

SURFACE PHENOMENA OF TEAR FILMS

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MANY ADVANCES HAVE BEEN MADE in general physical and surface chemistry in this century. For the most part these advances have not been applied or even considered by the average clinical ophthalmologist in his everyday practice. The purpose of this thesis is to briefly review a few points in physical and surface chemistry and to mention a few recent advances in this field; to report some clinical and experimental observations on tear films in human and animal eyes; and to explain these observations in the light of the advances in chemistry.

PHYSICAL CHEMISTRY

SOLUBILITY

Solubility refers to the ability of two different substances to mix freely with one another on a molecular level. For example, oxygen and nitrogen in the gaseous state freely mix. Forces of attraction between similar molecules in a gas are not great because of the great distances between the molecules. Therefore, no work is required to separate the molecules of oxygen, for instance, so that the nitrogen molecules can get in between them. If a container is divided by an impermeable partition containing oxygen on one side and nitrogen on the other side, and the partition is removed, free diffusion of the two gases occurs and the mixture is in a lower state of energy (more disorganized) than before. The solution occurs readily.

When a gas is dissolved in a liquid solvent, on the other hand, the attractive forces between the molecules of the liquid (van der Waals forces) must be overcome in order to permit the gas molecules to intersperse themselves evenly. Assuming that no chemical reaction occurs between the gas and the liquid solvent, the amount of gas going into solution will be proportionate to its partial pressure above the liquid. If chemical reaction occurs in such a way that the products are taken out of solution, such as in the formation of an insoluble

precipitate, the gas will continue to be dissolved, manifesting greater solubility than really exists.

When a solid is dissolved in liquid, the attractive forces between the solvent molecules must be overcome, but more important, force is required to break down the strong forces between the molecules or ions of the crystalline structure. The amount of energy required to separate these particles corresponds to the heat of fusion of the substance, that is, the amount of heat needed to melt a substance from a solid to a liquid state of the same temperature. This energy is absorbed by the solution. "However, this energy condition may be more than offset by the heat liberated by the interaction of the solute with the solvent in those cases where reaction occurs, such as in NaOH with water."¹²

Factors which determine solubility are basic to the molecular and atomic structures of the solute and the solvent. For example, the van der Waals forces between water molecules are greater than the attraction of water molecules for non-polar substances such as hydrocarbon chains, so that these non-polar substances will not separate water molecules and will not dissolve. So-called polar substances, such as NaCl, have a much greater attraction for water molecules than water molecules have for themselves. Therefore, they go into solution readily.

VAPOR PRESSURE

The vapor pressure of a liquid is a quantitation of the tendency for molecules to escape from the surface of the solution into the surrounding gaseous environment. The higher the vapor pressure of a liquid, the more readily it will evaporate. When a solute is dissolved in a solvent, the vapor pressure of the solvent is depressed. This requires that the solution be raised to a higher temperature for its vapor pressure to equal the atmospheric pressure (760 mm Hg). In other words, the boiling point is raised. Dissolved particles also lower the freezing point. This depression of the freezing point and raising of the boiling point is proportional to the number of dissolved particles and is therefore equal for a gram molecular weight of any two un-ionized substances or proportional to the number of ions of ionized substances. The depression of the freezing point or elevation of the boiling point produced by a known quantity of solute can be used to determine accurately the molecular weight of the solvent. Presence of ionized and un-ionized particles within the tear film should serve to reduce its vapor density and thereby slow down evaporation. When the gas above the liquid has a high vapor pressure, escape of the liquid mole-

cules into the gas is inhibited. For example, water films evaporate more slowly in a moisture-laden atmosphere than in a dry atmosphere.

VISCOSITY

A liquid is intermediate between a solid and a gas. In a gas the molecules are far apart and molecular adhesive forces play little role in preventing full molecular movement. In a solid, on the other hand, strong intermolecular forces restrict molecular motion to certain definite patterns within the crystalline framework of the solid. Only intense heat can break down these forces and produce a liquid state. In liquids the van der Waals forces of intermolecular adhesion are less than in solids because of the greater intermolecular distances, and, thus, the molecules are free to slide around.

There is a difference between various liquids in the relative ease of flow of molecules past one another. This may be regarded as an internal friction between adjacent layers of molecules and is called viscosity. Viscosity can be measured by determining the time needed for a given volume of fluid to flow through a capillary tube (Ostwald viscometer) or by measuring the time it takes for a small metal ball to fall through a given distance in the liquid. Poise or centipoise and stokes or centistokes are units of viscosity. The poise is the viscosity of a liquid such that a force of one dyne/cm² causes two parallel liquid surfaces 1 cm² and 1 cm apart to slide past one another with a velocity of 1 cm/sec². Water, for example, has a viscosity of 0.00895 poise at 25° or 0.895 centipoise; benzene, 0.61 centipoise at 25°.⁴ Viscosity decreases with an increase in temperature.

SURFACE TENSION

Liquids behave as if covered with an elastic membrane. (Witness the ability to float needles or razor blades on the surface of water.) This behavior is due to the surface molecules' attraction to one another, and to the fellow molecules beneath the surface, which tends to pull the surface molecules into as small an area as possible. For this reason, a drop of fluid in a vacuum assumes a spherical shape. A bead of mercury, which has a very high surface tension, gathers itself into little spheres when placed on a glass slide. This resistance to expansion of the surface area is called surface tension and is measured by the force (in dynes per linear centimeter) required to enlarge the surface (Table 1).

TABLE 1. EXAMPLES OF SURFACE TENSION

Substance	Surface tension (dynes per cm)
Water	72.6
Fluorocarbons (Teflon)	8-15
Hydrocarbons	18-30
Polar organic compounds	22-50 ¹¹
Aqueous detergents	24-40
Molten glass	200-400
Molten metal	350-1800
Tears	50 ⁸

Interfacial tension between two liquids is another variation of surface tension. The amount of the interfacial tension depends on the two solutions. The more similar they are the less will be the interfacial tension.

The addition of inorganic electrolytes, such as sodium chloride to water, increases the surface tension. Active agents which are adsorbed at the surface, such as detergents and soaps, dramatically lower the surface tension of water, even in a very dilute solution.

ADSORPTION

The attraction and holding of one molecule, ion, or atom at the surface of a liquid or solid is called adsorption. There are several kinds of forces which cause adsorption. They may be physical in nature, such as unsatisfied intermolecular attractions (van der Waals forces), or they may be chemical such as hydrogen-bond formation, ion exchange, or covalent bond formation. Adsorption always occurs in such a way as to reduce the free energy of the surface involved. Since the free energy of a surface equals area times surface tension, a reduction in either area or surface tension results in a lessening of the free energy of the surface. In a homogeneous solution which has molecules of differing activities, the molecules orient themselves at the surface in such a way that their least active part is exposed, thus reducing the surface energy. This is similar to the behavior of the molecules in a solution, where those molecules with the least energy, producing the greater drop in surface tension, will concentrate at the surface.

The process of adsorption occurs at surfaces and may occur at the interface of a liquid or a solid with a gas, liquid, or solid. Adsorption at the surface of a liquid or at a liquid-liquid interface may occur from solution in the case of a soluble adsorbent. In the case of an insoluble adsorbent, adsorption may occur at the surface as a mono-

molecular layer, or as a multimolecular layer, or by a process of condensation into pores or capillaries in the case of a solid surface.

