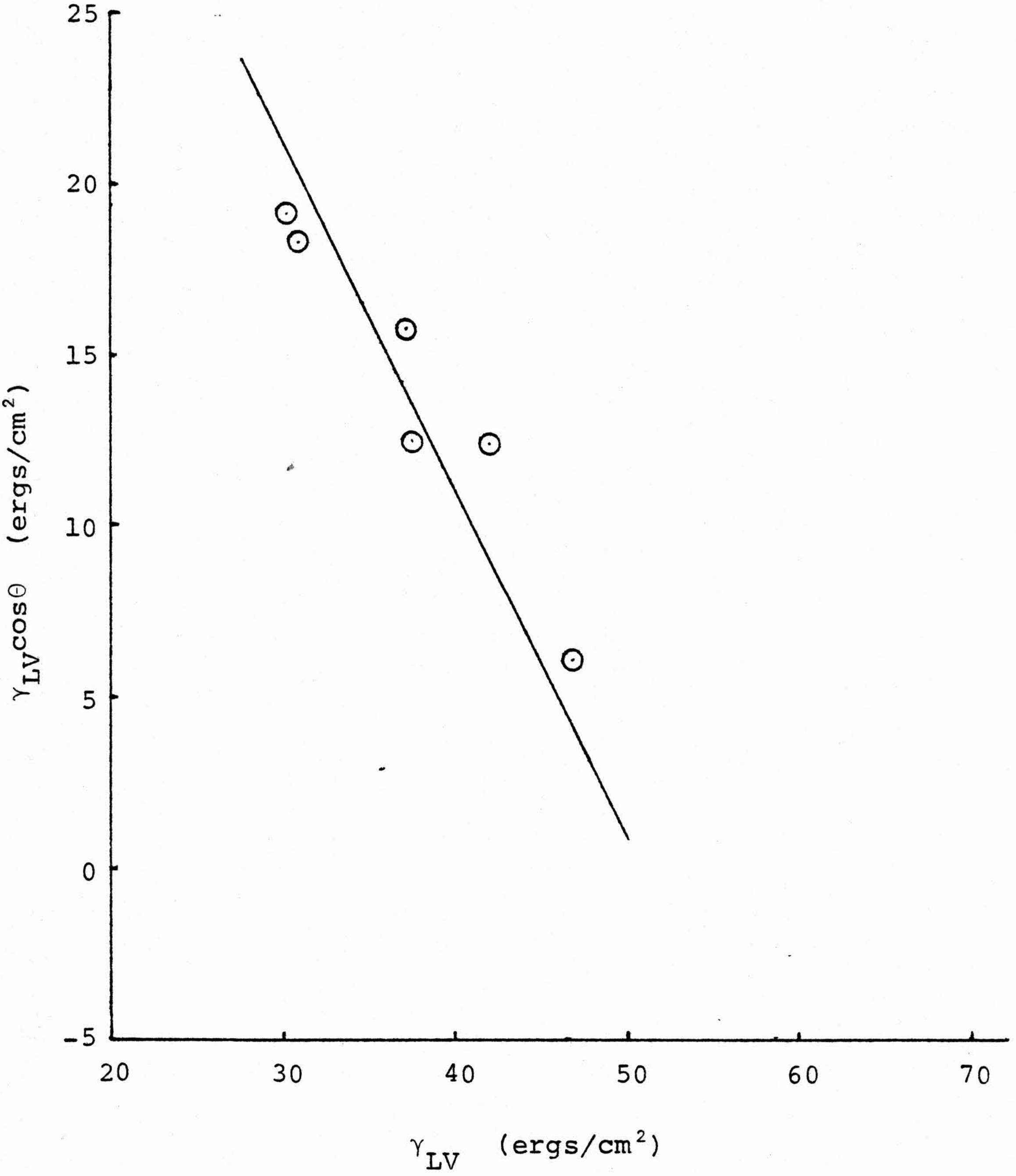
The accuracy of these values was further confirmed by subjecting them to a plot of $\gamma_{LV}\cos\theta$ vs. γ_{LV} (Fig. 7) which had been shown previously to follow a straight line with slope of approximately -1 (38, 39). Indeed, in Fig. 7 such a plot gives a straight line with values reasonably close to a slope of -1.

