Structure and Properties of Surfactants
Theoretical Background

By G. M. GANTZ
Antara Chemicals Division
General Aniline & Film Corporation*

INTRODUCTION

Soap is the oldest surfactant, perhaps 2,000 years old, and until very recently dominated the field. Synthetic detergents or surfactants are more than 100 years old but they were insignificant until a shortage of soap in Germany during World War I sparked their development.

After the war, a tremendous number of synthetic detergents were made and patented, particularly in Germany. The greatest application for these new products occurred in the textile industry. By the end of World War II it is estimated that production and consumption of synthetic detergents in this country was 90-100 million pounds per year. This was still small compared to an annual soap production of three billion pounds.

Starting in 1945 a very marked growth occurred in synthetics and by 1947 soap sales began to decline. This is shown in *Figure* 1. Built detergents based on synthetic surfactants continued to displace soap powders until synthetics surpassed soap in 1953. Most evidence points to a continuation of this trend.

As might be expected, the marked growth of synthetic surfactants since the war prompted more and more research and development by the chemical industry. An increasing number of new surfactants is being patented and very large numbers of tradename products are offered for sale.[1, 2, 3] It is becoming much more difficult, therefore, to classify and discuss surfactants.

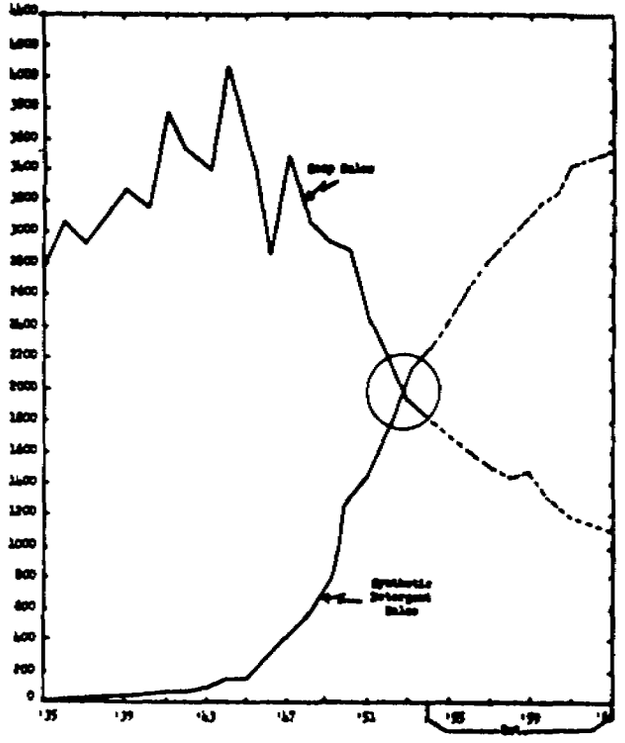
GENERAL NATURE OF SURFACTANTS

The theory of surfactants has been studied and developed as an important part of the field of surface chemistry. The contributions of Adam, Alexander, Harkins, and McBain plus many other eminent colloid chemists, have led to a much better understanding of the physico-chemical properties of surfactants.

Concurrently with the scientific studies of surfactants by chemists, physicists, and biologists, a vast technology has developed related to the application of surfactants in many different industries. This work includes studies of the effect of surfactant structure on wetting, detergency, emulsification, dispersion of pigments, and foaming. Unfortunately, a large gap exists between our scientific knowledge and our practical knowledge. When one is confronted with a practical problem involving surfactants, it is quite often necessary to try a great many of the products available. Correlation of molecular structure with surface activity and performance in specific applications is a fruitful field and one may expect more work of this type.

A surfactant may be defined as a material which will greatly reduce the surface energy of a solvent at a very low concentration. A good wetting agent, for example, will reduce the surface tension of water from 72 to 30 dynes/cm, at a concentration of less than 0.01%. In general, surfactants can be defined also as molecules containing a hydrophobic group and a hydrophilic group. *Figure* 2 illustrates this hydrophobic-hydrophilic balance in sodium laurate, a soap molecule.

If the molecule of sodium laurate were severed between the 11th and 12th carbon atom, one would obtain n-undecane and sodium formate. As



Source: 1953-54—Association of American Soap Producers; 1955-62—J. Ralph Macon, The Atlantic Refining Co.
Reference: *Chemical Week*, Oct. 22, 1960, p. 46.

Figure 1—Soaps vs. synthetic detergents. The balance tipped in 1953

* 435 Hudson St., New York 14, N. Y.
The registered trade-names used in this paper include: "Ethomid"—Armour & Co.; "Span" and "Tween"—Atlas Powder Co.; "Tergitol"—Carbide & Carbon Chemicals Co.; "Gardinols" and "Duponols"—E. I. du Pont de Nemours & Co.; "Igepal CO" and "Igepon"—General Aniline & Film Corp.; "Miranol"—Miranol Chemical Co.; "Ninol"—Ninol Laboratories; "Orvus"—Procter & Gamble Co.; "Triton"—Rohm & Haas Co.; and "Pluronic"—Wyandotte Chemicals Corp.

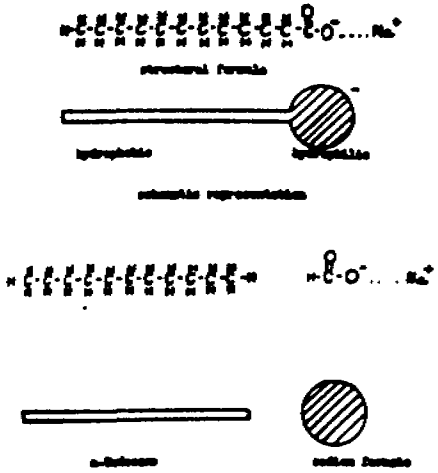


Figure 2—Hydrophobic-hydrophilic balance of sodium laurate

a straight chain hydrocarbon, n-undecane might be found in kerosene or mineral oil. It would be insoluble in water and highly polar solvents but quite soluble in oils. Sodium formate on the other hand is quite soluble in water but oil insoluble. Neither fragment of this soap molecule would have any surface active properties. The unique character of surfactants depends upon the presence of both an oil soluble and a water soluble group within the molecule.

