CHEMISTRY AND TECHNOLOGY OF SURFACE ACTIVE

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SURFACE SCIENCE: FUNDAMENTAL CONCEPTS AND APPLICATIONS

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SYNOPSIS

The domain of surface science is perhaps one of the most interdisciplinary areas of modern science and technology. Monolayers provide a unique system to determine experimentally the cross-sectional areas of surface-active molecules and to study reactions and molecular interactions at surfaces. The relevance of monolayers to many biomedical and engineering systems is described.

The engineering applications of surface science range from agricultural sprays to oil recovery including areas such as catalysis, coatings, detergency, dispersions, electronics, flotation of minerals, lubrication, and retardation of evaporation from lakes and reservoirs. Among biomedical areas, the applications of surface science extend from anesthesiology to zoology including fields such as artificial implants, biomembranes, biolubrication, lipoproteins, lung surfactant, ophthalmology, pharmaceuticals and pharmacology.

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Although the importance of surface science has been recognized for more than a century, it is only during the last few decades that we have seen rapid advances in the understanding of surface phenomena. In this presentation I would like to review briefly various principles of surface science and where appropriate would like to present the highlights of the research carried out in my laboratory during the past decade.

Let me begin with a quotation of an oriental proverb which says, "The color of the world you see depends upon the color of the glass you look through." In general, a scientist attempts to look at the Universe through his own glass. When one looks at the Universe through the glass of surface science (Figure 1), one sees that it consists of Sun, Earth, Moon, Stars, Galaxies, etc. When one looks closer to the Earth, one finds that it is full of objects; and that each object is surrounded by a surface or an interface. Fortunately, all the interfaces can be grouped into five major classes, namely, gas/liquid, liquid/liquid, solid/liquid, solid/gas, and solid/solid. All objects are surrounded by one or more of these basic five interfaces. All of these interfaces have a common property called surface tension or surface free energy. There is also a class of compounds called surface-active compounds (or surfactants) that decreases strikingly the surface tension or surface free energy of these interfaces.

A surfactant molecule has two functional parts, namely, a hydrophilic (water soluble) or polar part, and a lipophilic (oil soluble) or non-polar part. The lipophilic part is usually a long hydrocarbon chain. Schematically, a surfactant molecule
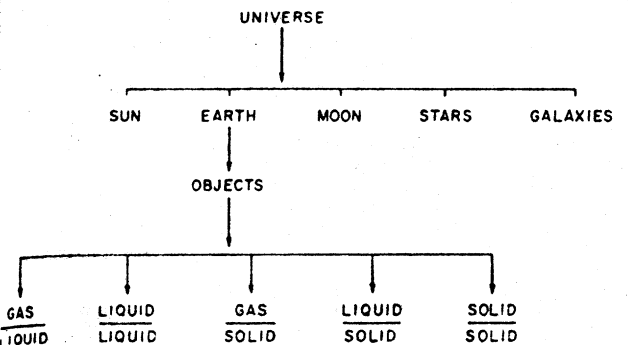
FIGURE 1. All objects are surrounded with one or more of these five interfaces.
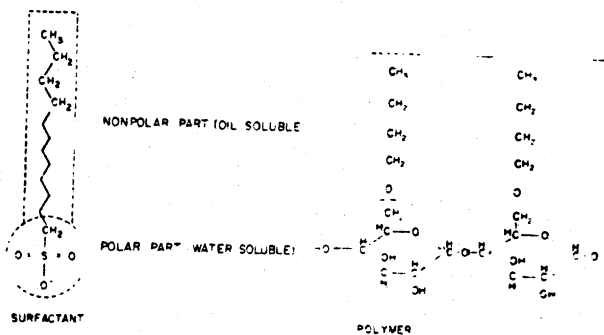

FIGURE 2. The structure of surface-active molecules. The broken line shows the separation of polar and non-polar parts of the molecule.

can be represented by a nonpolar (tail) and a polar group as shown in Figure 2. A polymer also can be surface-active if it has two functional groups, one hydrophilic and the other lipophilic (Figure 2). The properties of a surface-active compound are determined by the balance between its hydrophilic and lipophilic characteristics. If the chain-length is relatively short (less than 12 -C-C- bonds in length), they are called water soluble surfactants since the polar group drags the entire molecule in water. However, when the chain-length is greater than 14 or 16 -C-C- bonds in length, the compounds are called insoluble surfactants. They do not dissolve in water because of the long hydrocarbon chains.