Adsorption at Liquid Surfaces of Substances from Solution

Many substances dissolved in aqueous or hydrocarbon solutions are attracted to and adsorbed at the surface of the solutions. Such surfactant solutes, although soluble in a fluid such as water, gather and concentrate at the surface or at an interface to reduce the surface tension or the interfacial tension. They usually have two different parts of their molecule, such as a polar group on one end of the molecule and a non-polar group on the other. The polar group is sufficiently strongly attracted to the water molecules to cause the entire molecule to be soluble. But the non-polar or hydrocarbon part is rejected toward the surface. Thus, these molecules orient themselves on the surface with the polar end in the aqueous phase and the hydrocarbon protruding into the air. Soluble surfactant materials can be classified as oil soluble or water soluble:

Oil-soluble surfactants

1. Long-chain, non-polar substances with polar groups (COOH, NH₂)
2. Fluorocarbons, long- or short-chain, non-polar substances with polar groups

Water-soluble surfactants

1. Anionic substances, the long chain has a negative charge (*a*) soaps (Na stearate) (*b*) sulfonates (Tide, Fab, Surf) (*c*) sulfates
2. Cationic surfactants, the long chain bears a positive charge (quaternary ammonium compounds)
3. Non-ionic substances
4. Amphoteric substances,⁹ the long chain may be either positive or negative, depending on the *pH*

Soluble surfactants take the orientation which gives the least surface energy. The surface-tension-reducing effect of these substances increases with increasing concentration of the surfactant. However, there is a point after which an increase in concentration does not further reduce surface tension. At this concentration it is postulated that adsorption at the surface is complete and that excess surfactant molecules then gather themselves into organized collections in the body of the fluid. These groups are called micelles (Figure 1). The

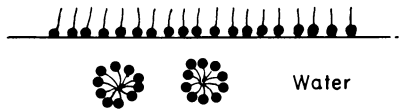


FIGURE 1

Micelles form in the body of the solution after saturation of the surface.

concentration at which dissolved surfactants begin to form micelles is called the critical micelle concentration (CMC). The formation of micelles is associated with a reduction in the free energy of the system. Detergent action is due to agents adsorbed at the surface, and micelles act as a storehouse which can be drawn upon to replenish surface activity. However, the micelles also engulf or adsorb water-insoluble substances and permit their solubilization. The longer the hydrocarbon chain and the more polar groups there are in the surfactant molecule, the lower is the CMC. The CMC increases with temperature.

When a substance is dissolved in water, the surface tension of the solution sometimes is higher than that of the pure solvent. In these cases, because powerful attractive forces between the ions concentrate in the body of the solution, a condition known as negative adsorption usually occurs. An example of this is an inorganic salt, such as sodium chloride, dissolved in aqueous solution. The calculation of the amounts of substances required to alter the surface tension of solutes at different temperatures leads to the conclusion that adsorption of soluble substances at liquid surfaces often takes place by the formation of a monomolecular layer of the substance adsorbed.

Adsorption at Solid Surfaces

Molecules in a solution may be attracted to and held by a solid surface immersed in a solution. Calculations show that the adsorptive capacity of a solid depends on its surface area. Further calculations show that when a monomolecular layer of the adsorbed molecules covers the entire surface, the saturation point has been reached. Such studies can be used to determine the surface area of irregular solids, by determining how much of an adsorbable substance is needed to reach saturation.

Adsorption at Liquid Surfaces of Insoluble Substances

When some insoluble substances, such as mineral oil, are floated on an aqueous surface, the oil is subject to several conflicting forces from

three different surfaces or interfaces (Figure 2). All three forces are trying to minimize their surfaces. These forces are (A) the surface tension of the water which tends to spread the oil out, (B) the surface tension of the air-oil interface which tends to pull up the oil into a sphere, and (C) the interfacial tension between the oil and water, also tending to draw the oil into a sphere.

When the horizontal resultant forces of B and C equal A, the oil is in equilibrium. If the force of A is greater than the sum of the horizontal vectors of B and C, the oil continues to spread out indefinitely until only the monomolecular layer is present. Other factors being equal, liquids with a high surface tension form better substrates for spreading of insoluble surface film than those with a low surface tension.

A multilayer, such as is formed when a drop of thin oil spreads on the surface of water, is a layer of varying thickness, perhaps a monolayer here, two or three layers there, and ten or a hundred molecular layers elsewhere. When these thin multilayers get thick enough that they are one-fourth the wavelength of visible light, interference effects begin to be noted and the thickness can then be calculated in each area (Figure 3). At a thickness of one-fourth the wavelength of violet

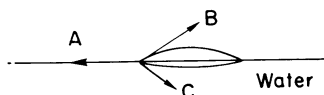


FIGURE 2

Forces acting on an oil lens in water.

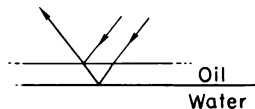


FIGURE 3

When the path through the oil film is $\frac{1}{2}$ the wavelength of light, that wavelength is cancelled.

light ($\frac{1}{4} \times 4000 \text{ \AA}$), the path through the film is one-half the wavelength of the violet light, and cancellation occurs. As the film thickness increases, the blue, green, yellow, and red colors are successively cancelled by interference. When the film reaches the thickness of 3 times one-fourth the wavelength of violet light (3000 \AA), the second order of spectrum begins. The next spectrum would represent five-fourths the wavelength or 5000 \AA .

At the leading edge of the oil film, successive complete spectra are noted very close to each other, indicating a rapid falling off in thickness (similar in manner to the isopters in the visual field near a steep-edged scotoma), whereas away from the edge the same colors appear as wide bands, indicating a uniform thickness of the oil film. One can

thus use the spectral interference pattern as a guide to the evenness or unevenness of a film surface, and if the order of spectrum is known, the exact thickness of the layer under observation can be determined.

Under certain conditions, some water-insoluble, long-chain hydrocarbon substances with a polar radical on the end (such as stearic acid) can be made to spread on the surface of water in a monomolecular layer. This is best accomplished by dissolving the polar hydrocarbon in an organic solvent of a low surface tension which will rapidly spread over the aqueous surface (attempting to reduce its surface-free energy), and then rapidly volatilize, having served as a vehicle for spreading the polar hydrocarbon. For formation of a monolayer, it is necessary that the substance be insoluble in water, but have a polar group which can attach to the water surface. Indeed, these long molecules are so oriented that the polar group sticks into the water and the long hydrocarbon chain protrudes into the air.³ Vertical orientation of these chains has been proved by the fact that lengthening of the chain of non-polar substances does not increase the area occupied on the surface by a given number of molecules. For example, it can be calculated that a molecule of palmitic acid ($\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$) has an area of about 21 \AA^2 , stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$), 22 \AA^2 , and cerotic acid ($\text{CH}_3(\text{CH}_2)_{24}\text{COOH}$), 25 \AA^2 . Lengths of the chain determined by film thickness are 24, 25, and 31 \AA , respectively.⁴ As with soluble molecules, these films always reduce the surface tension of the water. Their spreading tendency is proportional to this reduction. Thus, if a substance markedly reduces the surface tension, it has a high spreading pressure (surface tension of water minus surface tension of the monolayer) and a great tendency to form a monolayer.

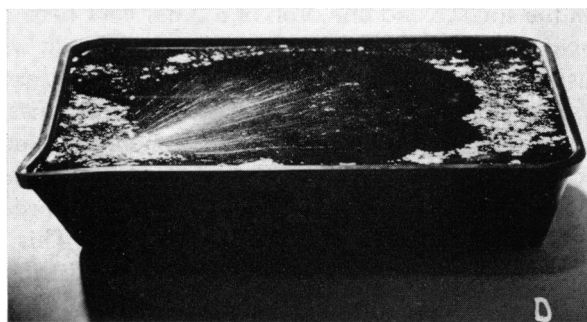
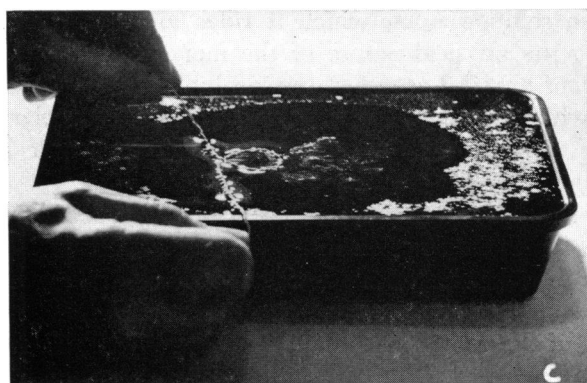
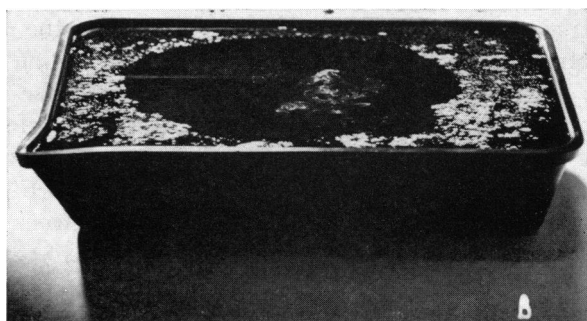
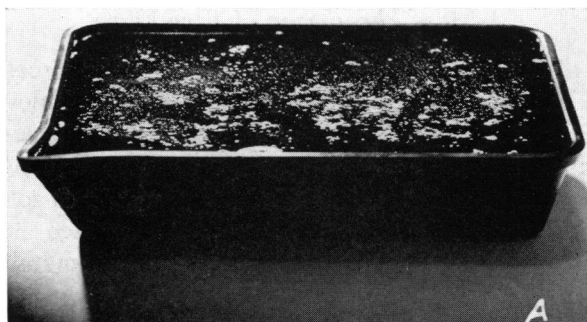
Insoluble monolayers can occur in any one of several states. Gaseous or vapor films are those in which the monolayer on the surface is well spread out over a large area and the molecules are free to move and act as a two-dimensional gas. When the surface film is compressed, as by movement of the surface barrier in a film balance, or by compressing such a film with a loop of non-wetted thread floating on the surface, molecules are brought closer together and show some degree of compressibility. This state of a monolayer is called a liquid expanded film. When such a film is further compressed, the film becomes condensed with the molecules closely packed together. This is known as the condensed film and further compression causes the film to collapse and become a multilayer. It is in the condensed state, before the collapse, that one can calculate the area occupied by each molecule.

