

4.5 Discussion of Specific Classes of Surfactants

This section lists some of the chemical reaction and stability characteristics of the various chemical classes of surfactants and notes several commercial products in each class. Note the disclaimer at the front of this book. Since the first edition was published in 1988 the World-Wide Web has expanded to become a showcase for most surfactant firms' products. Now you may copy from the Web version of this book the chemical class of a surfactant and paste it into a search engine window to get a list of links to manufacturers, suppliers, research articles, and applications.

More detailed descriptions of the chemical classes can be found in Rosen [ref list], Osipow [ref list], and the Surfactant Science series (Schick and Fowkes [ref list]). McCutcheon [ref list] and Ash and Ash [ref list] provide extensive listings of surfactants and their uses.

4.5a Nomenclature and Structural Abbreviations

The names used in commerce tend to retain archaic names related to the raw material sources. I have tried to use IUPAC nomenclature, noting the archaic names in several tables in Appendix C. A number of molecular structures are included to illustrate the major classes of surfactant. The abbreviations used to represent chemical structures are given below:

- R- is a terminal hydrocarbon chain. Unless otherwise noted, it means a linear chain, $\text{H}(\text{CH}_2)_n-$. Where there are several R groups in a molecule, the convention is to distinguish one from another with prime marks (').
- Z- is an organic ester fragment $\text{R}(\text{CO})-$ or other group whose structure is given in the discussion of the surfactant class.
- Ph- is a doubly substituted benzene ring $-\text{C}_6\text{H}_4-$. Unless otherwise specified, substitution is para- (two groups on the 1,4 carbons, opposite each other).
- PEO- is a poly(ethoxy) chain, $-(\text{CH}_2\text{CH}_2\text{O})_x-$. Ethylene oxide molecules are often inserted at active hydrogen sites to increase the water solubility (or hydrophilic character) of a surfactant. Some texts use a name putting the oxygen first, polyoxyethylene (POE), and PEO chains are also called polyethylene glycols (PEG's) because the same structure can be obtained by a dehydrating condensation of ethylene glycol (1,2-ethanediol).
- PPO- is a poly(propoxy) chain, $-(\text{CH}_2[\text{CHCH}_3]\text{O})_x-$, which could also be called a 1-methylethoxy chain. These are often inserted at active hydrogen sites to increase the oil solubility (or lipophilic character) of a surfactant. They are sometimes called polyoxypropylene (POP) chains.
- M^+ is a positive ion. Na^+ , K^+ , and NH_4^+ are often used in water-soluble surfactants, and Mg^{++} , Ca^{++} , and Ba^{++} are often used in oil-soluble surfactants
- X^- is a negative ion, often Cl^- or Br^-

4.5b Aliphatic Molecular Structures

When Ziegler catalysis is used to form long chain alcohols, the addition of ethylene to the chains gives a Poisson distribution of $-\text{C}_2\text{H}_4-$ units.

Acids derived from natural fats and oils contain only even numbers of carbons in the chain, and the distribution of chain lengths varies not only with the plant or animal used as a raw material

source, but also with season in which the raw material was collected. Double bonds (unsaturation) in the acid make the surfactant subject to degradation through air oxidation. The non-IUPAC names and typical percents of the major acids whose esters are found in common natural fats and oils are given in a table in Appendix C.

Many fatty acid, sorbitol, and glycerol derivatives have been approved by the United States Food and Drug Administration for human consumption, so they can be used for dispersions that will be used in food, pharmaceutical, and cosmetic applications. Synthetic fatty acids with odd numbers of carbons in the main chain aren't used in food products because they are indigestible.

4.5c Ethoxylated and Propoxylated Surfactants

Ethylene oxide may be inserted at an active hydrogen site in an organic acid, amine, phenol, or alcohol surfactant. The normal reaction gives a Poisson distribution to the probability that a molecule will contain a certain number of ethylene oxide units, but reaction conditions may be adjusted to get a wider distribution, and distillation or selective adsorption of the product stream may be used to get a narrower distribution. Since the HLB value increases with the number of ethylene oxide units in the molecule, a commercial product mix may include molecules with a wide variety of HLB values.

A PEO "backbone" contains oxygen links that can be solvated by water, trapping the water in a solvation sphere. Since water forms even stronger solvation bonds with inorganic ions, the solubility of a surfactant containing a PEO chain will decrease if salt is added to the system. Since thermal jostling breaks the weak solvation bonds, surfactants with PEO chains are less soluble at high temperatures than at low temperatures. The temperature at which they become relatively insoluble and condense to a separate phase is known as the cloud point. This factor makes surfactants that contain PEO chains unsuitable for high temperature applications.