MOLECULAR AGGREGATES

If the concentration of a soluble surfactant in water is increased gradually, at a specific concentration of the surfactant, (i.e., in a very narrow range of concentrations), the solution properties such as osmotic pressure, surface tension, viscosity, electrical conductivity, and density abruptly change [1]. This concentration is called critical micelle concentration
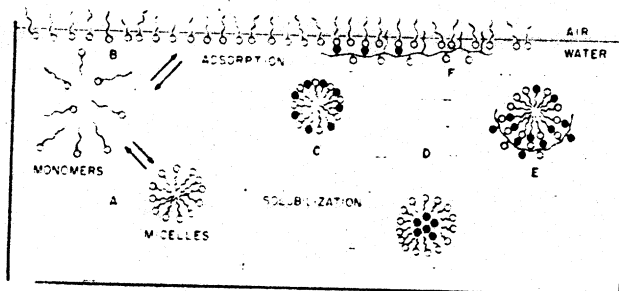
FIGURE 3. A schematic presentation of adsorption, micelle formation, and solubilization processes in surfactant solutions.

(CMC). It has been well established from theoretical considerations as well as experimental determinations that surfactant molecules begin to form aggregates, called micelles, when surfactant concentration is increased beyond the critical micelle concentration (Figure 3A). In general, the micelles are spherical aggregates of surfactant molecules about 40-100 Angstrom in diameter and are in equilibrium with single molecules (or monomers) in the bulk solution (Figure 3A). The critical micelle concentration depends upon the structure of surfactant molecules as well as physicochemical conditions such as temperature, pH, and the ionic composition of the solution.

If a soluble surfactant is dissolved in water, it tends to adsorb at the gas/liquid, liquid/liquid, or solid/liquid interfaces. The adsorption phenomenon results in a greater concentration of surfactant molecules at the interface as compared to that in the bulk solution (Figure 3B). For many surface-active drugs and pharmacological agents, their concentration at the membrane surface will be considerably greater than their bulk concentration [2].

The formation of micelles in an aqueous solution creates a

local nonpolar environment within the aqueous phase. Oil soluble molecules such as dyes, pigments, nonpolar oils, or oil soluble vitamins can be dissolved within the micelles (Figure 3C,D). The solubilization of such molecules in micelles is greater if they also possess polar groups.

If a surfactant solution contains a surface-active polymer, then adsorption of the polymer can occur at the micellar surface (Figure 3E). The structure of lipoproteins, particularly low density lipoproteins in blood serum, resembles this situation in which a protein is adsorbed on the aggregates of lipid (i.e., biological surfactant or fat) molecules [3]. If a surface-active polymer is present in the solution, then a mixed, absorbed film of polymer and surfactant also can occur at the interface (Figure 3F). In several biological membranes, the protein-lipid association is believed to resemble this type of association [4].

The solubilization of polar and nonpolar "dirt" in detergent micelles play an important role in detergency process. The role of surface-active agents in changing the wettability of the fiber surface is also important in detergency.

Surfactant molecules can be considered as building blocks. One can make various types of structures of surfactant molecules by simply increasing the concentration of surfactant in water and adjusting proper physicochemical conditions such as temperature, pH, and the presence of various electrolytes [5, 6]. Figure 4 schematically shows various structures that are formed in the surfactant solution upon increasing the concentration of a surfactant. Upon increasing the concentration of surfactant,
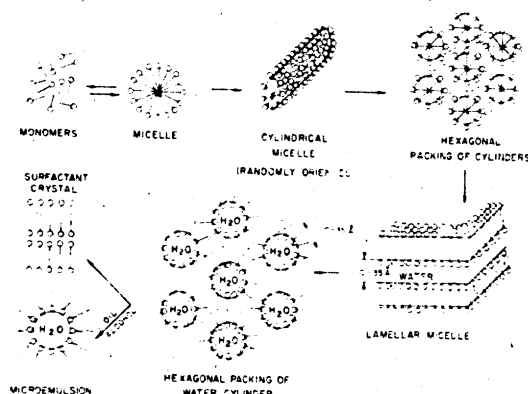
FIGURE 4. A schematic presentation of structure formation in surfactant solution depending upon the concentration of surfactant as well as physico-chemical conditions.