Equilibrium Advancing Contact Angles on PMMA

Advancing contact angles of water, ethylene glycol, and methylene iodide were measured on PMMA using Method III for different volumes (Table VI). The PMMA samples used were heated in the cleaning process; except in the case of water as there was no statistically significant difference (p=0.005) in the contact angle values whether the samples were heated or not. There was no statistically significant difference (p=0.25) in the advancing contact angle values due to differences in volume for water and ethylene glycol on PMMA. The average advancing contact angle values using grouped values of 80.5^0 for water, 50.5^0 for ethylene glycol, and 31.6^0 for methylene iodide compared

TABLE V - AVERAGE ADVANCING CONTACT ANGLE VALUES OF AQUEOUS AEROSOL OT SOLUTIONS

SOLUTION	CONCENTRATION (M)	SURFACE TENSION (dyne/cm)	CONTACT ANGLE
A	7.2×10^{-6}	46.93	82.6°
B	4.5×10^{-5}	37.44	70.5°
C	1.6×10^{-4}	30.81	53.4°
D	1.6×10^{-4}	30.25	50.7°
E	5.3×10^{-4}	41.94	72.8°
F	1.0×10^{-3}	37.02	64.6°



<u>Figure 7</u>. $\gamma_{LV}\cos\Theta$ <u>vs</u>. γ_{LV} for Aqueous Aerosol OT Solutions

Solid line has theoretical slope of -1

TABLE VI - ADVANCING CONTACT ANGLES ON POLYMETHYLMETHACRYLATE

	LIQUID		
DROP VOLUME	WATER	ETHYLENE GLYCOL	METHYLENE IODIDE
10 µℓ		49.9°	
17 µℓ	75.7°	51.0°	
22 µℓ			32.3°
25 µℓ	75.1°	50.2°	31.0°
34 µℓ	80.3°	51.0°	
42 µℓ	76.1°	50.0°	
51 µℓ	82.1°	52.3°	
Average	80.5°	50.5°	31.6°

favorably with previously reported values (Table VII).

Equilibrium Advancing Contact Angles on Nylon

Advancing contact angles of water, ethylene glycol, and methylene iodide on nylon were measured using Method III for different sessile drop Volumes (Table VIII). The advancing contact angle values appeared not to depend on the drop volume used. The average advancing contact angles of 64.8° for water, 44.8° for ethylene glycol, and 39.6° for methylene iodide compared favorably with those previously reported (Table IX).

Equilibrium Receding Contact Angles on Paraffin

Receding contact angles of water and ethylene glycol on paraffin were measured using Method III for different sessile drop volumes (Table X). There was no statistically significant difference ($p=0.25$) due to volume in the contact angles. The average receding angle of 97.0° compares favorably with the reported values of 95° (47) and 99° (19) as does the 72.8° for ethylene glycol with 74° (19).

Equilibrium Receding Contact Angles on Polymethylmethacrylate

Receding contact angles of water, ethylene glycol and methylene iodide on PMMA were measured using Method III for different sessile drop volumes (Table XI). Again, the PMMA

TABLE VII - REPORTED ADVANCING CONTACT ANGLES ON POLYMETHYLMETHACRYLATE

WATER

CONTACT ANGLE	REFERENCE
80.5°	This work
62.6°	Zografi (25)
67°	Andrade (40)
71°	Panzer (31)
72°	Pyter (26)
74°	Dann (35)
78°	Craig (41)
80°	Owens (33), Fox (34), Shafrin (32)
86°	Herzberg (42)

ETHYLENE GLYCOL

50.5°	This work
51°	Panzer (31)
52°	Dann (35)

METHYLENE IODIDE

31.6°	This work
31.5°	Panzer (31)
34°	Dann (35)
41°	Owens (33), Jarvis (43), Shafrin (32)

TABLE VIII - ADVANCING CONTACT ANGLES ON NYLON

	LIQUID		
DROP VOLUME	WATER	ETHYLENE GLYCOL	METHYLENE IODIDE
25 μℓ	64.8°	44.8°	40.0°
34 μℓ		45.2°	39.4°
42 μℓ		44.7°	
Average	64.8°	44.8°	39.6°