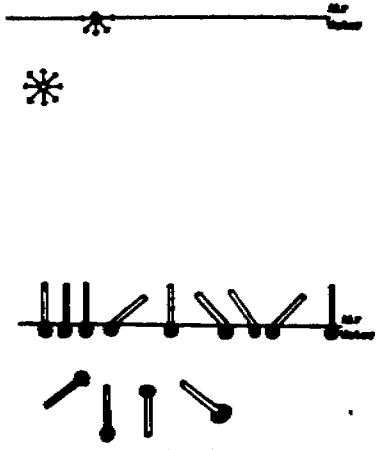


Figure 3—Molecular forces in a liquid and orientation of soap molecules

Consider the forces acting upon a single molecule in a solvent such as water (a) when the molecule is in the body of the liquid and (b) when the molecule is at liquid-air interface (*Figure* 5). In the body of the liquid, cohesive forces will uniformly attract the molecule on all sides. For a molecule at the surface, however, there will be an attractive force down into the liquid so that the surface acts as if it were under compression.

If a few molecules of soap are added to the liquid, they will tend to collect at the surface. Water molecules have little or no attraction for the hydrocarbon tail of the soap molecule and they get squeezed out and line up at the surface as shown in *Figure* 5. As more and more soap molecules collect at the surface, the surface tension is reduced until the surface is completely covered with soap molecules.

The quantitative relationship between the degree of adsorption at the surface and the lowering of surface tension was developed by J. Willard Gibbs by thermodynamic methods. For dilute solutions the Gibbs equation can be given as follows:

$$e = -\frac{C}{RT}\frac{d_\sigma}{dC}$$

where e is the excess concentration in the surface layer, σ is the concentration in solution. R is the gas constant, T is absolute temperature and $\frac{d_\sigma}{dC}$ is the rate of change of surface tension with concentration.

A typical curve of surface tension versus concentration for a surfactant is shown in *Figure* 4. The concentration at which no further reduction of surface tension occurs is known as the "critical" micelle concentra-

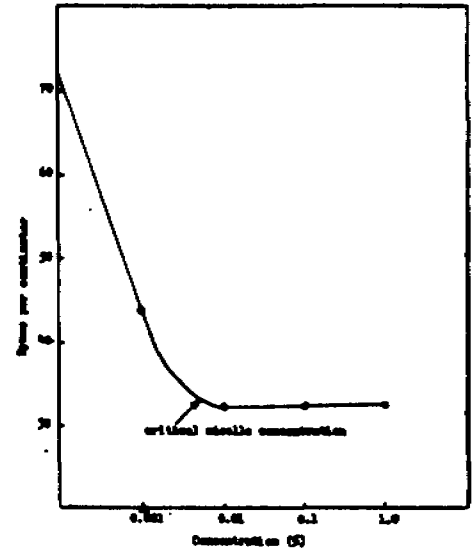


Figure 4—Surface tension of Igepal CO-630 in water at 25°C.

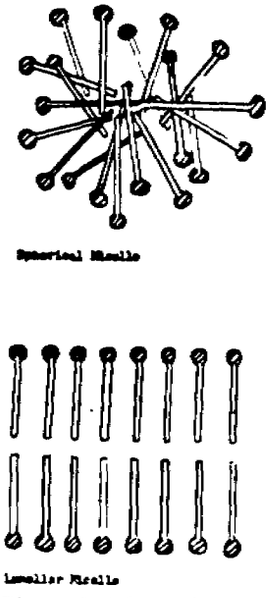


Figure 5—Schematic representation of surfactant micelles

tion. When no additional concentration of surfactant at the surface takes place, it must remain in solution. However, surfactant molecules do not diffuse separately throughout the liquid but clump together in micelles.

Surfactant micelles are shown schematically in *Figure* 5. They may be spherical, lamellar, or even rod shaped. Although the theory of micelle structure is still being developed, their existence is no longer questioned. Measurements of conductivity, osmotic pressure, as well as both X-ray and optical studies confirm the presence of surfactant micelles. These micelles are believed to be important in detergency, emulsification, and solubilization.

CLASSIFICATION OF SURFACTANTS

The majority of surfactants can be classified into four main groups: anionic, cationic, nonionic, and amphoteric. A schematic representation of these types is shown in *Figure* 6. Anionic molecules are so called because they bear a negative charge and migrate toward the anode or positive pole in solution. Cationic molecules migrate toward the cathode and therefore contain a positive charge.

Nonionic surfactants do not contain an ionizable group and have no electrical charge. The hydrophilic end of this type of surfactant is usually made up of several hydroxyl groups or ether linkages. As indicated in *Figure* 6, the hydrophilic part of a nonionic molecule is usually

larger than that of anionics or cationics and may even be much larger than the hydrophobic part of the molecule.

Amphoteric surfactants contain both a positive charge and a negative charge. These changes may neutralize each other so that at a given pH, the surfactant behaves as if it were nonionic. These surfactants usually exhibit cationic properties in acid solutions and anionic properties in alkaline solutions. Although amphoteric surfactants have been known for a long time they have become commercially important only recently.

Many classification systems have been devised to cover surfactants. Perhaps the most comprehensive system is that devised by Schwartz and Perry in their book on surfactants.[4] The classification shown in *Table* 1 is by no means comprehensive but an effort has been made to include structures which are commercially important.

1 — Anionic Surfactants

It will be noted in *Table* 1 that anionic surfactants include just three hydrophilic groups: carboxyl, sulfate ester, and sulfonic. Although anionic surfactants containing a variety of other solubilizing groups have been made and patented, none are believed to be of commercial importance except the phosphate esters. The phosphate esters are expected to become more important in the future. In addition to good emulsifying properties, they are particularly useful as antistatic agents for textiles and plastics.