spherical micelles become cylindrical and subsequently the cylindrical structures become hexagonally packed. If concentration is further increased, the lamellar structures are formed. Upon further addition of surfactant, the lamellar structures are converted to a hexagonal packing of water cylinders. Upon addition of oil
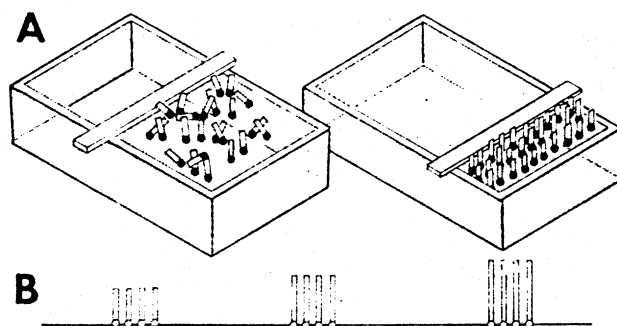

FIGURE 5. (A) schematic illustration of a monomolecular film at air-water interface.
(B) orientation of surface-active molecules with increasing chain-length at air-water interface.

and a short-chain alcohol, one can convert such water cylinders into a water-in-oil microemulsion. The structures of these systems are well established from X-ray diffraction studies [7, 8]. It is possible to induce a transition from one structure to another by changing the physicochemical conditions such as temperature,

pH, addition of monovalent or divalent cations in the surfactant solution [9]. The cylindrical and lamellar structures often are called liquid-crystalline phases since they have flow properties as liquids and a certain degree of crystallinity as solids. They have very unusual electrical and rheological properties [10, 12]. It should be emphasized that the scheme shown in Figure 4 is a general scheme and a surfactant may skip several phases depending upon its structure and the physicochemical conditions.

INSOLUBLE SURFACTANT AND MONOLAYERS

If the hydrocarbon chains are sufficiently long (greater than 16 -C-C- bonds), the surface-active molecules will be insoluble in water. When such insoluble surfactants are dissolved in organic solvents, and a drop of the solution is placed on the water surface, these molecules will spread at the air/water interface. In general, the surfactant molecule does not evaporate because the polar group is anchored on the water surface and it does not dissolve because the long hydrocarbon chain prevents the molecule dissolving into water. In this way, one can produce a monomolecular film of floating molecules of an insoluble surfactant at the air/water interface. In general, one can fill a tray of Teflon or plexiglas with water up to the rim of the tray. A measured quantity of surfactant solution in an organic solvent such as chloroform, benzene, or hexane can be placed by a microsyringe on the water surface. The solvent molecules evaporate or diffuse into the water leaving the insoluble surfactant molecules at the surface. A glass slide is placed at one end of the trough (Figure 5A). By horizontal movement of the glass slide one can compress this monomolecular film and bring molecules

closer to one another. However, as the film is compressed, at a specific film area, the molecules will stand side by side with their polar groups in water and hydrocarbon chains in the air. By measuring the area of the film as well as calculating the number of molecules deposited on the surface, one can determine the average area per surface-active molecule in the monolayer. In a closed packed state, the average area per molecule is close to the cross-sectional area of the surfactant molecule. Thus, an insoluble monolayer is a system which allows the direct experimental determination of the cross-sectional area of the molecules.

Monomolecular films or monolayers represent a two-dimensional state of matter since their height, which is about 20-25 Angstrom, is negligible compared with their length and width. Analogous to the states of matter in three dimensions, monolayers also can exist as two-dimensional solids, liquids or gases and can undergo temperature-dependent phase transitions from one state to another [13, 14].

When the monomolecular film is compressed by moving the glass slide, the surface tension decreases (Figure 5A). The decrease in surface tension often is called surface pressure which indicates the state of compression of the monomolecular film. The higher the surface pressure, the higher the state of compression of the monomolecular film. The surface tension is measured by a torsion balance from which a thin platinum blade is suspended in water at the air/water interface.