TABLE IX - REPORTED ADVANCING CONTACT ANGLES ON NYLON

VALUE	REFERENCE
WATER	
64.8°	This work
61°	Baier (44)
66°	Bernett (45)
75°	Dann (35)
76°	Zografi (25)
89°	Fort (46)
ETHYLENE GLYCOL	
44.8°	This work
31° or 41° †	Baier (44)
51°	Dann (35), Zografi (25)
METHYLENE IODIDE	
39.6°	This work
31°	Bernett (45)
32° or 42° †	Baier (44)
37°	Dann (35)
40°	Zografi (25)

† Value depends on the solvent used in forming the nylon film.

TABLE X - RECEDING CONTACT ANGLES ON PARAFFIN

	LIQUID	
DROP VOLUME	WATER	ETHYLENE GLYCOL
20 μℓ	96.3^0	70.9^0
30 μℓ	96.2^0	71.9^0
35 μℓ	99.6^0	
40 μℓ	97.9^0	73.1^0
50 μℓ		74.1^0
Average	97.0^0	72.8^0

TABLE XI - RECEDING CONTACT ANGLES ON POLYMETHYLMETHACRYLATE

		LIQUID	
DROP VOLUME	WATER	ETHYLENE GLYCOL	METHYLENE IODIDE
10 μℓ		16.9°	7.0°
15 μℓ			17.6°
17 μℓ		28.2°	23.0°
20 μℓ	34.1°		
25 μℓ	55.6°	36.8°	
34 μℓ	56.0°	37.0°	
42 μℓ	71.0°	44.8°	

samples used were heated in the cleaning process except in the case of water where both heated and non-heated PMMA samples were used. The receding angles were not constant for each liquid, as was the case for paraffin, but instead decreased with decreasing drop volume.

Equilibrium Receding Contact Angles on Nylon

Receding contact angles of water, ethylene glycol and methylene iodide on nylon were measured using Method III for different sessile drop volumes (Table XII). As for polymethylmethacrylate the receding contact angles were not constant for each liquid, but instead decreased with decreasing drop volumes.

In view of the apparent dependence of receding contact angle on the volume of the drop for both PMMA and nylon in contrast to the relatively constant receding contact angle on paraffin, further studies were carried out with these systems. To be sure that these did not reflect any time - dependent processes, studies were conducted as a function of residence time of the drop on the solid surface. A more systematic study of volume dependency was also conducted.

Contact Angle Hysteresis as a Function of Residence Time

Residence time defined as the time between applying

TABLE XII - RECEDING CONTACT ANGLES ON NYLON

	LIQUID		
DROP VOLUME	WATER	ETHYLENE GLYCOL	METHYLENE IODIDE
10 μℓ	12.8°	23.8°	12.8°
15 μℓ	33.6°	30.4°	21.8°
20 μℓ	26.6°	37.8°	30.4°
25 μℓ	48.4°		

the liquid to the solid sample (creating a sessile drop with an advancing contact angle) and removing liquid from the sessile drop (creating a receding contact angle) was varied from 1 to 60 minutes for both water and ethylene glycol on PMMA (Tables XIII and XIV). The sessile drop volumes used for each run were the same; the initial volume, V_i was 34 μl and the final volume, V_f was 25.5 μl. The liquids were delivered by Method III to PMMA samples that had been heated during the cleaning process. The Θ_a, Θ_r, and H values in Tables XIII and XIV were determined for each side of the sessile drop for each run. The variation in the advancing and receding contact angles for the different runs was probably due to the different solid samples used. There appeared to be no significant difference in the contact angle hysteresis, H values; thus the receding angle is independent of residence time.