A. Carboxylic Acids: The fatty acid soaps will not be considered in any detail. They are made by saponification of natural fats and oils and the most useful products contain between 12 and 18 carbon atoms. A major drawback of the fatty acid soaps, of course, is their sensitivity to hard water. Rosin soaps and tall oil soaps are also sensitive to hard water

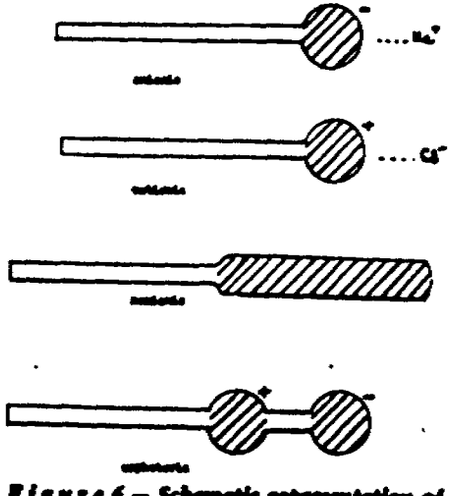


Figure 6* — *Schematic representation of surfactant types

Table 1—Classification of Surfactants

I—Anionics
- A. Carboxylic Acids
  - 1. Soaps; fatty acid, rosin, naphthenic
  - 2. Misc
- B. Sulfuric Acid Esters
  - 1. Alkyl sulfates, alcohols and olefins
  - 2. Sulfated oils and esters
  - 3. Sulfated amides and ethers
  - 4. Misc
- C. Sulfonic Acids
  - 1. Alkyl sulfonates
  - 2. Alkyl aryl sulfonates
  - 3. Sulfonated amides and esters
  - 4. Misc.
- D. Misc. Hydrophilic Groups, Phosphates, Sulfamates

II—Cationic
- A. Simple Amine salts
- B. Quaternary Ammonium Salts
- C. Amino Amides and Imidazolines
- D. Misc.

III—Amphoteric
- A. Amino and Carboxyl Groups
- B. Amino and Sulfuric Ester or Sulfonic Groups
- C. Misc

IV—Nonionics
- A. Alkyl, Alkylaryl Ethers and Thioethers
- B. Esters and Amides
- C. Misc

but they are quite cheap and are used in many industrial operations where color and odor are not important. Naphthenic acids are used primarily as their heavy metal salts. The copper salt is a fungicide while the lead, cobalt, zinc, and manganese salts are used as driers in paints and varnishes.

B. Sulfuric Acid Esters (Figure 7). Sulfated fatty alcohols were among the first synthetic surfactants to become commercially important. These products, known by such tradenames as "Gardinols," "Duponols," and "Orvus," are used primarily as detergents in the textile industry, as fine fabric detergents or in shampoos. Fatty alcohols required for sulfating are usually obtained by catalytic hydrogenation or reduction with sodium of the corresponding fatty acids.

Secondary alcohol sulfates can be made by sulfating olefins obtained from petroleum. The secondary alcohol sulfates marketed under the tradename "Tergitol" are believed to be made, however, by aldol condensation, dehydration, and reduction. Some of the products of this type are particularly good as wetting agents in strong acid, alkali, or salt solutions. In general, sulfate esters are not stable in acid solutions.

Oxo process alcohols produced by the Fischer-Tropsch oxidation of paraffins are growing in commercial importance. These primary alcohols, particularly the tridecyl product, can be sulfated to give surfactants.

Sulfated oils, usually referred to as sulfonated oils, are the oldest synthetic surfactants. As early as 1834 it was discovered that treatment of olive oil with sulfuric acid then neutralizing with potassium hydroxide produced an oily, water dispersible product very u[illegible]yeing calico reds. These sulfated triglycerides from various oils became known as Turkey Red oils. Products of this type are still used in the textile industry as dyeing assistants, particularly sulfated castor oil.

Sulfated oils and fats such as tallow are used in the textile industry for finishing yarns and fabrics. They provide surface lubrication and softness.

Many valuable surfactants are produced by sulfating esters such as the methyl, propyl, butyl or amyl oleates or ricinoleates. These products foam more, and are better wetting and rewetting agents than the sulfated triglycerides. Sulfation of the hydroxyl group in a mono or diglyceride or a glycol monoester produces surfactants useful in household detergents, shampoos, and cosmetics. In general, sulfation of any polyhydric alcohol partially esterified with a fatty acid will yield a surfactant.

A variety of surfactants can be made by reacting fatty acids with ethanolamines and sulfating the resulting alkylolamides. These products are easily manufactured and have been offered by a number of companies for various textile and industrial uses.

Sulfated ethers represent a fairly recent development in the field of surfactants. Sulfation of the terminal OH group of an alkyl phenol or a fatty alcohol ethylene oxide condensate yields surfactants with good wetting, foaming, and detergent properties. These products are used extensively in the formulation of liquid household dishwashing compounds.