From the surface pressure measurements one can prepare a plot of surface pressure vs. average area per molecule. This plot is equivalent to pressure vs. volume curve for gases in

three-dimensional state. In 1910, the concept of the specific

molecular orientation at interfaces was a novel idea, but there

was no experimental proof for this concept. Langmuir [15] used

monolayer approach to establish that surface active molecules

have a specific molecular orientation at the air/water interface.

He studied monolayers of various fatty acids of different length

containing 16 to 32 carbon atoms. Experimentally, he determined

the cross-sectional area of molecules in the compressed mono-

layers of these fatty acids. To his surprise, he observed that

although the fatty acids studied were of different chain-length,

the cross-sectional area determined was the same for all fatty

acids suggesting that they must be oriented vertically to the

surface (Figure 5B). If they were oriented in any other way,

the increasing chain length would have caused an increase in the

average area per molecule. For estabishing this concept of the

specific molecular orientation at interfaces, Langmuir later

was awarded a Nobel Prize [16].

APPLICATIONS OF MONOLAYERS

Since it is difficult to visualize at a molecular level how

properties of a monolayer are related to various phenomena, I

have prepared the following few diagrams to emphasize the role

of monomolecular films in these phenomena.

Figure 6 shows two conceptual models for molecular arrange-

ment of lipids and proteins in biological membranes [17, 18].

In the Davson-Danielli model (Figure 6A), the lipids (i.e., bio-

logical surfactant) are arranged as a continuous bilayer and

protein is believed to be adsorbed on both sides of the lipid
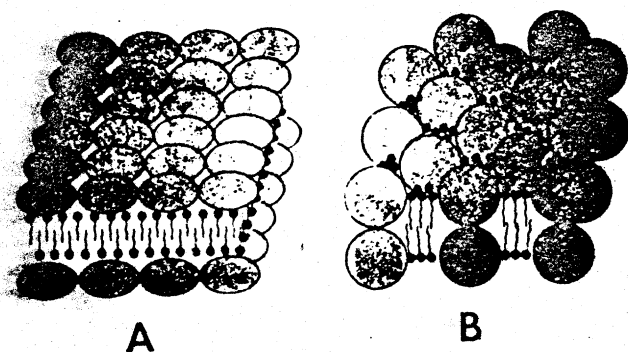
FIGURE 6. (A) Davson-Danielli model for structure of biological membranes.
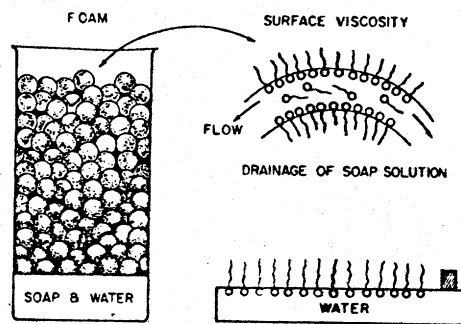(B) Lipid-protein mosaic model for the structure of biological membranes.

FIGURE 7. The schematic presentation of factors influencing foam stability.

bilayer. The second model, (Figure 6B) which is based upon the current thinking about the structure of biological membranes, visualizes a discontinuous lipid bilayer interdigitated by protein molecules. Irrespective of which of these models is a more accurate description of molecular arrangement in membranes, the orientation and packing of lipid molecules in membranes are similar to that in monomolecular films of the lipids at the interface. Using a monolayer approach, one can determine lipid-lipid, lipid-protein and lipid-metal ion interactions that may occur in biological membranes [19-21].

Figure 7 schematically shows a foam column produced by a surfactant solution. The stability of the foam column depends upon the stability of individual soap bubbles. A soap bubble is a thin layer of surfactant solution which has the adsorbed film of surfactant on both sides of the soap film. The stability of the soap film depends upon the rate of drainage of solution in the film, which subsequently depends upon the state of adsorbed
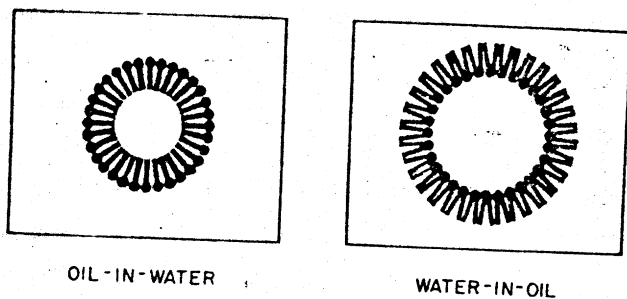
OIL-IN-WATER   WATER-IN-OIL