Contact Angle Hysteresis as a Function of Drop Volume

Both the initial drop volume, V_i used for establishing the advancing contact angle and the volume decrement, ΔV used to create the receding angle were varied for ethylene glycol on PMMA (Table XV). Ethylene glycol was delivered to PMMA samples that were heated in the cleaning process using Method III and a residence time of 10 minutes. There appeared to be a significant difference in H when comparing

TABLE XIII - CONTACT ANGLE HYSTERESIS AS A FUNCTION OF TIME : WATER ON POLYMETHYLMETHACRYLATE

RESIDENCE TIME (MINUTES)	Θ_a †	Θ_r †	H
1	84.5° 80.5°	65.9° 63.6°	18.6° 16.9°
5	91.2°	74.3°	16.9°
10	79.6° 83.5°	63.1° 66.0°	16.5° 17.5°
30	78.4°	59.2°	19.2°
60	90.6° 91.4°	72.2° 72.5°	18.4° 18.9°

† Contact angles are individual Θ_{Left} and Θ_{Right} for a particular sessile drop.

TABLE XIV - CONTACT ANGLE HYSTERESIS AS A FUNCTION OF TIME : ETHYLENE GLYCOL ON POLYMETHYLMETHACRYLATE

RESIDENCE TIME (MINUTES)	Θ_a †	Θ_r †	H
1	57.0° 52.5°	44.3° 42.7°	12.7° 9.8°
10	47.7°	36.7°	11.0°
30	53.2° 54.0°	40.9° 43.5°	12.3° 10.5°
60	53.8° 54.9°	42.7° 44.3°	11.1° 10.6°

† Contact angles are individual Θ_{Left} and Θ_{Right} for a particular sessile drop.

TABLE XV - CONTACT ANGLE HYSTERESIS AS A FUNCTION OF VOLUME : ETHYLENE GLYCOL ON POLYMETHYLMETHACRYLATE

V_i/V_f §	ΔV §	Θ_a †	Θ_r †	H
34/25.5	8.5 μℓ	47.7°	36.7°	11.0°
34/17.0	17.0 μℓ	48.0° 48.4°	25.4° 25.9°	22.6° 22.5°
42.5/25.5	17.0 μℓ	48.8° 46.7°	30.7° 30.4°	18.1° 16.3°
42.5/25.5	17.0 μℓ	48.7° 50.3°	31.9° 32.7°	16.8° 17.6°

§ V_i is the initial volume; V_f is the final volume; ΔV is the volume decrement such that $\Delta V = V_i - V_f$. All volumes are in μℓ's.

† Contact angles are individual Θ_{Left} and Θ_{Right} for a particular sessile drop.

different initial volumes, V_i and/or different volume decrements, ΔV. However H seemed fairly consistent if both V_i and ΔV were the same. Due to the preceding observation all previous runs of both water and ethylene glycol on PMMA were also examined with respect to V_i and ΔV. Contact angles having similar initial volumes and volume decrements were averaged to obtain the values given in Table XVI and XVII. It was observed that for a given volume decrement ΔV, the contact angle hysteresis H increased as the initial volume V_i decreased; and for a given initial volume V_i, H increased as ΔV increased for both water and ethylene glycol.

TABLE XVI - CONTACT ANGLE HYSTERESIS AS A FUNCTION OF VOLUME : WATER ON POLYMETHYLMETHACRYLATE

V_i/V_f §	ΔV §	Θ_a †	Θ_r †	H
51/42.5	8.5 μℓ	81.3°	71.4°	9.9°
42.5/34	8.5 μℓ	74.8°	61.6°	13.2°
34/25.5	8.5 μℓ	79.1°	62.2°	16.9°
51/34	17.0 μℓ	81.3°	59.8°	21.5°
42.5/8.5	34.0 μℓ	73.4°	19.1°	54.3°

§ V_i is the initial volume; V_f is the final volume; ΔV is the volume decrement such that $\Delta V = V_i - V_f$. All volumes are in μℓ's.