C. Sulfonic Acids. Petroleum sulfonates obtained from the manu-

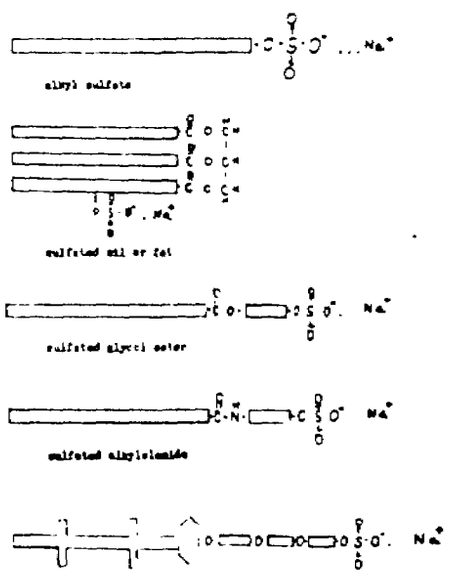


Figure 7—Sulfate ester surfactants

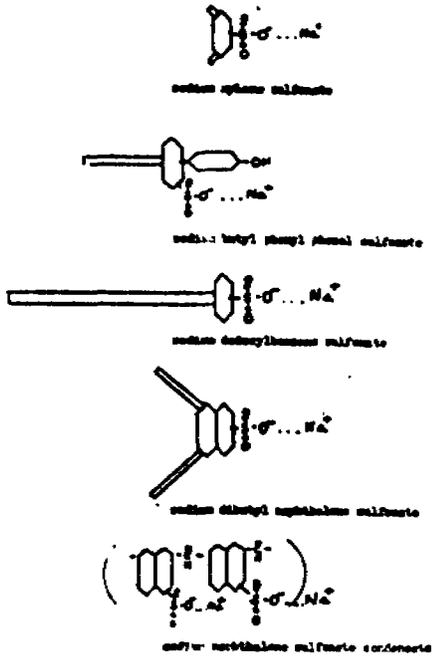


Figure 8—Alkyl aryl surfactants

facture of white oils are complex mixtures of alkyl sulfonates. These are produced in large tonnages and are used to make soluble cutting oils, textile spinning lubricants, and detergents for motor oils. Alkyl sulfonates can be made also from refined petroleum oils by the Reed-Horn process involving sulfur dioxide and chlorine. Many products of this type were made in Germany during World War II,[5] and du Pont has pioneered their development in this country. Properties of the alkyl sulfonates are similar to the alkyl aryl sulfonates.

The alkyl aryl sulfonates have attained the largest tonnage among surfactants as a result of their use in packaged household detergents. Alkyl benzene types are most important and vary from xylene sulfonates to trialkyl benzene types (*Figure* 8). These products are used in a great many applications because they are very low in cost, versatile, and chemically stable. The dodecyl benzene or keryl benzene sulfonate is the most effective type for detergency. Larger alkyl chains reduce solubility while smaller alkyl chains reduce detergency but increase wetting action.

Alkyl naphthalene sulfonates such as the dibutyl or diisopropyl products represent another important type in this class of surfactants. They are used in a variety of applications for wetting, detergency, emulsification, and dispersing action.

An interesting class of surfactants is made by condensing naphthalene sulfonates or alkyl naphthalene sulfonates with formaldehyde. These low

molecular weight polymers are extremely useful as dispersing agents. They are used in the manufacture of water dispersible dyestuffs as well as in paints, plastics, and rubber manufacture.

One of the most versatile surfactants is made by condensing fatty acids with n-methyl taurine to give a sulfonated amide.[6] These products, developed and sold by GAF under the tradename "Igepon" have been used extensively in the textile industry for many years and are perhaps more like soap than any other surfactant, yet they have none of the disadvantages of soap. The related esters made from fatty acids and hydroxyethanesulfonic acid developed and sold by GAF under the trademark "Igepon A" (*Figure* 9) are less stable in hot acid or hot alkali solutions. In recent years these sulfonated amides and esters have found many non-textile applications.

Another important class of anionics is the sulfosuccinic esters developed and sold by American Cyanamid Co. under the tradename "Aerosol" and "Deceresol." These products are made by esterifying maleic anhydride with an alcohol and treating the diester with sodium bisulfite. The sulfosuccinic esters are particularly efficient wetting agents, as Caryl has shown.[7]

II — Cationic Surfactants

Cationic surfactants are used for quite different purposes than the anionics. Perhaps their most unique property is affinity for various surfaces. In textiles they react with many direct dyes (anionic) to improve water resistance, they are powerful softening agents presumably because they orient strongly on individual fiber surfaces. Other important textile uses for cationics are as water repellents, moth proofers, bactericides, and antistatic agents. The major industrial uses are as germicides or sanitizers, corrosion inhibitors, and emulsifiers. Typical structures of cationic agents are shown schematically in *Figure* 10.

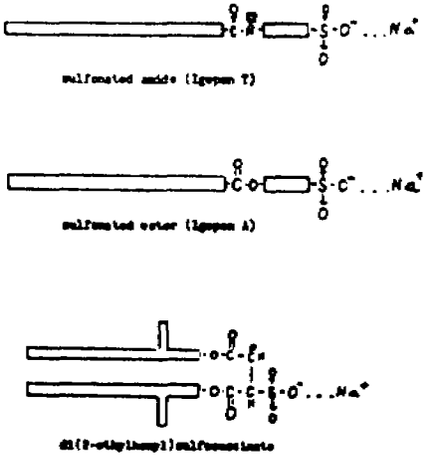


Figure 9—Sulfonated amides and esters

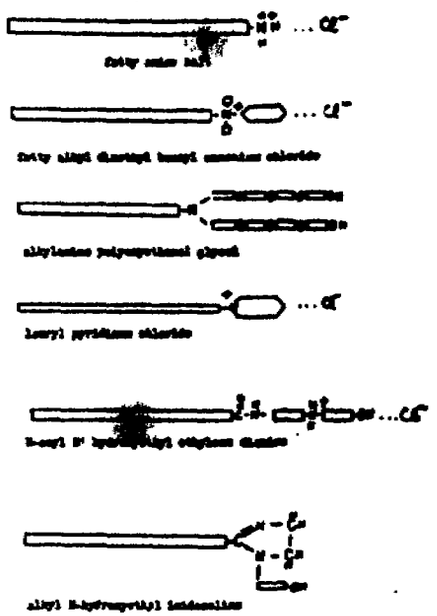


Figure 10—Cationic surfactants

A. Simple Amine Salts: Straight chain fatty amines with 8 to 18 carbon atoms are rather insoluble in water but their hydrochloride or acetate salts have wetting, foaming and detergent properties. Actually these amines are not often used as such but serve as starting materials for preparing more effective surfactants. Reaction of fatty amines with ethylene oxide yields products which are used as emulsifiers and detergents.

B. Quaternary Ammonium Salts: Alkylation of fatty amines with methyl chloride, dimethyl sulfate, benzyl chloride, etc. gives quaternary ammonium salts. These are much more soluble than the amine salts and retain their cationic nature in alkaline solutions. Products of this type are most widely used as germicides. However, a variety of products for special applications fall in this classification. Lauryl pyridium chloride is a spin bath additive in viscose rayon manufacture. Methylolstearamide pyridium chloride is used as a water repellent. Quaternized amine-ethylene oxide types are used as dye stripping agents.