FIGURE 8. A schematic presentation for the structure of emulsion droplets and orientation of surface-active molecules at the oil-water interface.
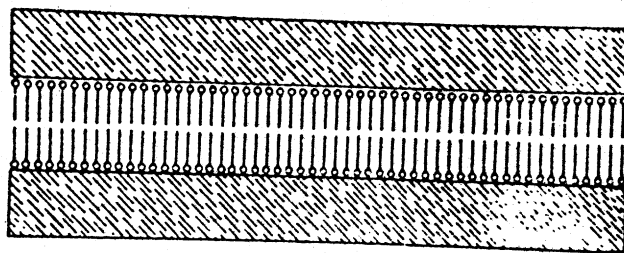

FIGURE 9. A schematic presentation of the orientation of surface-active molecules at the metal surface in boundary lubrication.

surfactant film. We have observed [22, 23] that a closer packing of surfactant molecules in the adsorbed monolayer leads to a higher surface viscosity of the adsorbed monolayer, which subsequently decreases the rate of drainage of solution within the soap film, and hence increases the foam stability.

Figure 8 schematically shows the role of monolayers in stabilizing oil/water emulsions. It has been known that oil and water do not mix. However, if a surfactant is added to oil-water mixture, one can produce a relatively stable emulsion. Depending upon the relative amounts of oil and water as well as the physicochemical conditions, one can produce oil-in-water or water-in-oil type emulsion. In either case, each droplet is coated with a surfactant monolayer (Figure 8).

Figure 9 shows the role of the monomolecular film in boundary lubrication of metallic surfaces. Here a surfactant attaches itself to a metal surface due to the interaction between the polar group of the surfactant with the metallic surface. When such monolayer-covered surfaces slide against one another, the frictional forces decrease considerably. Since sliding of hydrocarbon chains past one another does not

offer too much resistance, the coefficient of friction decreases strikingly. Moreover, the adsorption of such monomolecular film of surfactant on metal surfaces also protects the surface against wear from friction.

The monomolecular films of fatty acids or fatty alcohols also are employed for reducing evaporation of water [24]. In many countries, such as India and Australia, this approach is used to decrease evaporation of water from lakes and reservoirs. Monolayers can be used also for contraction and containment of oil spills. For this application, insoluble surfactants with higher surface pressure than that of the oil spill are spread around the oil spill.

Monolayers can cause significant damping of capillary waves at the air/water interface. Since light reflection from a stationary surface would be much higher than that with an oscillating surface, a monolayer can be used as a "spot marker" on the ocean surface. If surfactants containing fluorescent or phosphorescent groups are used, then such films can be spotted at night.

In summary, monolayers provide an extremely useful system to study cross-sectional area of surfactant molecules and to elucidate the effect of unsaturation on the intermolecular spacing, and hence on the reactions and molecular interactions at interfaces.