† Contact angles are averaged values; includes several runs

TABLE XVII - CONTACT ANGLE HYSTERESIS AS A FUNCTION OF VOLUME : ETHYLENE GLYCOL ON POLYMETHYLMETHACRYLATE

V_i/V_f §	ΔV §	Θ_a †	Θ_r †	H
51/42.5	8.5 μℓ	52.3°	44.8°	7.5°
34/25.5	8.5 μℓ	49.2°	38.8°	10.4°
25.5/17	8.5 μℓ	52.3°	39.0°	13.3°
51/34	17.0 μℓ	52.3°	37.0°	15.3°
42.5/25.5	17.0 μℓ	48.6°	31.4°	17.2°
34/17	17.0 μℓ	47.1°	25.7°	21.4°
25.5/8.5	17.0 μℓ	52.3°	23.0°	29.3°
51/25.5	25.5 μℓ	52.3°	29.6°	22.7°
34/10	24 μℓ	45.0°	13.1°	31.9°
51/17	34.0 μℓ	52.3°	21.2°	31.1°

§ V_i is the initial volume; V_f is the final volume; ΔV is the volume decrement such that $\Delta V = V_i - V_f$. All volumes are in μℓ's.

† Contact angles are averaged values; includes several runs

DISCUSSION

As shown by the contact angle data presented earlier, the apparatus designed for measuring contact angles on flat solid surfaces provides excellent flexibility and very good results. An important feature is the capability to measure both the advancing and receding contact angles of sessile drops of varying sizes at a constant temperature in an atmosphere saturated with the liquid vapor. The latter significantly decreases the evaporation rate of the drop. It was shown, further, that in all cases both the advancing and receding contact angles are independent of the delivery method used.

The advancing contact angles of all solid/liquid systems studied showed excellent agreement with previously reported values. Of the receding angles studied only those on paraffin were shown to be independent of the drop volume, and these values likewise agreed with those previously reported. In contrast, all the receding contact angles on PMMA and nylon showed a distinct dependence on the drop volume even though the three liquids used ranged widely in polarity.

Theoretically, in order for the receding contact angle to be independent of drop volume; the radius of the sessile drop base, a, must decrease as the drop volume is decreased. This describes the behavior of liquids on paraffin and is depicted as Case A in Figure 8. However, if the drop base radius, a, remains the same upon retraction of the liquid i.e. the three phase line (TPL) remains stationary as in Case B, Figure 8, the contact angle must change as the volume changes due to simple geometric conditions. This may be seen from the mathematical relationship between the volume, V, the radius of the base, a, and the angle Θ for a spherical segment (spherical cap), where:

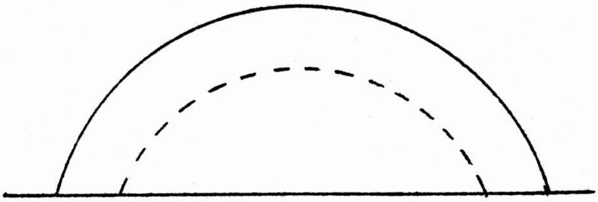
$$V = \frac{\pi a^3 \, (1-\cos\Theta)^2 \, (2+\cos\Theta)}{3 \sin^3\Theta} \qquad \text{(Eq. 8)}$$

The derivation of this equation, from simple geometric relations, is given in Appendix I.

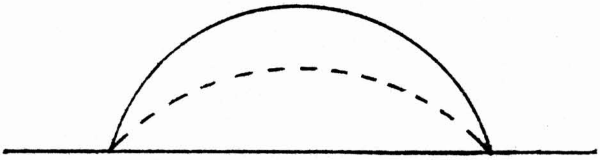
Rearranging the terms gives:

$$a = \left[\frac{3 V \sin^3 \Theta}{\pi \, (1-\cos\Theta)^2 \, (2+\cos\Theta)} \right]^{1/3} \qquad \text{(Eq. 9)}$$

Using measured receding contact angles and volumes for ethylene glycol on the three solids, and assuming the drop shape to be a spherical cap values of base radius, a, were calculated, as shown in Table XVIII. The values cal-



Case A. Receding Drop with moving Three Phase Line (TPL): The drop base radius, a decreases and the contact angle, θ stays the same.



Case B. Receding Drop with stationary Three Phase Line (TPL): The drop base radius, a stays the same and the contact angle, θ decreases.

Figure 8. Receding Contact Angle Behavior:

Drop profile changes from solid line to dashed line when the drop volume decreases.