Surface layers have their own physiochemical properties separate

from those of the underlying liquid. For example, the viscosity of such a layer can be tested by dusting talc on the surface and blowing gently on the surface with a jet of air from a pipette. If the surface layer acts as a two-dimensional liquid of low viscosity, the talc particles are easily moved about on the surface. If the surface film is solid and acts like a two-dimensional crystal, blowing on the surface either causes no movement of the talc, or else causes the talc to blow about just as if it were on a solid dry surface. Another method of testing the viscosity of a surface layer is applicable if the layer is thick enough to cause interference patterns with reflective light. In this case, the disturbance of the spectral patterns with a jet of air is an indication of surface movement. Since surface properties may differ from the underlying liquid, it is not correct to quote one value for both the surface and the body of the liquid. When these solid films are disturbed mechanically, as by a glass rod, the entire surface moves as a rigid sheet. The viscosity of these surface films may also lie anywhere between these two extremes, as in the case of the oil film on tears.

In some conditions, a given solid monolayer may be converted into a liquid by changing the *pH*. Such factors as *pH*, temperature, and contents of the solution upon which it rides are important factors in determining the physical nature of the monolayer at any given moment. Another physical aspect of the insoluble monolayer is its refractive index which can be determined by measuring its polarizing angle (the angle of incidence for maximum polarization of a reflected beam).

Many of these interesting properties of insoluble monolayers can be seen by the ophthalmologist with a minimum of equipment. A hydrophobic and oleophobic surface, such as a Teflon cooking utensil, may serve as a container for distilled water. The water may be brought to the surface of the container so as to invert the meniscus, but for certain demonstrations this is not necessary. Household talc can be spread upon the surface and one drop of a 3 per cent benzene solution of stearic acid may be dropped on the surface. The talc will immediately be pushed to the side of the tray by the rapidly spreading benzene-containing stearic acid. The benzene rapidly disappears by volatilization, leaving a solid stearic acid monolayer. Under certain lighting conditions, the fast volatilization of the benzene may be seen by a rapidly changing spectral interference pattern proceeding from the edge of the benzene multilayer as it evaporates. This process all may occur in four or five seconds, leaving an evenly distributed monolayer at the surface for study.



THE CRUMPLE PHENOMENON

Most monolayers are invisible, but when a monolayer is laterally compressed sufficiently, it becomes visible by increased reflectance of its surface. Langmuir and Schaefer⁵ noted this in a film balance and named it the crumple phenomenon. They interpreted it as the point when the monomolecular layer crinkled and lost its orderly arrangement. The lateral pressure overcomes the adhesive forces of the film molecules on the surface of the film. This crumple phenomenon can be seen in a stearic acid monolayer in a film balance or by looping a paraffin-waxed thread on the surface and gradually reducing the area available to the monolayer within the loop (Figure 4). Looking at the film with the light at an angle of about 120 to 140°, one will notice that the previously invisible surface becomes visible at a certain point in the compression. Its visibility corresponds to the collapse of the monolayer. If the monolayer is not solid but is only condensed, loosening of this loop will cause the surface phenomenon to disappear. If it is solid, the crumpled monolayer remains. The crumple phenomenon occurs at a certain lateral pressure. Because these monolayers are of uniform thickness, less than one-half the wavelength of visible light (stearic acid, 25 Å), they produce no spectral interference pattern with reflected light.

The crumple phenomenon does not always occur with sufficient lateral pressure on a monolayer. Sometimes an orderly multilayer of the molecules is produced instead. Indeed, under certain conditions, especially when building multilayers, as on a glass slide, one can get an even, regular arrangement up to one hundred molecules thick. Crumple patterns are characteristic of the surface molecule and of the solution. According to Langmuir and Schaefer,⁵ crumple patterns can be dramatically affected by the addition to the solution of metallic ions, even in extremely dilute concentration. The assumption is that these metallic ions intersperse themselves in the molecular layer and are factors in affecting the appearance of this layer.

An extension of the crumple phenomenon is the rolled up scum phenomenon. The orderly monolayer, having been collapsed by overwhelming lateral forces, still has enough cohesive force to gather into rolls as the lateral compression continues. When the lateral forces stop or are reversed, the role of oil then serves as a source of material for

FIGURE 4

A, powdered talc on surface of distilled water. B, spreading of talc by stearic acid monolayer. C, crumpling of monolayer by reducing surface. D, after blowing talc to show rigidity of monolayer.

reformation of the orderly monolayer. These phenomena can be demonstrated in the oil layer of the tear film in animal and human eyes.

Monolayers of insoluble, poorly volatile, or non-volatile substances which spread on water surfaces retard the rate of evaporation of the water. The phenomenon is used in the preservation of reservoirs of water in arid areas, and in the eye the oil layer on the tear film certainly retards the evaporation of the aqueous phase of tears.^{1,6,7,9,10} Resistance to evaporation increases with the chain length of the fatty acids involved.

EMULSIONS

The mixture of two insoluble liquids may result in one liquid being dispersed in the other, an emulsion. Because the liquids may be of different densities, they tend to separate by gravity. The globules may tend to gather together without becoming one (flocculation), or they may tend to coalesce, smaller globules bumping each other and becoming one large globule. Since the area of such globules is much greater than the area of two large separate phases, such emulsions are thermodynamically unstable, the more so, the greater the interfacial tension. Surfactants that lower the surface and interfacial tension tend to act as emulsifying agents and permit greater dispersion of the solution. Globules of oil are often seen in the lacrimal lake—a form of emulsion.

FOAMS

A foam is a collection of gas bubbles. These may be temporary as in the foam on top of a glass of beer or permanent as in gelfoam or styrofoam. Like emulsions, foams are thermodynamically unstable, because the great increase in area caused by the bubbles is not the condition of minimum free energy. "Foams collapse as a result of drainage of liquid in the bubble wall until part of the film reaches a thickness of 50-150 Å when the random motion of the molecules is sufficient to cause a sudden breakdown of the film."¹¹ Foam is often seen at the margin of the eyelid, especially near the inner and outer canthus. There are agents which tend to stabilize foams by increasing the surface viscosity and others which act as antifoams.

WETTING

When a drop of mercury is placed on a clean glass slide, the drop gathers itself almost into a sphere. This is due to the high cohesive force between the mercury molecules, which results in an extremely

high surface tension. The forces opposing this sphere formation are the adhesive forces between the mercury and the glass surface, which tend to satisfy unfilled van der Waals forces and to cause a spreading out or wetting of the surface. In this case, because of the relatively low surface activity of glass, no wetting takes place. The angle between the tangent of the mercury surface and the glass slide as measured from inside the drop is called the contact angle (Figure 5).

If, instead of glass, a surface of higher activity such as polished metal is substituted, the contact angle is smaller. The contact angle is determined by the surface activities of the solid and the liquid. The

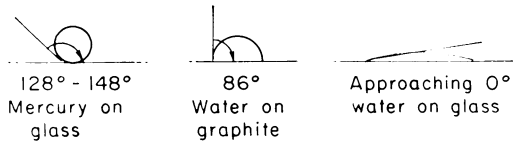


FIGURE 5
Contact angles.

molecular characteristics of the solid surface determine its surface activity. For example, polished metallic surfaces have a very high surface activity and are easily wetted. If the high-energy, polished metallic surface is covered by an adsorbed hydrophobic monolayer (stearic acid), the surface shows a marked reduction in energy and its surface tension is reduced. Hence, oil or grease on an ordinarily wettable surface will cause poor and uneven wetting of this surface. In the eye, the adherence of hydrophobic grease or oil spots to a contact lens prevents smooth wettability. The addition of soluble surfactants or wetting agents lowers the surface tension of the film and augments wettability, as will be noted later. Different parts of the eye and the adnexa oculi display different surface activities to the tear film, so that some parts of the eye are normally wetted and other parts are not. In certain eye diseases, this distinction sometimes breaks down.