More than 10^9 tons of ore are processed each year by flotation process to separate desired minerals. As shown in Figure 10, ore is ground into small particle size, and mixed with water containing appropriate surfactant. When air is bubbled through the ore suspension, the surfactant molecules adsorbed at the
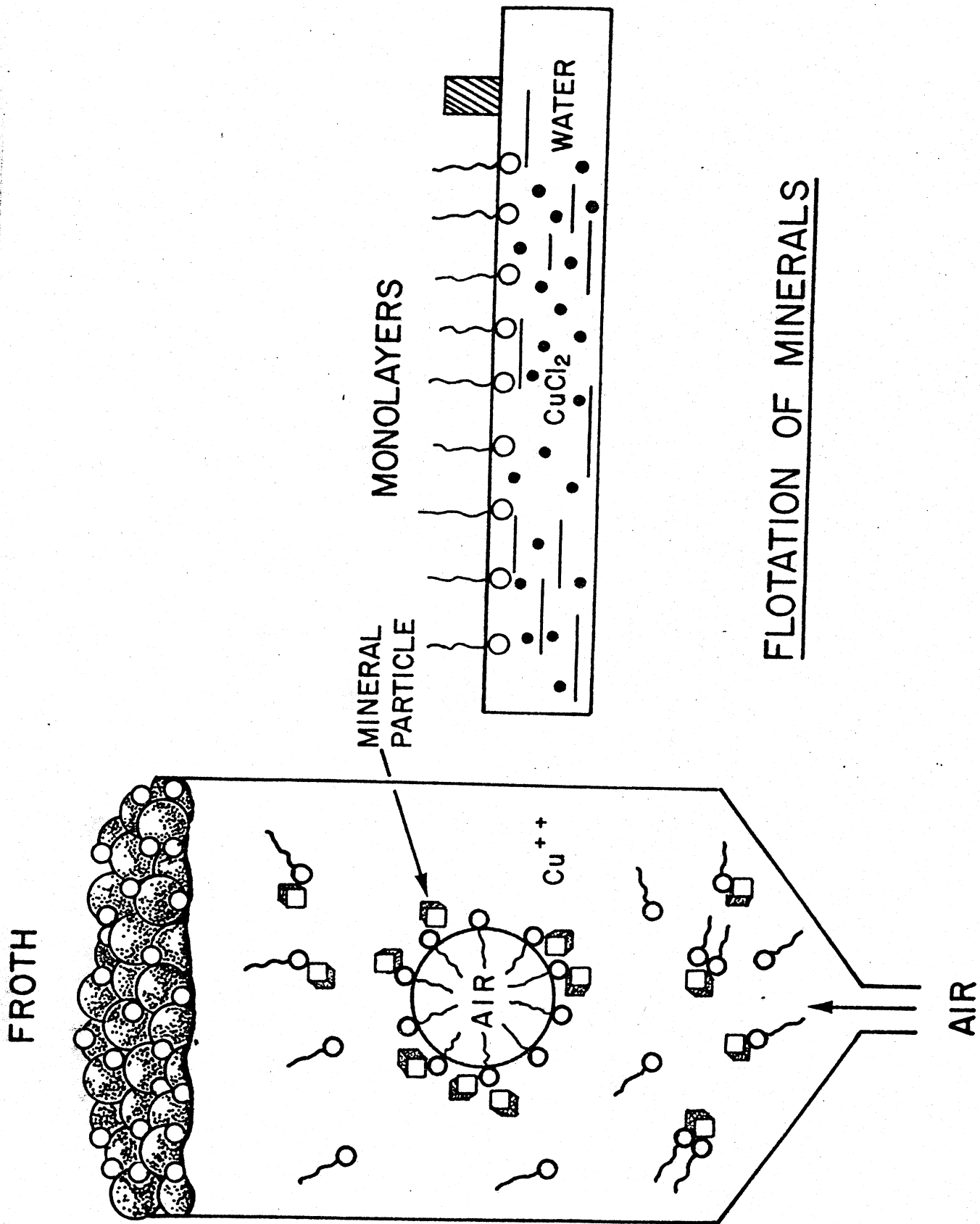
FIGURE 10

air/water interface around the bubbles with bound minerals.
Thus, the froth becomes richer in the desired mineral. For
many systems, it has been noticed that the pH for optimum flo-
tation is the same as that required for maximum interaction
of metal ion with the surfactant monolayer.

Figure 11 shows one of the concepts of surface science,
namely, contact angle and wettability. When a drop of water
is placed on wax, Teflon, or plexiglas, the drop rests on the
surface with a finite angle called contact angle. If the con-
tact angle is greater than 90°, the liquid does not wet the
surface. If one adds a surfactant or "wetting agent" in water,
the contact angle on wax or Teflon decreases dramatically and

WITHOUT SURFACTANT   WITH SURFACTANT (wetting agent)

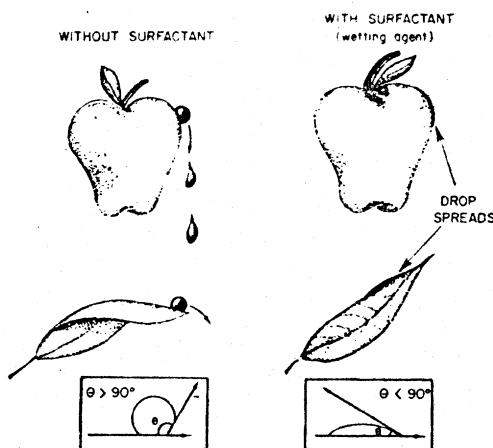DROP SPREADS

θ > 90°   θ < 90°

FIGURE 11: A schematic presentation of the role of contact angle and
wettability in influencing the effectiveness of agricultural
sprays.