TABLE XVIII - CALCULATED DROP BASE RADII FOR ETHYLENE GLYCOL ON PARAFFIN, POLYMETHYLMETHACRYLATE AND NYLON

	CALCULATED DROP BASE RADIUS, a (mm)	
DROP VOLUME	PARAFFIN †	PMMA
25.5 μl	2.65	3.64
17.0 μl	2.32	3.62
11.0 μl	2.00	3.79

DROP VOLUME	PARAFFIN †	NYLON
21.2 μl	2.49	3.41
16.2 μl	2.28	3.39
11.9 μl	2.06	3.39

† a was calculated using $\Theta_r = 72.8^0$

culated are very consistent for both PMMA and for nylon whereas values for paraffin change as expected. Indeed, while measuring contact angles on PMMA and nylon using the goniometer-telescope, it was observed that the TPL remained stationary as the sessile drop volume was decreased. Also, the drop base radius of ethylene glycol on nylon was ∿ 3.5 mm when measured externally with a ruler which agrees with the calculated values of about 3.4 mm in Table XVIII for the same drop.

The concept that the receding contact angle is dependent on only the drop volume within the constraints of a stationary TPL is further strengthened by the observations in Table XIX of water on PMMA. Here it can be noted that receding contact angles for the 42.5 μl drop were very consistent whether created by a decrease or an increase in volume.

Other authors have observed receding contact angle behavior similar to that observed on PMMA and nylon in this study but have not analyzed possible reasons in any depth. For example Slabaugh (48) studying sessile drops of aqueous solutions of acetone and ethanol on organoclays, reported reproducible advancing contact angles; but irreproducible receding angles. However, no receding data was actually reported, nor was an explanation provided. Herzberg and Marian (42) measured advancing and receding

TABLE XIX - CONTACT ANGLES OF WATER ON POLYMETHYLMETHACRYLATE AS THE VOLUME IS INCREASED AND DECREASED

DROP VOLUME	VOLUME CHANGE	Θ_{Left}	Θ_{Right}
51.0 µl †	increase	82.1°	78.1°
42.5 µl	decrease	71.0°	69.5°
34.0 µl	decrease	58.7°	60.5°
42.5 µl	increase	71.0°	69.1°
34.0 µl	decrease	57.5°	60.0°
42.5 µl	increase	70.1°	68.4°
34.0 µl	decrease	56.7°	59.1°

† 51.0 µl was the maximum volume used, and thus established the position of the three phase line (TPL).

contact angles of sessile drops for a polethylene/water system using a procedure similar to Method III. The advancing contact angles gave consistent results when the drop volume was 20 μl or greater, but the receding contact angles decreased as the drop volume decreased. The authors attributed this behavior to possible roughness and surface charge on the solid surface. No further analysis was presented.

Oliver and Mason (49) using a delivery system similar to Method IV measured advancing and receding contact angles on aluminum. They observed large variations in the contact angle hysteresis, $(H \equiv \Theta_a - \Theta_r)$ even for polished aluminum having surface asperities less than 0.5 μm. They attributed this to the surface roughness, and particularly to edge effects (50, 51). No further quantitation of the observed differences in receding angles has appeared in the literature.

In the present study no effort was made to smooth the solid surfaces or to obtain a measure of their roughness; however, the paraffin samples appeared to be much smoother than the PMMA and nylon samples used. Another important difference between paraffin on the one hand and PMMA and nylon on the other is that paraffin is essentially completely nonpolar while the latter solids contain polar groups. Solid-liquid polar interactions seem unlikely to have an effect in these studies, however, as the liquids used, ranging from very polar water to nonpolar methylene iodide, gave similar contact angle behavior. Penetration also does not seem to account for this behavior since contact angle hysteresis, H, showed no time dependency, i.e. was not a function of residence time. Thus an explanation for the results of this study must be based on properties of the solid surface.

The effects observed for receding angles can be due to surface chemical heterogeneity, to surface roughness, or to both. Surface chemical heterogeneity can not be ruled out for the samples used in this study, but due to observations of others, previously discussed, at this point surface roughness seems more likely to predominate.