C. Amino Amides and Imidazolines: The majority of textile softeners are made by reacting fatty acids with various polyamines. These amino amides may then be alkylated to eliminate any primary amine group or fully alkylated to the quaternary. It is obvious that a variety of complex products can be made and a very large number of proprietary cationic softeners are offered to the textile trade.

By modifying reaction conditions, fatty acids and polyamines will

condense to form substituted imidazolines. In general, the imidazolines discolor more on aging or at high temperatures than the corresponding amino amides and have not been used as widely as textile finishes. Quaternized imidazolines also have this disadvantage. Alkyl oxazolines are prepared by condensing fatty acids with amines like 2-methyl-2-amino-1,3 propanediol. Products of this type are marketed by Commercial Solvents Corp. under the tradename "Alkaterge."

III — Amphoteric Surfactants

As noted earlier, amphoteric surfactants, also called ampholytes or ampholytic surfactants, contain both a positively charged and a negatively charged group (*Figure 11*). The cationic group is usually an amine salt or a quaternary nitrogen. The anionic group is usually a carboxyl, a sulfate ester, or a sulfonic acid. This classification excludes such products as the fatty amine ethylene oxide condensates which may be cationic or nonionic and the alkylolamides which may be anionic or nonionic. The former are considered cationic while the latter are classed as nonionic.

A. Amino and Carboxyl: Reaction of an alkyl amine with chloroacetic acid produces an alkyl glycine with typical amphoteric properties.

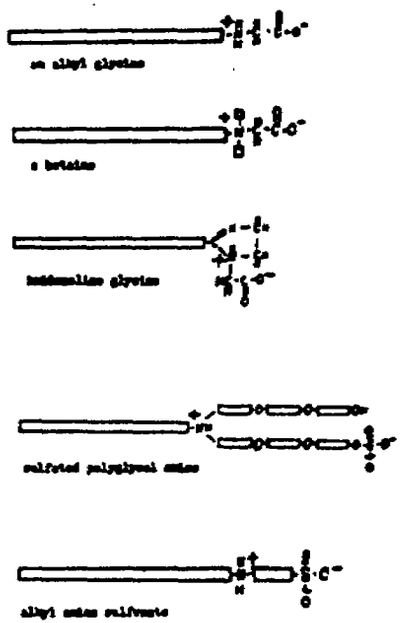


Figure 11—Amphoteric surfactants

...er reaction will produce a betaine which contains the quater... nitrogen group. As might be expected the betaines are more cationic in nature than the simple glycines. A variety of other methods may be used to make both betaines and alkyl glycines from fatty amines.

Reaction of a fatty acid with a polyamine gives an amino amide which can be reacted with monochloroacetic acid to produce an amphoteric product. Likewise the amino amide may first be converted to an imidazoline and then used to make an ampholyte. A number of products marketed under the "Miranol" tradename are claimed to be of this type.[9] The amino amides or imidazolines may be alkylated before or after reaction with monochloroacetic acid to give betaines. Neu[8] has indicated that many useful ampholytes have a structure which may be N-alkyl poly (aminoethyl) glycines.

B. Amino and Sulfuric Ester or Sulfonic Groups: Surfactants containing an amino group plus a double bond may be sulfated readily to give an ampholyte. Similarly amino compounds containing hydroxyl groups may be sulfated. The alkyl amine-ethylene oxide condensates contain two terminal OH groups so that one or both might be sulfated. Amino-amides made with hydroxyethyl ethylene diamine or the corresponding imidazolines can be sulfated at the hydroxyl group.

Amphoteric surfactants containing an amino group and a sulfonic acid group can be made by using a halogenated alkyl sulfonic acid in place of monochloroacetic acid. Although many other types of amphoterics containing a sulfonic group appear in the patent literature, it is not believed that any have become commercially important.

Probably the outstanding feature of the amphoteric surfactants is the fact that they behave like cationics without the disadvantage of being incompatible with anionic materials. They are substantive to protein and cellulosic fibers and exhibit softening and lubricating properties. They also have a bactericidal action. Amphoteric surfactants may never become as important as the anionics or nonionics but they should find many applications where cationics would be useful and cannot be used because of incompatibility.

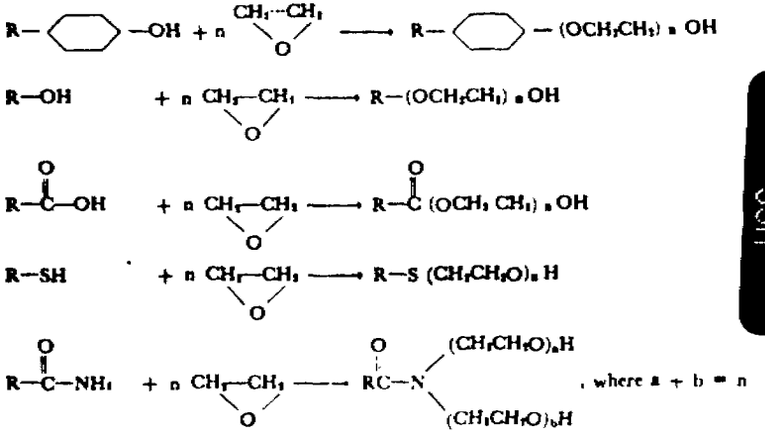
IV — Nonionic Surfactants

The hydrophilic group in anionics and cationics bears an electrical charge and it is usually small relative to the hydrophobic group. The electrical charge must have a marked solubilizing action because the hydrophilic group in nonionics must be quite large if the surfactant is to be water soluble.