If any surface is covered by a hydrocarbon with a fluorinated group exposed, such as Teflon, surface activity is at a minimum. The contact angle of such surfaces is very high and they are not wet by water or oil, hence the value of the Teflon frying pan. Thus, in order to wet a surface, a fluid must have a surface tension below the critical surface tension of the solid to be wetted.

The physical, chemical, and surface phenomena noted above have applicability and counterparts in the tear film of the eye. These will be discussed under the headings of clinical observations and experimental observations.

CLINICAL OBSERVATIONS

WETTING

The human eye is wet by tears over the entire corneal and conjunctival surfaces with one continuous tear film. The wetting of this film stops midway on the lid margins at a line joining the meibomian orifices. This line is convex to the front, extending forward between the orifices. The skin of the lid margin anterior to these orifices corresponds to the margin of the keratinizing squamous cells and is not wetted by the tear film. Even if tears are dropped or placed on the lid outside of this boundary, the tears collect in droplets, exhibiting a large contact angle, and the outside lid margin remains unwetted. This indicates that the outside lid surface anterior to the meibomian orifices has a critical surface tension below that of the tears and is therefore not able to attract tears sufficiently to wet the surface. Such a hydrophobic surface might be caused by the greasy keratinized squamous cells characteristic of this area. It does not seem to be caused by meibomian secretions, as will be demonstrated later. The shape of the tear film and the lacrimal river or prism can be more easily appreciated under the slit lamp when fluorescein is used to color the tears. If a few drops of fluorescein-tinted tear film get on the lid anterior to the non-wetting line, isolated discrete droplets are noted on this area of the lid in the manner of droplets of rain on a newly waxed car hood or water rolling off a duck's back. Behind this line, however, there is continuous smooth wetting.

SURFACE CURVES AND CONTACT ANGLES

When a light is held in front of the eye under examination through the slit-lamp microscope, a reflex is noted in front of the lacrimal prism.¹ When the lighted object is moved up, the image in front of the lacrimal prism moves down, indicating the formation by the vertically concave tear film of a real image in air. The curve of the tear film extends gradually to become almost tangential to the corneal surface, indicating a contact angle of zero at the tear-corneal junction. The cornea is thus perfectly wettable by tears and must have a high surface tension attracting the tear film. On the lower border of the lacrimal prism, on the lower lid, one can get a "with" movement of the reflex when a lighted object is moved vertically. This indicates the formation of a virtual image behind the convex reflecting surface of the tear film at its lower border, which in turn indicates an anterior curve to this portion of the lacrimal prism. The tears do not wet this

lower border. This is sometimes difficult to demonstrate and depends on the presence of a sizable lacrimal lake. If the tears are drained off rapidly, for example, the lacrimal prism may be pulled backward, leaving what appears to be a zero contact angle at the wetted surface. However, this only represents the high water mark of the tears.

INTERFERENCE PHENOMENA

The tear film is a compound layer consisting of a superficial oil layer and a posterior aqueous phase. Many of the characteristics of this surface layer can be determined by studies of interference patterns. This is best accomplished by mirroring a large light, such as a fluorescent light or a gooseneck lamp (Figure 6A), held close to the cornea, and studying with the slit-lamp microscope the phenomena on the surface of the cornea in front of the virtual image of the lamp. Under such conditions, spectral interference patterns are seen in the surface oil film.

These interference patterns can also be seen by self-inspection with a concave microscope mirror placed on an x-ray viewing box (Figure 6B). One has to move back and forth while looking at the eye to focus on the corneal surface in front of the virtual image of the illuminated glass. Spectral interference patterns can easily be noted on the surface in most eyes, at least on part of the illuminated area of the cornea. At first inspection, the oil film appears gray with varying shades, suggesting various thicknesses of the oil-film layer. This gray background suggests also that the surface layer is not thick enough to cause interference (less than one-fourth the wavelength of visible light). Certain parts of the tear film usually are coloured. For example, where the oil film appears red, the color results from annihilation of the blue waves occurring at a thickness of 1000 Å. When the oil layer of the tear film shows interference patterns it is at least 1000 Å thick. When the lid is partially closed, the gray area of the surface film usually produces a red color which may then, with further compression, become orange, yellow, green, blue, and ultimately even red again with further compression. This implies that the oil film is made thicker by lateral pressure on the film by the lids. The first color denotes the formation of a first order spectrum, indicating destructive interference with the blue end of the spectrum. If a complete spectrum is seen, a film thickness of 1000–1750 Å is indicated. Sometimes two complete spectra (from the red end of one spectrum to the blue of the other) lie adjacent to each other, indicating a varying thickness of the oil film over the cornea (1000 to 5200 Å). That the thickness of the oil

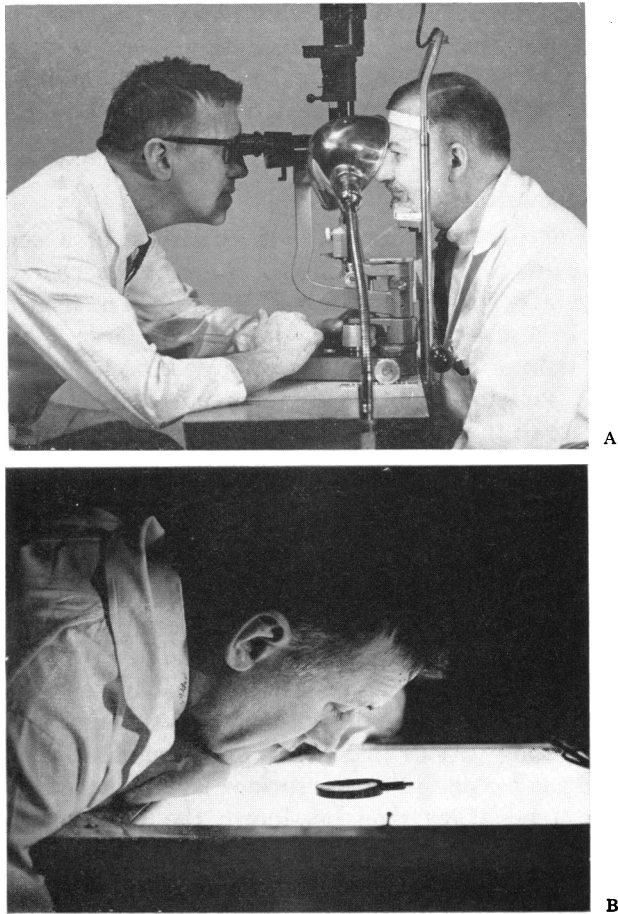


FIGURE 6

Top, examination for interference pattern using gooseneck light. *Bottom*, examination for interference pattern using x-ray view box and concave microscope slide.

film is increased by lid closure is readily apparent from this change in spectral colors (Figure 7).

These spectral patterns are easily seen on the smooth corneal surface. With some effort, one can pick up interference patterns everywhere on the conjunctiva by focusing in front of or behind the highlights. Even when the lid is inverted, the tear film presents to the examiner an oil film capable of exhibiting these interference patterns.

When the surface over the lacrimal lake is studied, similar inter-

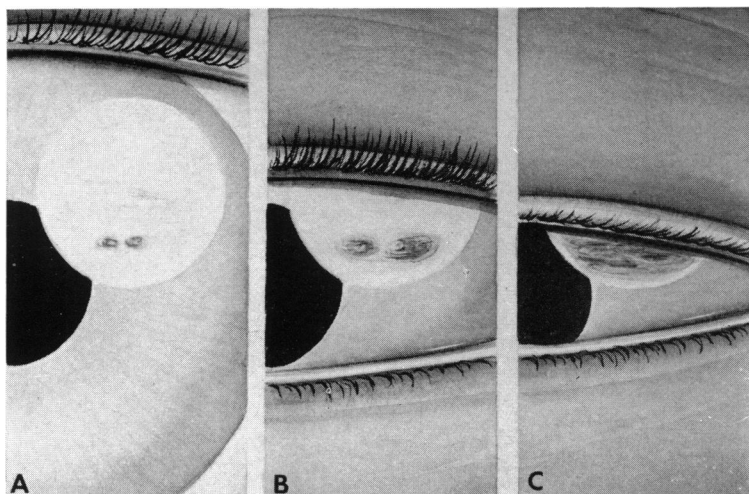


FIGURE 7

Interference patterns increased by lid closure.

ference colors are produced. These colors are continuous with the corneal interference colors, showing no abrupt change when the corneal tear film deepens in the lacrimal lake. This shows that these interference patterns are surface phenomena related to the thickness of the oil layer and not to the thickness of the aqueous phase of the tear film.