The best explanation of the receding contact angle behavior in this work appears to be based on the premise that a stationary TPL, and thus a constant value of a, can account for the θ_r data. The roughness of the surface could provide a physical barrier to the movement of the TPL, such that removing liquid from the drop with a centrally located needle may not result in a force large enough to retract the drop along the solid surface; i.e. the TPL will not move. Instead the liquid would be removed preferentially near the needle tip resulting in Case B behavior, previously described. Thus the force balance required to form a "stable" receding contact angle must include the force needed to overcome the physical barrier, the force applied through the needle to remove the liquid, and the interfacial forces which are normally manifested as a contact angle. If this is true, receding contact angles obtained by an evaporation process may be expected to be different from those obtained by mechanically reducing the drop volume with a needle as in Method III and IV; since during the evaporation process liquid is removed over the entire liquid-vapor interface instead of locally near the needle tip.

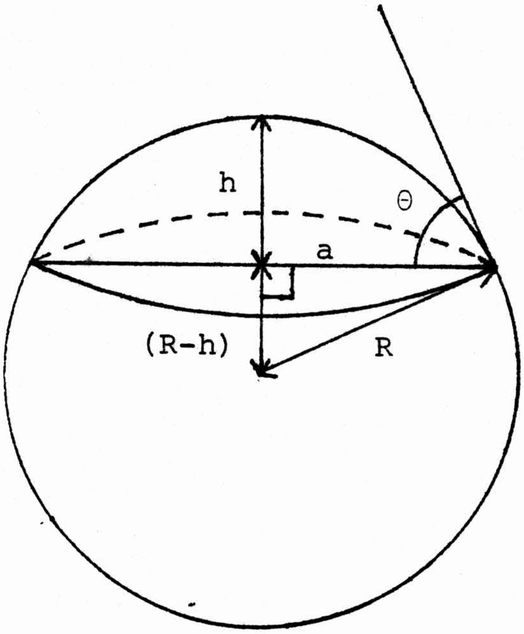
Mangel (52) reported that drop evaporation was a reliable method for measuring receding contact angles as the values obtained agreed with those obtained by the tilted plate method. Preliminary work in this study showed that appreciable water evaporation of the sessile drop in the saturated chamber occurred in three hours resulting in a receding contact angle. For the paraffin/water system reproducible receding contact angles of 96^0 were obtained which agreed with the receding angles previously reported (Table X). A receding contact angle of 61^0 for PMMA/water and 33^0 for nylon/water were obtained after 9 and 14 hours respectively. Both of these values were higher than some of the receding contact angles obtained by mechanically decreasing the sessile drop volume by Method III (Tables XI and XII). More systematic studies of this type must be carried out to analyze the situation in greater detail.

CONCLUSION

Recognizing the nonhomogeneity of a solid surface whether it be chemical or physical, is important when studying contact angles. With the apparatus designed in this study it was found that on a surface which appears rough the receding contact angle was dependent on the initial volume and volume decrement of a sessile drop due to a stationary three phase line (TPL). It is proposed that the forces used in advancing and receding the sessile drop as well as the surface roughness and interfacial forces must determine the movement of the TPL and, therefore, that the contact angles obtained on rough surfaces are dependent on the exact method in which the advancing and receding angles are established. More work is needed to characterize the exact nature of the surface roughness and to quantitate the forces operating at the TPL.

APPENDIX I

Derivation of the Volume of a Sphere Segment



The volume of a sphere segment (53) as shown above is:

$$V = \frac{1}{3} \pi h^2 (3R - h) = \frac{1}{6} \pi h (3a^2 + h^2) \qquad (a)$$

$$a = R (\sin\Theta) \qquad (b)$$

$$\cos\Theta = (R - h)/R \qquad (c)$$

(b) and (c) are trigonometric relationships for a right triangle. Rearranging (c) gives:

$$h = R - R\cos\Theta = R (1 - \cos\Theta) \qquad (d)$$

Substituting (d) into (a) gives:

$$V = \frac{1}{3} \pi R^3 (1 - \cos\Theta)^2 (2 + \cos\Theta) \qquad \text{(e)}$$

By substituting $R = a/\sin\Theta$ from (b) into (e) Equation 8 is obtained:

$$V = \frac{\pi a^3 (1 - \cos\Theta)^2 (2 + \cos\Theta)}{3 \sin^3\Theta} \qquad \text{(Eq. 8)}$$

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