An important method of making nonionics involves reaction of ethylene oxide with a hydrophobe group containing an active hydrogen. After one mole of ethylene oxide has reacted with the active hydrogens, further reaction takes place until any desired mole ratio is obtained. This is illustrated in *Table* 2.[10]

A. Alkyl, Alkylaryl Ethers and Thioethers: Nonionics made from alkyl phenols were first produced in this country before the war. Their output has continued to rise and their price has continued to drop. Since they are manufactured from phenol, nonene (or diisobutylene) and eth-

Table 2—Preparation of Nonionic Surfactants from Ethylene Oxide



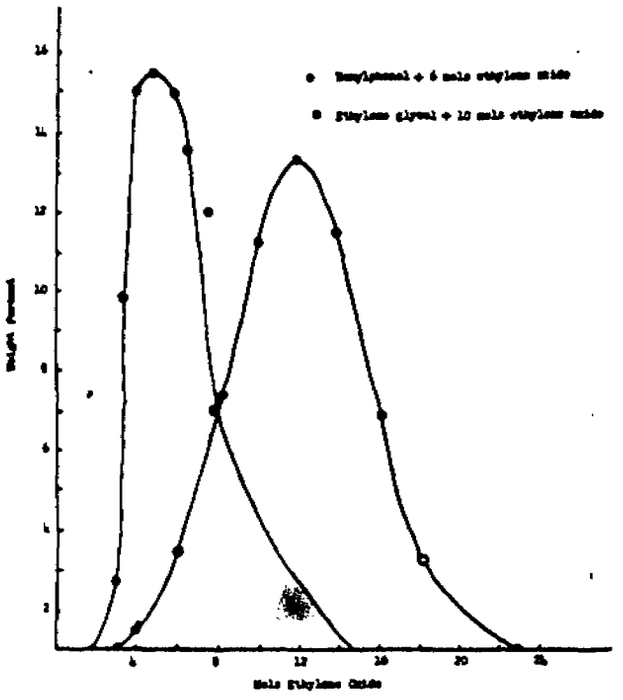
ylene oxide, they may be considered as petroleum base surfactants. It is interesting to note that at the present time sales of nonionics are increasing faster on a percentage basis than the alkylarylsulfonates.

A variety of products can be made by adding various amounts of ethylene oxide to an alkyl phenol. There are eight nonylphenol products of this type available under the "Igepal CO" trademark varying from a water insoluble 4 mole product to a highly water soluble 30 mole product. A similar series of octylphenol nonionics is available under the "Triton" trademark. As the hydrophobic-hydrophilic balance is shifted the surface activity changes. In the nonylphenol series, the most versatile surfactant is obtained with a mole ratio of 8-10.

Surfactants prepared from ethylene oxide are not single compounds but mixtures of compounds with different mole ratios of ethylene oxide. Mayhew and Hyatt[11] showed that the composition of a nonylphenol nonionic follows the Poisson distribution formula (*Figure* 12). Thus the mole ratio for an ethylene oxide nonionic refers to an average value.

Fatty alcohols may be used to prepare nonionics and many products of this type have found specific applications such as stabilization of rubber latices. The Oxo process alcohols may be used to prepare nonionic surfactants with good wetting action and detergency. Alkyl mercaptans such as dodecyl mercaptan react with ethylene oxide to give good surfactants.

A new type of nonionic has been developed recently by adding ethylene oxide to polypropylene glycol.[12] A polypropylene glycol having a molecular weight of 900 or more is water insoluble and can serve as the hydrophobic base for producing high molecular weight nonionics. Products of this type, marketed under the "Pluronic" tradename, can be produced in a solid form.



Reference: R. L. Mayhew and R. C. Hyatt, General Aniline and Film Corp., *Journal of the American Chemical Society*, Sept. 1952, no. 9, p. 957-962.

Figure 12—Mole ratio distribution of ethylene oxide in polyoxyethylated surfactants

B. Esters and Amides: Ethylene oxide reacts with fatty acids (or fats and oils) to yield nonionic surfactants. These esters, however, in contrast to the ethers, are not stable in strongly alkaline solutions. Nonionic ester surfactants may also be made by esterifying a fatty acid with a polyethylene glycol. These glycol esters can be made in rather simple equipment and a great many manufacturers offer nonionics of this type. The predominant use for the fatty ester nonionics is in emulsification and textile yarn lubrication.

The tall oil ethylene oxide condensates should be noted because they are produced in large quantities. A built tall oil nonionic is used in one of the popular low foaming household detergents. Tall oil products are cheaper than the alkyl phenol products but they are less efficient in most applications.

Fatty acids may be reacted with polyhydric alcohols such as glycerol, sorbitol, pentaerythritol, and glucose. These esters are sparingly soluble in water but are used extensively as oil soluble emulsifiers. The polyhydric alcohol partial esters may be reacted with ethylene oxide to give water soluble nonionics. Combinations of the partial esters and ethoxylated esters such as those available under the trademarks "Span" and "Tween," can be used for a variety of emulsion problems.

The reaction of ethylene oxide with fatty amines to yield cationic surfactants has been mentioned. Ethylene oxide also reacts with fatty amides to yield nonionic surfactants. Such products available under the trademark "Ethomid" are used primarily for emulsification and dispersing action.

A class of compounds variously known as amine condensates, alkanolamides, or Kritchevsky compounds and available under the trademark "Ninol" are produced by reacting one mole of a fatty acid with 2 mols of diethanolamine. The structure of these compounds has not been established definitely but they are usually considered as nonionic. A variety of products can be made by using various fatty acids and various hydroxy amines. These nonionics are used extensively in detergent formulations as foam stabilizers as well as in many textile and cosmetic applications.

STRUCTURE AND SURFACE ACTIVITY

Although a vast amount of work has been done on correlating chemical structure with surface activity, there is a lack of general test methods which permit prediction of performance in specific applications. The lowering of surface tension by surfactants does not always correlate with wetting action. Lowering of interfacial tension does not always correlate with emulsification. Dispersing action for one pigment does not correlate with dispersing action for other pigments. In spite of these difficulties it is well to review the results that have been obtained and draw some broad generalizations.

A. Solubility: Like other organic compounds, surfactants of higher molecular weight are less soluble than those of lower molecular weight. Solubility increases with temperature and any given surfactant will usually show a maximum efficiency at a certain temperature. Selection of a surfactant for use at a given temperature should be based on tests made at the same temperature. Nonionic surfactants exhibit a phenomenon known as a cloud point. As the temperature of a nonionic solution is raised, a point is reached where the solution becomes cloudy. This cloud point increases with ethylene oxide content (*Figure* 13).