One must conclude that the tear surface in the human, whether it is small as with partial lid closure, or large as when the open lids are pulled away from the eyeball, is covered with an oil film of variable thickness. These surface phenomena suggest that the oil film is not a monolayer but a multilayer, varying in thickness from less than 1000 Å to 3700 Å. The usual monolayers of fatty acid are much thinner, about 25–30 Å. If the oil film is made up of these fatty acids we might expect that the thickest part is 72 molecules thick and that the thinnest part is less than 20 molecules thick. The insolubility of this oil layer in the tear film is established by its surface-spreading characteristics and its multilayered nature shown by its variable interference patterns.

Surface phenomena noted near the orifices of the meibomian gland establish that it is the source of the oil-film layer. Adjacent to these orifices at the tear surface several spectra are sometimes seen, indicating a pouring forth of a thick layer of oil from these glands (Figure 8). The oil spreads from the meibomian glands over the surface of the

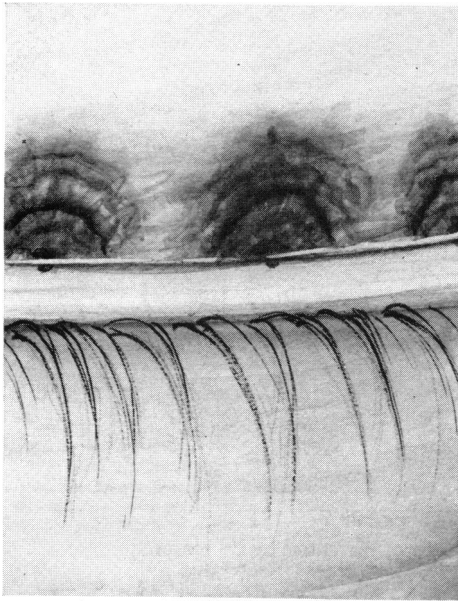


FIGURE 8
Meibomian glands secreting
oil on surface.

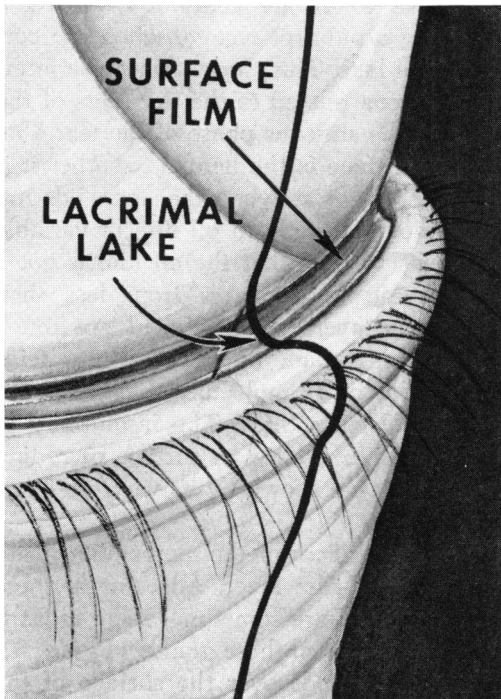


FIGURE 9
Rigidity of surface over lac-
rimal prism.

tear film because the oil lowers the surface energy. The multicolored film at each orifice indicates a thickness of the secreting stream of 3700 Å, which spreads out to a layer 1000 Å thick.

VISCOSITY

That the viscosity of the surface of the oil layer is very much greater than that of the underlying aqueous phase can be demonstrated by focusing the microscope on the surface of the lacrimal prism in the area of specular reflection, using surface debris as a focusing pattern. Fluorescein helps to identify the shape of the lacrimal prism. It will be seen that this surface is firmly attached at the wetting-non-wetting border of the lid. The surface remains rigid and immobile in spite of lid motion. When partial lid closure causes the "pumping of the tears" to the punctal drainpipe, the surface does not move, but behind it, tears and tear debris flow toward the puncta. When this movement is labeled with conjunctival cells or globules of fat, it is very dramatic. The tear flow in the lake, and indeed everywhere, takes place under a membrane-like oil multilayer firmly attached to the lid margins (Figure 9). This oily multilayer is "elastic" enough to stay intact whether the lids are opened or closed. The implication is that each successive oil monolayer has a great tendency to slide easily over its neighbor. The general similarity of colors in a given area suggests strong cohesion within a molecular layer. The oily multilayer, however, is viscous enough not to be affected by rapid submarine currents.

If the eye has a slight excess of tears and is studied under the slit lamp with the reflective lighting described above, the oil film is quickly and easily floated away from the cornea by having the upper and lower lacrimal lakes meet by lid partial closure. When the lids are open again, the viscous oily multilayer drops down again, hugging the precorneal tear film with an even, optically-acceptable, refracting surface. Its ease of separation from the cornea by such techniques attests to the fact that the oily layer is subject to the laws governing surface films. Continuity of such an oily layer might be of more importance than the watery tear film base, for it blocks tear evaporation and prevents dessication of the cornea.

EMULSIONS AND MEIBOMIAN MASSAGE

When a normal upper lid is everted and the eye is examined under a slit lamp, there is a very greasy appearance to the precorneal film. This is presumably due to the milking effect of the lid eversion on the meibomian glands, causing them to empty, as during the lid massage



FIGURE 10
Foam at outer canthus.

for blepharitis. Interference phenomena show that the oil film is thicker and has several orders of spectral color that are not present before lid eversion. Indeed, it seems that the oil has reached a greater amount than can be handled by an orderly multilayer. Globules of oil are produced which may be seen caught in the rapid subsurface currents under the immovable oil film covering the lower lacrimal lake. Such "emulsification" of the excess oil secretion could be a regular method of turning over the oily multilayer or of disposing of the water-insoluble, oily debris.

Rubbing of the eyes occasionally produces the same increase in the oil surface layer and must not be confused with a pathologic condition, such as the greasy appearance of a tear film in seventh nerve paralysis (which may be due to accumulated meibomian oil).

OIL LAYER FRACTURE

In a few of the many hundreds of eyes studied, certain definite

channels which permitted movement through the surface membrane were noted. These movements were similar to the movements of ice floats on a frozen lake after passage of a steamer. The phenomenon is apparently caused by a local breakdown in the viscosity of the oil layer, possibly due to a low surface-tension contaminant. Similar phenomena were noted in the laboratory by blowing hard enough to create a channel.

FOAMS

The oily surface of the tear film forms posteriorly at the orifices of the meibomian glands so that the oil is spilled onto the surface. Usually, one can see bubbles at the orifice of some of the glands in the lower lid. When these bubbles flocculate, foam is formed. This foam may be clinically evident in many eyes and in these cases it tends to collect along both the lateral and the medial extremities of the lower lid. The white, rather stable foam has bubbles about 0.05 mm in diameter. The foam tends to wet the outer canthus and seems to cause a breakdown in the hydrophobic barrier allowing wetting by tears at the lateral canthi (Figure 10).

OTHER PHENOMENA

Other surface phenomena noted in the laboratory can, under certain circumstances, be demonstrated in the human eye, especially when the oil film is thicker than usual. These include the crumple phenomenon and the rolled up scum phenomenon described by Langmuir and Schaefer⁵ and other observations explained by surface chemistry. These will be described in the next section.

EXPERIMENTAL OBSERVATIONS IN ANIMALS

Although most of the studies described below were done on rabbit eyes the observations were also made on cat and dog eyes.

OIL FILM INTERFERENCE PHENOMENA

Accurate observation of interference patterns on the surface of the tear film requires the mirroring of a large illuminated object, such as a long fluorescent or gooseneck lamp, which has been placed approximately 6 inches from the eye of the animal. A microscope observation system of a slit lamp is focused on the tear surface either in an area in front of the virtual image of the illuminated object or in front of the virtual image of the mirror of the illuminating system. In the latter

case, the area of blinding specular reflection of the filament, which is located in the same place, must be avoided.