may approach zero. Hence, normally nonwettable surfaces can be
wetted by water if surfactants are added to water [25, 26]. This
phenomenon is of considerable importance in agricultural sprays
since the herbicide or insecticide will not be effective if the
drops from the spray do not stay on the leaves or fruits (because
of their waxy surface) and fall on the ground. However, if one
adds a surface-active agent to the spray, it changes the contact

angle and permits droplets to stick and spread on the leaves and fruits providing protection from insects and other diseases (Figure 11). This phenomenon is also of central importance in the wetting of contact lenses and in many problems related to cornea and tears [27].

Figure 12 shows the three-dimensional view of the application of surfactant solutions or microemulsions in tertiary oil recovery from petroleum reservoirs. Usually the oil wells are drilled in a five spot pattern in such a way that the microemulsions or surfactant solutions are injected into the central injection well. The surfactant formulation solubilizes the oils or decreases the interfacial tension at the oil/brine interface in the reservoir and displaces the oil towards the production wells at the four corners. If appropriate surfactants are injected, then the sandstone and rocks in the reservoir are cleaned and the oil is displaced effectively towards the production wells.
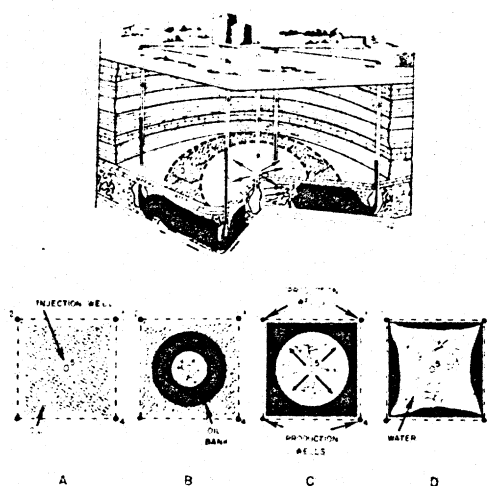

FIGURE 12. A schematic presentation of a petroleum reservoir. The lower part of the diagram shows how injection of a surfactant formulation moves the oil towards the four production wells.

Only about 30 to 35 percent of the original oil-in-place is recovered during primary and secondary water flooding oil recovery stages. About 65 to 70 percent of the oil is left behind in the reservoir. The oil remaining in the reservoir is distributed as discontinuous oil ganglia trapped in narrow channels between sand particles. The interfacial tension between crude oil and reservoir brine can be as high as 20 to 30 dynes/cm. The injected surfactant formulation is designed to decrease this interfacial tension to a few millidynes/cm level. This decreases the work for deformation of oil ganglia and its subsequent movement through narrow channels. Surfactant behavior for interfacial tension, interfacial viscosity, coalescence of oil glanglia, wettability alteration of rocks and adsorption and precipitation loss is important for tertiary oil recovery [28-32].

APPLICATIONS OF SURFACE SCIENCE

Agriculture and food technology --- The effectiveness of various herbicides and insecticides in agricultural sprays are determined by their wetting of leaves and fruits. The presence of surfactants (wetting agents) in agricultural sprays strikingly improves the effectiveness of the sprays and contributes to a greater production of crops. The emulsions also find considerable application in food products such as salad dressings, margarine, whipped cream, puddings, etc. Surface chemical aspects of protein-lipid associations also are important in determining the texture of food such as cakes and pastries and work is being done in this direction using the principles and techniques of surface science .

Energy --- The surfactant solutions and microemulsions are important in improving oil recovery from petroleum reservoirs. Another interesting application is in the area of combustion efficiency of various oils. Recently, it has been shown that if one injects a fine dispersion or emulsion of water and oil in furnaces, the efficiency of conversion of oil into heat is improved considerably. Although the exact mechanism is not established, the fact still remains that emulsification of oil and water improves the combustion efficiency.