B. Surface Tension Lowering or Wetting: Probably the most extensively studied feature of surfactants is their ability to lower the surface tension of water. A variety of methods have been devised to measure this property and the du Noüy ring method is most widely used. Many articles can be found in the literature relating chemical structure of surfactants to their ability to lower the surface tension of water. Surfactant manufacturers often furnish such data in their technical bulletins.

The Draves-Clarkson test[13] has been used extensively to indicate the wetting power of surfactant solutions. This test measures the time required for a cotton skein to wet out and sink in a dilute surfactant solution. Although Gruntfest, Hager, and Walker[14] have pointed out some shortcomings of the Draves test, it usually correlates quite well with surface tension and contact angle measurements.

The excellent work by Caryl[1] on the wetting power of sulfosuccinic

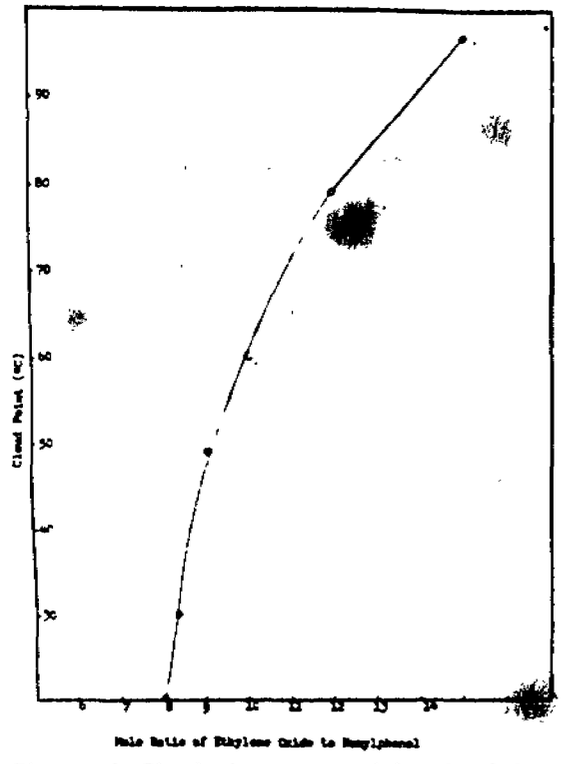


Figure 13—Cloudpoints of nonylphenol ethylene oxide products

acid esters may be cited to illustrate the conclusion that maximum wetting occurs for molecules with a branched chain structure. Thus the 2-ethyl hexyl diester gives a 25 second wetting time at only 0.20 grams/liter while the normal octyl diester requires 0.52 grams/liter.

C. Dispersion: The fact that well dispersed solid particles remain suspended in a liquid is of great importance in paints, varnishes and printing inks. It is first necessary to wet out the solid particles in the liquid medium and then to coat the surface of each particle so that agglomeration does not occur. It is rather difficult to differentiate between surfactants and protective colloids as to the part they play in preventing agglomeration.

Protective colloids may contain ionizing groups, for example carboxymethyl cellulose, or they may be nonionic such as methyl cellulose. One can visualize that protective colloids function by coating finely divided solid particles with a film. This film effectively reduces attractive forces between the solid particles and they remain dispersed.

Anionic or cationic surfactants may be adsorbed on solid particles and provide them with charged surfaces. Repulsion between like charged particles prevents agglomeration. In the case of sulfonic acid surfactants, dispersing action in aqueous systems increases from alkyl to alkyl benzene to alkyl naphthalene and is greatest for the naphthalene sulfonate condensates. From this and other evidence, it may be concluded that increased aromaticity of the surfactant structure increases the adsorption on solid surfaces.

Nonionic surfactants are quite effective dispersants also, particularly the alkyl phenol ethylene oxide condensates. In this case the hydrophobic groups are adsorbed on the solid surfaces and the polyglycol chains form a film around the particles more or less like protective colloids.

Although these simple concepts are useful for explaining the role of surfactants as dispersing agents, the actual mechanism is believed to be quite complex.

D. Emulsification: Many of the concepts about surfactants as dispersing agents apply equally well to their use as emulsifiers. Hydrophobic groups dissolve in the surface of oil droplets with hydrophilic groups oriented outward into the water phase (conversely for water-in-oil emulsions). The most important concept in emulsions is that of an interfacial film between the water phase and oil phase. A strong film prevents coalescence of the dispersed droplets. Charged droplets, like charged solid particles, are stabilized by virtue of repulsion between charged bodies of the same sign.

Nonionic surfactants as a class are quite often superior to anionics or cationics for emulsification. Their ability to form tough interfacial films must be more important than the electrical repulsion factor provided by ionic surfactants. Perhaps the most important structure factor in emulsification is hydrophobic-hydrophilic balance. The ease with which this balance can be altered in nonionics is one reason for their extensive use as emulsifiers.

The technique of making an oil emulsion with triethanolamine oleate by dissolving the oleic acid in oil and the triethanolamine in water can be used with synthetic surfactants. A combination of an oil soluble nonionic and a water soluble nonionic, such as the sorbitol esters and ethylene oxide adducts mentioned earlier, often surpasses a single surfactant. Anionic-nonionic combinations are very effective in many applications. Protective colloids are used for stabilizing emulsion systems.

E. Foam and Detergency: The ability of surfactants to foam has important uses such as ore flotation and firefighting and is quite important in detergent formulation. Although foaming has been studied scientifically as well as in practical applications, no completely satisfactory explanation of foaming has been developed and little or no correlation with surfactant structure is possible.