Under such conditions of observation, one sees a surface of different shades of gray with movable whorls, suggesting an oil cover of variable thickness. When the gray is particularly intense, it often takes on a spectral color, indicating that it is thick enough to cause interference phenomena. If the lids are closed or partly closed, the superficial tear film is compressed and the color of these areas changes from gray, where there is no interference, to red (indicating an annihilation of the blue waves) to orange, green, and blue, and again to red if the compression continues. The areas of lighter gray pick up color as compression continues and go through the same spectral changes until even a second-order spectrum may appear. This phenomenon indicates the exact thickness of the oil film, 1000 Å at the first red color (Figure 11).

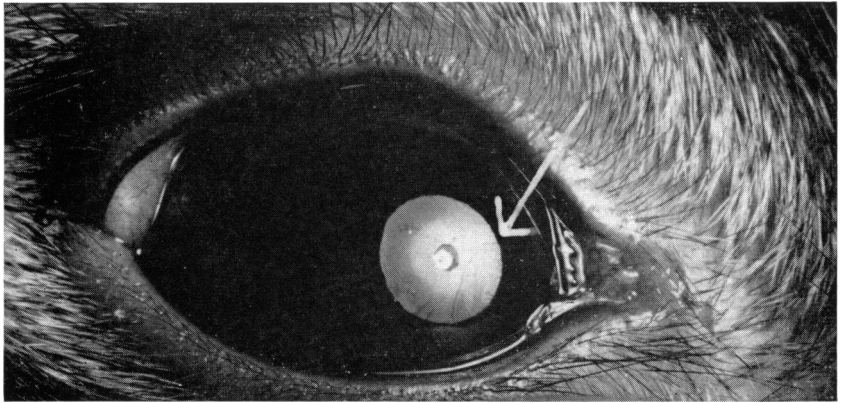


FIGURE 11

Photo of rabbit interference patterns due to oil film.

When a normal or partial blink occurs, the colors change rapidly, indicating a thickening of the oil layer. When the blink is over, the original colors are resumed, so that with each partial blink there is a rapid change in interference colors.

Because of the curvature of the lacrimal prism in animal eyes, it is more difficult to get the surface illuminated for the purpose of showing interference patterns. However, the spectral patterns can be seen by carefully focusing on the surface behind the real image of the illuminated object which lies in front of the surface. The pattern

is continuous, over both the cornea and the lacrimal lake, with no change in colors in spite of the great increase in depth of the aqueous phase over the lacrimal lake. The surface oil layer is of uniform thickness up to the lid itself, as in the human eye.

At the meibomian orifices, the pouring forth of the oil onto the surface is evident from the successive spectral colors near each orifice, as noted in the human eye and also as seen in cat and dog eyes. This oil pours onto the surface and can be seen to form the outer tear covering. One can conclude from the spectral colors in "delta" of each meibomian orifice that the oil layer is thicker here than elsewhere in the cornea (approximately 3700 Å).

By careful focusing on the surface of the bulbar or palpebral conjunctiva in the region of highlights, the spectral interference colors indicative of an oil film can be seen everywhere. One must conclude, therefore, as in the human, that rabbit, cat, and dog eyes do not expose the aqueous phase of tears to air, but expose a continuous, unbroken oil film which exhibits the surface phenomena suggestive of an oily multilayer. As in the human, this oily multilayer very rapidly adjusts itself to great differences in surface area exposed, ranging from small exposure in partial lid closure to extreme exposure when the lids are pulled from the globe.

WETTING

The tear film in animal eyes, as in humans, looks like it is attached to each lid margin at the junction of the line joining each meibomian orifice. By using a fluorescent or gooseneck lamp for illumination and by carefully focusing on the area of spectral reflection, interference patterns can be seen over the lacrimal lake. Using the light from the slit lamp, one can focus on surface contaminants. Either the surface contaminants or the spectral colors can be used as indicators of the surface in this area and their observation shows that the surface is fixed to the lid all along this hydrophilic hydrophobic border. The aqueous phase of the tears is contained behind this layer as under a membrane, as in the human (Figure 12).

The surface tension of the tears, which is reduced by the oily multilayers, determines its wetting ability. The lower the tension, the more substances it will wet. If the critical surface tension of a tissue is greater than the tears, it will be wet as are the cornea and the conjunctiva. If the tissue has a lower surface tension than the tears, it will not wet, as on the outer aspects of the lid. The attachment of the surface oil film to the lids seems quite firm, almost like an organic attachment



FIGURE 12

Wetting limited by lower surface tension anterior to meibomian orifices.

of the vitreous base to the periphery. However, we know that this is only the result of surface tension and the physical qualities of the multilayer (Figure 12).

VISCOSITY OF THE SURFACE

Viscosity of the surface of the rabbit eye can be tested by dusting a little talc on the surface of the eye and preventing lid closure. Using a pipette, a fine jet of air is directed to the talc on the surface. No movement of the talc is noted in relation to the surface, indicating a rather rigid multilayer. This is in contrast to the ease of moving talc particles on the surface of water. The oil interference pattern can also be used for viscosity measurements. In the rabbit it is very difficult, even when blowing with all one's force, to cause any movement of the surface layer.

The viscosity of the surface film is demonstrated also by observing the surface membrane over the lacrimal lake, using interference phenomenon or surface contaminants to identify the lake. The surface

is immobile, but underneath, as in the human, there is a great rush of liquid, now one way, now the other. These submarine movements are related to lid movement and for the most part are directed toward the puncta. The viscosity shown here is a surface phenomenon.

If the surface is brought into focus by the direct light of the slit lamp, viscosity of the multilayer can be demonstrated by slight movements of the upper lid. A slight downward movement of the upper lid moves the surface film two-thirds of the way down the cornea with a slight change in the interference pattern, indicating some "elasticity" of the multilayer. When the lid is raised, ever so slightly, the film moves upward over the whole cornea. Therefore, the multilayer has much viscosity, but also has the characteristics of an elastic membrane.

FAT STAINING OF TEAR FILM

If the surface layer of tears is oil, it should dissolve oil-soluble substances but not water-soluble substances. Sudan IV is a dye which is soluble in oil but not in aqueous solution. The end of a hair was wetted with a 0.5 per cent solution of Sudan IV in mineral oil and placed in the conjunctival sac. The lid was passively blinked two or three times to spread the oily solution. The red-coloured mineral oil did not mix with the tears but it did immediately wet and stain the hydrophobic (and apparently oleophilic) part of the lid, including the hairs and skin. Each meibomian orifice seemed to stain pink, as if the oil waiting to be discharged at the orifice took a little of the dye out of the mineral-oil vehicle. On first looking at the area of the lacrimal prism, especially at the upper lid, one can see that the tears are not stained but that there are red globules of oil which move to and fro underneath the rigid surface of the lacrimal prism. These globules even change shape to allow their passage through narrow channels or past debris in the same manner as red blood cells adjust their shape for passage through a narrow capillary. These movements of globules are intermittent, sometimes in one direction and sometimes in another, as in the human, and are related to lid movement.

The red, oily globules are too high in surface tension to form a surface layer on the tear film. They gather themselves into spheres to reduce the free energy of their surface. Since the oil molecules are incapable of overcoming the van der Waals forces of the tear molecules, they are rejected out of the aqueous solution and presumably discharged through the puncta as an oil-water emulsion. The chemicals or factors which contribute to emulsification in tears are unknown.

The fat dye did not stain the conjunctiva or corneal tissue and avoided all tissue capable of being wet by tears. However, by virtue of their lower surface tension, it wetted and stained the oleophilic and hydrophobic portions of the lid. The fat of the skin molecules allowed the mineral oil molecules to intersperse themselves, the attraction for the oil being as great as the attraction of the fat molecules for each other.