Environment --- Principles and techniques of surface science find many applications in environmental problems. The dewatering of phosphate slimes, sludge formation, coagulation, and flocculation in many waster-water treatment plants rely on the surface interactions. The surface reactions and adsorption on activated carbon are very effective methods for removal of trace contaminants. Fibrous coalescers also are used for the removal of oil droplets from a few parts per million concentration in the effluent streams of many industries. Here the attachment of oil drops to the fiber and their subsequent coalescence play an important role in the separation of oil. The use of surface films as oil herder for the contraction of oil-spills has been discussed. The presence of films at the air/water interface also causes wave-damping of small ripples. This observation has been used in developing the instrumentation for remote sensing of oil-spills. In all these systems and processes, the principles of physics and chemistry of surfaces and surface-active agents are involved.

<u>Industries and engineering</u> --- The surface science is involved in coating processes. For example, the production of magnetic tapes in which a dispersion of magnetic oxide is coated on polyester tapes. The stability of the dispersion and the strength of adhesion depend on the surface interactions. Other applications of surface science are found in the manufacture of inks, paints, pigments, nonstick cooking wares, etc. The textile industry also utilizes considerable quantities of surface-active substances in the form of wetting agents, emulsions, dye-solubilization and other processes. The contact angle and wettability also enters into water-proofing of textiles, roofing material and similar systems. Many lubricants also involve the use of hydrocarbon oils and various surface-active agents as additives. The physics and chemistry of thin films are used extensively in the electronics industry. As discussed previously, the production of petroleum and petrochemicals also utilizes many processes which are in the general domain of surface science. The field of catalysis is based on surface interactions between the substrate molecules and the catalyst surface. The formulations of soaps and detergents for household uses also are based on surface properties of surfactants. In the world about 10^9 tons of minerals are processed every year by the use of flotation technology which again relies on the adsorption of surfactant on mineral particles. Many office stationeries, such as NCR papers (no carbon required papers), use microencapsulation of powders to coat these papers. The microencapsulation is one of the most interesting applications of surface and colloid science to industrial processes.

Biology and medicine --- Many principles and techniques of surface science are relevant to the understanding of the properties and functions of biological membranes. It has been suggested [17] that the spontaneous formation of membranes played an important role in the origin of prebiological cells during the chemical evolution which was followed by the biological evolution. These techniques are being used to elucidate the mechanism of action of many drugs, anesthetic agents, and pharmacological agents on membrane properties. It has been established during recent years that conduction of electrical signal along a nerve fiber is strictly a surface phenomenon occurring in nerve cell membrane. As discussed previously, the surface properties of polymers are also relevant to the performance of tear substitutes in the eye. These concepts can be also extended to the wetting of contact lenses and the comfort for the eye. The solubilization of oil soluble vitamins in micelles, the fat absorption in intestine, lung stability and the function of pulmonary surfactant, synovial fluid and lubrication of bone joints, dental integuments, and the development of various nonthrombogenic surfaces for artificial organs and implants all draw significantly on surface science.

Pharmaceuticals --- Various pharmaceutical products such as ointments, skin lotions, creams, microencapsulation of drugs for sustained drug-delivery, birth control foams, etc. are being formulated and developed using principles and techniques of surface science. Some of these have been discussed previously.

In summary, I would like to emphasize that from the research activities I have carried out in the past decade, I have become

convinced that the surface science is one of the most important facets of science. It is related to many natural processes and systems; it is one of the unique branches of science that finds so many diverse and wide-ranging applications in engineering, biology and medicine.

It is only during the past few years that we have seen rapid advances in understanding the complexities and unique properties of surfaces. I believe we are still at the shores of surface science, and we have a whole ocean to explore! Over the years I have also become convinced in my belief that "research is an art. Just as an artist enjoys painting a picture, or a poet enjoys writing a poem, a scientist does research for his own enjoyment, regardless of its appreciation by others, although it is nicer when it is also appreciated and enjoyed by others." As I began this article with a quotation, I would also like to end it with a quotation from a poem by Tagore, which very appropriately says, "My friend, drink my wine in my own cup to appreciate its sparkling bubbles."

ACKNOWLEDGEMENTS

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