Detergency is one of the most important properties of surfactants from a practical standpoint and it is an extremely complex subject. Certainly wetting, dispersing action, and emulsification are all involved in detergency. It is not difficult to measure the relative scouring power of a homologous series of surfactants for soiled cotton and wool (*Figure 14*), but it is generally recognized that laboratory testing methods do not show

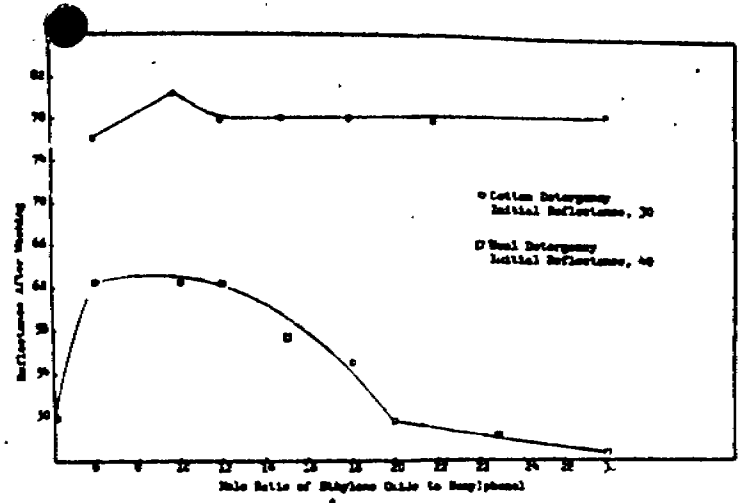


Figure 14—Cotton and wool detergency of nonylphenol ethylene oxide products (0.2% detergent)

which surfactants or formulations are best for all around performance as household detergents.[18]

IDENTIFICATION OF SURFACTANTS

Accurate identification of surfactants is extremely difficult and requires a variety of analytical tools. It is often possible, however, to obtain a general idea about surfactant structures from simple laboratory tests. As a first step, the manufacturer's technical literature should be studied. The practice of revealing exact structures is growing, at least among the larger manufacturers. Specifications on individual surfactants can be obtained from the manufacturer in many cases and they may furnish analytical procedures upon request.

A clue to the type of structure is often given by a product's price or its recommended uses. Products recommended as germicides or corrosion inhibitors are usually cationic. A detergent would be anionic or nonionic. An edible product would be nonionic. A powerful wetting agent is probably anionic whereas a substantive textile softener would be cationic.

Several compilations are available which list surfactants by tradename.[1-4] For example, McCutcheon lists over 1600 products by tradename and in most cases gives the ionic type, activity, and type of structure. It is interesting to note that about half this group are anionic, one third are nonionic, 11% are cationic and less than 1% are amphoteric.

Preliminary examination of an unknown surfactant would include physical form, color, odor, ash, density, per cent volatile by oven drying, water content by xylene, and solubility in water and common solvents. Portions of a 1% aqueous solution of the unknown should be tested by adding an equal amount of a 1% anionic and also a cationic surfactant.

Precipitation immediately or after 24 hours, will indicate the ionic nature of the surfactant whereas no precipitation suggests a nonionic. The following generalities may be used as a guide:

(1) Nonionics are usually oily liquids or low melting waxy solids and would show only a trace of ash. A 1% aqueous solution of a nonionic may exhibit a cloud point at some definite temperature upon heating. If a nonionic is suspected and shows no cloud point, repeat the test in a 5% sodium sulfate solution.

(2) Products in powder form are most apt to be anionic. Products giving very high foam are probably anionic. Anionics are frequently cut with sodium sulfate and will not be soluble in alcohol, xylene, or carbon tetrachloride.

(3) Cationics are often sold as waxy pastes containing water or isopropanol or both. They are substantive to cellulose and will impart a soft, slippery feel to cotton cloth soaked in a dilute aqueous solution.

A qualitative test for nitrogen, sulfur, and chlorine by sodium fusion can be helpful. Most anionics are sulfates or sulfonates and would show positive for sulfur. Most cationics contain nitrogen but nonionics usually contain neither sulfur or nitrogen. Most cationics are chlorides but acetates, sulfates, phosphates, and bromides may be encountered.

Surfactants differ in stability to acid, alkali and salt solutions. Soaps are precipitated by calcium solutions and separate as an oily layer upon acidification. Sulfate esters are usually hydrolyzed by acid solutions but are stable to alkali. Carboxylic esters are saponified in alkaline solutions. Nonionic ethers are stable in both acids and alkalis but are often insoluble in strong solutions of acids, alkalis or salts.

REFERENCES

(1) McCutcheon, J. W., *Soap & Chem. Specialties*, July-Oct., 1955.
(2) Technical Manual and Year Book, AATCC, Vol. XXXI, Howes Publishing Co., New York (1955).
(3) Sisley, J. P. and Wood, P. J., "Encyclopedia of Surface-Active Agents," Chemical Publishing Co., New York (1952).
(4) Schwartz, A. M. and Perry, J. W., "Surface Active Agents," Interscience Publishers, Inc., New York (1942).
(5) Hoyt, P. B. 3868, Office of Technical Service, U. S. Department of Commerce, Washington, D. C.
(6) Kastens, M. L. and Ayo, J. J., *Ind. Eng. Chem., 42* 1626 (1950).
(7) Caryl, C. R., *Ind. Eng. Chem., 33*, 731 (1941).
(8) U. S. Patent No. 2,528,378.
(9) Neu, R., *Manufacturing Chemist*, January, 1954.
(10) Jelinek, C. F. and Mayhew, R. L., *Textile Res. Journal, 24*, 765 (1954).
(11) Mayhew, R. L. and Hyatt, R. C., *J. Am. Oil Chem. Soc., 29* 915 (1952).
(12) Vaughn, T. H., Jackson, D. R., Lundsted, L. G., *J. Am. Oil Chem. Soc., 29* 240 (1952).
(13) Draves, C. Z., and Clarkson, R. G., *Am. Dyestuff Reporter, 20*, 201 (1931) also *28*, 421 (1939).
(14) Gruntfest, I., Hager, O. B., and Walker, H. B., *Am. Dyestuff Reporter, 36*, 225 (1947).
(15) Lambert, J. M. and Sanders, H. L., *Ind. Eng. Chem., 42*, 1988 (1950).