THE CRUMPLE PHENOMENON

Under certain conditions an invisible, insoluble monomolecular layer can be made visible by lateral pressure on the surface film, as previously mentioned. The lateral pressure needed to collapse the orderly arrangement of the monolayer can be quantitated with a film balance or by a "piston" oil (an oil that has a known spreading pressure and is used to compress surface films).⁵ A similar surface phenomenon is here noted in the rabbit eye, even though this layer seems to be a multimolecular layer. Using a wide, bright beam of the slit lamp shining obliquely on the cornea at about 45° to the line of sight of the observer, this surface phenomenon can be noted spontaneously without touching the rabbit, when the animal partially blinks or tends to close the nictitating membrane over the cornea. This is seen as a fleeting increase in reflection of the tear surface, as if the invisible surface film suddenly became like shining silk (Figure 13). It occurs

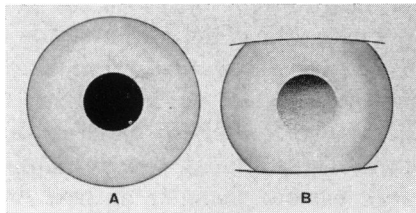


FIGURE 13
Crumple phenomenon with partial lid closure.

when the surface film is laterally compressed with partial lid or nictitating-membrane closure. The sudden increased visibility of the surface disappears as rapidly as it came when the lateral pressure on the oil layer is relieved by lid or membrane retraction. This pattern can be repeated indefinitely. The phenomenon should not be confused with the increase in reflection caused by the concentration of accumulated surface debris; as such a concentration can be seen to be built up

gradually, whereas the crumple phenomenon is an all-or-none condition for a given area of the corneal film. Nor should it be confused with the increased visibility of the virtual image of the lashes and lid borders which occurs when the lids are approximated.

By the use of the slit lamp (best for the crumple phenomenon) and also the reflected light of the gooseneck lamp (best for interference phenomenon), one can see that prior to the collapse of the multilayer, the spectral interference pattern seems generally blue. This indicates a thickness of the multilayer of one-fourth the wavelength of red light (1,790 Å), which is cancelled out. It is difficult to make out any spectral interference color because of the shimmering reflection from the collapsed surface.

The oil film, whether crumpled or not, maintains the polarity of incident polarized light, just as the normal tear surface does. No polarization phenomenon was noted at the surface of the crumpled film when a single piece of polaroid was placed in the path of either the incident or the reflected beam. The use of blue light does not seem to alter the appearance of the crumpled pattern.

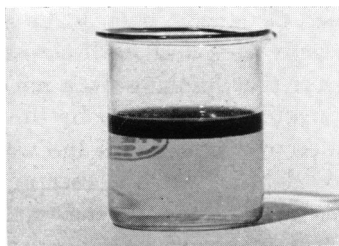


FIGURE 14

Floating oil dissolves Sudan IV dye, and water dissolves fluorescein.

The entire tear film seems to stain with water-soluble sodium fluorescein. When the surface oil layer was compressed to produce the crumple phenomenon, it was seen that the aqueous portion of the tears is stained with fluorescein, but the oily tear film is not. Since the surface is usually invisible, this rejection of the fluorescein by the oil surface is not usually noted. Also, when oil-soluble Sudan IV stain is used in the eye, the surface oil is not visibly stained red in its normal state (Figure 14), but when the layer is thickened by the crumple phenomenon, it is possible to see that the surface oil is indeed stained with the red, oil-soluble dye. When both stains are used, one can see

an apparently yellow surface giving way to the red as the crumple phenomenon proceeds.

These changes in the multilayer in a rabbit are similar to the Langmuir and Schaefer description⁵ of the crumpling of insoluble monolayers. If the observations in the eye are explicable in terms of crumpling of molecular layers, as I believe they are, they imply the interaction and involvement of profound physical forces on atomic and molecular levels. The parameters which operate to regulate these forces in the rabbit, cat, dog, or occasionally in the human are unknown.

A related surface phenomenon of the oil layer can be called the pleated drape effect. This is noted at times in the area of the superior lacrimal lake of rabbits, by the illumination of the slit lamp. As the lid descends, actively or passively, the invisible oil layer is pushed ahead in bunches, just as pleated drapes gather together as they are opened. When the lids are raised, the collection of oil serves as a source of oil for the reformation of the orderly multilayer, in the same manner as the pleats in drapes disappear as they are drawn across the window. The use of a fat-soluble stain makes the phenomenon easier to see. In this case the red-stained oil layer is seen to be gathered into itself at the upper lid as it sweeps back and forth across the corneal surface.

These findings suggest that blinking does not cause a sweeping of debris across the surface of the tear film by the upper lid but rather seems to cause an undercover renewal of the water phase of the tear film with its submarine debris. Thus the escape of the surface debris is not explained by this interpretation of the blinking mechanism. Perhaps a breakdown of the rigidity and the viscosity of the layer occurs when such debris is present. The factors involved in such a hypothetical breakdown might be similar to those factors, such as temperature, *pH*, and various chemical contaminants, which affect the physical characteristics of an insoluble monolayer in the laboratory.

In the laboratory, Langmuir and Schaefer found that some insoluble monolayers continued to be compressed after the collapse phenomenon had occurred (the rolled up scum effect). This surface effect can also be seen in the oil tear film of the rabbit as an extension of the crumple phenomenon. When the film is crumpled and the lids continue to be compressed, occasionally a roll of oil develops at right angles to the direction of compression. This can be seen with the direct slit-lamp beam or the gooseneck reflective light. As compression continues, the crumpled layer seems to be gathered into a rolled up, scum-like area,

which appears as a line or surface collection of scum (Figure 15). As the lids are retracted, this collection of oil serves as a source for the reformation of the orderly multilayer. The phenomenon implies, as the crumple phenomenon does, that there is a limit to the amount of oil that a rabbit's tear film can accommodate in an orderly manner. A strong lateral cohesiveness of the oil molecules is also implied. Factors which would affect the occurrence of this phenomenon or vary it are unknown.

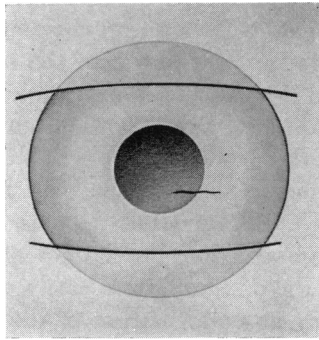


FIGURE 15
Rolled up scum effect.

The crumple phenomenon was seen spontaneously in the rabbit, and was reproducible. These phenomena were also noted in cats and dogs, but not as easily as in the rabbit. In the human, a true crumple was seen only in three patients, all of whom had an excess of oil at the time of examination.

EPITHELIAL SURFACE

On focusing in front of the specular reflection of a bulb, one sees a vague, patterned effect under the tear film in the rabbit, which is easier to visualize when the tear film is moved up or down by lid motion. What appeared as a very smooth reflecting surface under the oil and aqueous phase now is seen to consist of a series of gentle ridges and craters, like ridges of sand under the water at the seashore. In other words, when the tear film is made to move, the surface particles are carried along with it, but these movements aside, one can see these irregularities in the residual stationary epithelial surface. Such subsurface contour variations do not usually produce irregularities in the

reflecting tear film, the difference presumably being taken up by the thickness of the aqueous tear layer. These epithelial surface irregularities are maintained for at least ten minutes, at which time observations ceased.

EPITHELIAL TOUCH PHENOMENON

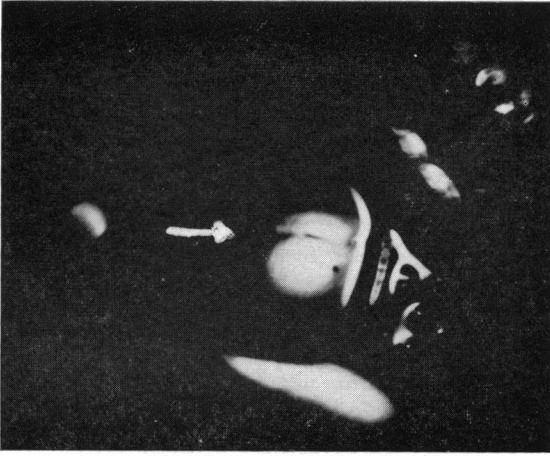
It was noted that when a hair riding on the tear film was pushed away by the movements of the lid, it left an indentation in the epithelial surface. This indentation was seen best by passively moving the tear film over it. The superficial color interference pattern was not disturbed by the submerged hair. The tear film over the indented area behaved in one of several ways. When the epithelial indentation was small, the tear surface maintained its curvature without any change in the thickness of the oil layer, indicating that there was a corresponding increase in thickness in the aqueous phase of the tear. If the indentation was larger, the surface curvature was altered, there being a depression in the surface partially compensating for the indentation of the epithelial surface. In these cases the oil film flowed easily over the altered indentation without changing its color pattern or thickness. These indentations disappeared in approximately four minutes.

Indentations of the corneal epithelial surface can apparently be produced in a fraction of a second by the weight of the hair alone without any pressure whatsoever on either end of the hair. When these indentations are large, as from a thick whisker, tear surfaces are distorted as they flow over the depressions. When they are small, there is no tear surface deformity. A series of 10 or 20 parallel linear indentations can be made by the same hair without exerting any pressure whatsoever on either end of the hair. One wonders if this epithelial indentation might not be a factor in calculations of tonometry, as originally suggested by Schiøtz,² especially in the small amounts of pressure applied as in applanation tonometry. The same phenomenon is noted with a piece of lint in the eye, which is approximately one-tenth as thick as hair, and also with 6-0 black silk and nylon sutures.

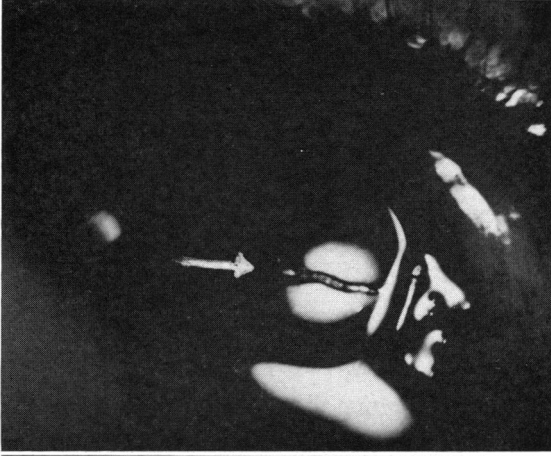
If a 22-gauge needle or a rabbit's whisker is touched longitudinally to the cornea while observing the spectrum of the corneal tear film through the microscope, the spectral colors in the area of the touch disappear. This indicates displacement of the oil layer of the tear film (Figure 16) by oil of low surface tension on the whisker or on the

FIGURE 16

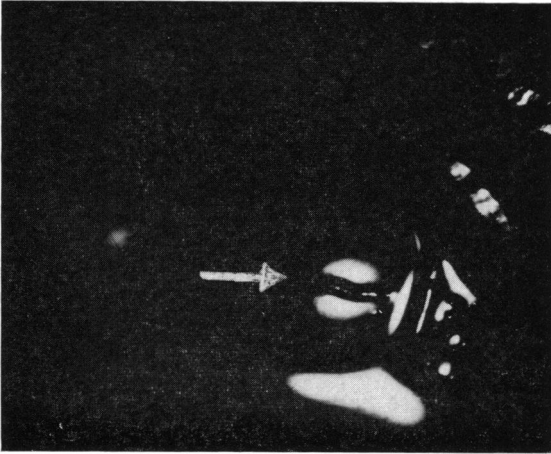
A, oil film displaced by whisker touch. B, tear film retracts under area of touch. C, further recession proceeds and causes stain lesion of epithelial surface.



A



B



C

needle. Subsequent to this, drying starts in one place under the oil-deficient area and spreads longitudinally until the whole area of the touch is dry and indented, although normal tear and oil films are on either side of the touch. Upon blinking, this area wets again. However, the surface of the epithelium and the tear film is still indented. The oil layer is reconstituted and is of normal thickness. The indentation is due to the compression of the epithelial cell surface and disappears in four minutes. In subsequent touches, if the needle or whisker is wet, the oil film is not easily displaced and the cornea seems less likely to dry, especially if the same area of the needle is used. Application of grease from one's skin to the needle will restart the phenomenon. Compression of the epithelial cell surface can be produced, however, without a rupture of the oil layer and without drying. The edge of a glass slide which was visibly wet with tear film showed no tendency to adsorb the multilayer or produce drying.

If the oil layer is made deficient by displacement with a low surface tension surfactant and if it is so viscid as not to repair the defect immediately, then the surface of the tear film becomes depressed and drying starts. The dry areas are stainable with fluorescein for half an hour, even if immediately wetted by lid closure. These findings confirm the observations of Maurice and Mishima,⁶ Mishima and Maurice,^{9,10} and Ehlers¹ that the oil layer protects against corneal desiccation.

INTERFERENCE PATTERNS ON CONTACT LENSES

Another type of interference phenomenon can be seen in front of a contact lens in the eye of a rabbit or a human. It is due to the drying of the entire thickness of the pre-lens tear film leaving the oil layer deposited on the dried surface in a crystalline-like pattern. This phenomenon consists of five or more orders of spectra whose colors sweep across the surface and then recede to extinction. These full-thickness interference phenomena are so intense and speedy that they are difficult to assess.

Rapid drying occurs by evaporation or recession of a rabbit's tear film over a contact lens. This is in marked contrast to my inability to dry the normal corneal tear film for one minute under a hair dryer. Full-thickness tear film interference patterns could not be produced under any circumstances when the natural corneal epithelial surface was the base. On the other hand, when the contact lens was the base for the aqueous film, these patterns were so prominent that it seemed possible for the patient to appreciate them. The mechanism of this

rapid drying in front of the contact lens is unknown, but there are several possibilities: (*a*) pre-lens film may have an oil film which is more permeable or more expanded than the oil film of the normal cornea, (*b*) normal tear renewal from behind or from the periphery may be inhibited by the contact lens, (*c*) the better wetting properties of the corneal epithelial surface may be a factor in the rate of surface drying. In this regard, it is interesting to note the pattern of drying. First a microscopic area dries and acts as a nucleus from which the tear film recedes. The rapidly receding borders of the still wetted area may show five or more orders of spectra near to their edges. This indicates a thickness of the pre-lens tear film of from 11,000 to 1000 Å near the edge of the drying tear film. These dry centers resist wetting when the lacrimal lake is raised up to them, and when wet, dry faster than the adjacent surface. This suggests that these areas have a lower surface tension and that the lower surface tension of a solid will produce an earlier drying of an overlying film as well as a resistance to wetting.

DISCUSSION

In the film balance, insoluble monolayers behave much like the oil layer on tear films. This is true in regard to surface tension, spreading pressure, and viscosity. However, because of its variability of thickness as measured here by interference techniques, the oil layer of tear films cannot be a continuous monolayer, but must be an orderly multilayer, at least when interference patterns are seen. This oily multilayer displays phenomena previously attributed to monolayers, such as the crumple phenomenon. Its thickness when no interference is present is less than 1000 Å. Our technique permits no finer measurement. If the oily molecules are 50 Å in length, we would expect this layer to be less than 20 molecules thick in those areas of the film that showed no interference.

An oil covering of variable but observable thickness is present over the aqueous phase and this somewhat rigid oil layer is firmly attached to the lids by molecular attractive forces. This is true of the human eye as well as of eyes in the rabbit, cat, and dog. The physical and chemical characteristics of the eye and adnexa are perfectly designed to maintain the continuity of this oil film and to renew it. Its presence seems necessary to the healthy eye. Our rabbit experiments confirm this. A greasy needle touched to the oil film breaks its continuity by displacement, profoundly disrupts the watery layer beneath, and wounds

the epithelial surface. The damage to the corneal epithelium when the oil film was washed away and blocked from renewal was very great indeed.^{1,6,9,10}

Some physical characteristics of surface films can be determined on a clinical level. The relative viscosity, the wetting properties relating to surface tension, the general appearance and thickness all can be described and documented with camera or brush.

It is not known what, if any, correlations can then be made with diseases and disabilities of the eye which hint at causal surface factors. It would seem that the surface tension of the eyelid must be raised at the outer canthus in those eyes whose canthi first wet, then macerate, then crack. The eye with superficial punctate staining, whose stain spots are harder to wet and dry earlier, seems to have a problem involving surface tension. It would be interesting to know if its oil layer were of normal thickness and viscosity. Other eyes that tear, when there is no excess of tears or drain pipe difficulty, seem to have trouble maintaining the hydrophobic border, probably due to surface tension factors. Even the presence of a good oil layer in normal eyes and its possible variations in disease are yet to be adequately studied.

Surface phenomena in relation to symptoms of drying in a contact lens or possible subjective appreciation of interference patterns during the process have not, to my knowledge, been systematically investigated. The dramatic irregularity and desiccation of the cornea with topical anesthesia, especially in the rabbit, must be related to surface phenomena. These items suggest the need for more investigation.

SUMMARY

A review of some phenomena and aspects of physical and surface chemistry is presented. A number of observations on human, rabbit, cat, and dog eyes are described and illustrated. An explanation for these phenomena is offered in terms of surface factors. The possible clinical importance of such surface phenomena is discussed.

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