Since PEO chains are solvated, powders treated with surfactants containing PEO chains are hygroscopic. The dry powders readily adsorb moisture from the air and gain enough surface conductivity to dissipate a static charge. Elimination of the charge on a powder reduces dustiness, provides reliable flow, and leads to a high bulk density. This leads to a cleaner, more reliable packout operation, with smaller bags needed to ship 20 kg of powder.

A PPO backbone is lipophilic because the oxygen in the ether linkage is shielded from the liquid by the methyl side groups. If a PPO chain is inserted into a fatty acid, alcohol, and alkyl phenol, the resulting surfactant will have properties similar to the PEO-substituted surfactants, but will be oil-soluble rather than water-soluble. If a PPO chain is inserted into a surfactant which also has a PEO chain, the lipophilic PPO will offset the hydrophilic character of a PEO chain and increase the surface activity.

Examples of PEO- and PPO-substituted surfactants are listed under the chemical classes of the unsubstituted surfactant.

4.5d Fluorinated Surfactants

These involve perfluorinated (all H's on the backbone replaced by F's) or multiply fluorinated hydrocarbon segments. The hydrophilic group may be carboxylate, sulfonate, phosphate,

quaternary amine, betaine, or an ethoxylated adduct. Perfluorinated acids are stronger acids than fatty acids, so they retain surfactant properties better at low pH or in the presence of divalent cations. They are resistant to biodegradation and to decomposition in hot acid or base.

Fluorosurfactants have very low surface energies and reduce the surface tension of water to below 20 mN/m.

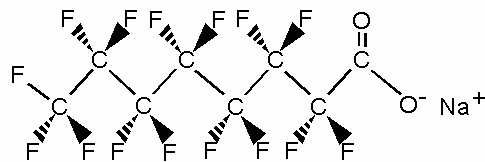
This is lower than any other surfactant. However, fluorocarbon chains are

incompatible with both water (and highly polar surfaces) and oil (and weakly polar surfaces), fluorosurfactants are

poor dispersants except for powders with low surface energies, such as

highly fluorinated or chlorinated solids. Low concentrations of fluorosurfactants are sometimes used to stabilize concentrated commercial dispersions of hydrocarbon surfactants.

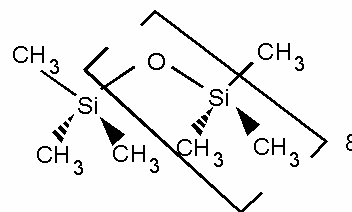
Examples: DuPont's Zonyl™ series, 3M's Fluorad™ series, Atochem's Foralkyl™ series



4.5e Siloxane Surfactants

Polydimethylsiloxanes have a backbone of silicon-oxygen bonds, $R-[Si(CH_3)_2O]_n-H$. Siloxanes combine low surface energies with better hydrophilicity than hydrocarbon or fluorocarbon chains.

Example: Dow Corning's series, Union Carbide's Silwet™ series



4.6 Nonionics

See Cross [ref list] for further discussion of synthesis and applications.

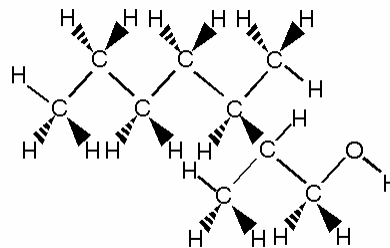
FATTY ALCOHOLS ROH

Primary alcohols have the -OH on a terminal carbon and are made by reduction of fatty acids or by Ziegler catalysis. Primary alcohols with C_{10} to C_{20} chains are good, biodegradable surfactants, but they are not convenient to use because they are solids at room temperature. Secondary alcohols have the -OH on a mid-chain carbon. Since they are liquids, they are easier to use than primary alcohols, but they are harder to make and thus cost more.

Example: Petrolite's Unilin™ series, Henkel's Lannette™ O

Inserting 6 to 12 ethylene oxide units in the alcohol makes a good low-foam detergent.

Example: Shell's Neodol™ 25-3, Alcolac's Siponic™ L series, DuPont's Merspol™ series



Recently, C_{30} to C_{50} alcohols have been ethoxylated. They are soluble in a wide variety of liquids and are better than the short-chain compounds for high temperatures applications.

Example: Petrolite's Unithox™ series, Sherex's Arosurf™ 42-E6

FATTY ACIDS R(CO)OH

These are rather reactive and easily degraded, so they are usually used in their ester (nonionic) or metal salt (anionic) forms. They may oxidize metal surfaces and can esterify metal oxide and hydroxide surfaces to convert them from high energy to low energy surfaces.

Example: Humko's Hystrene™ series

Polyethoxylated fatty acids, R(CO)O-PEO-H hydrolyze in either acid or base. They are not as good detergents as the polyethoxylated alcohols. The best ones are the C₁₂ to C₁₈ acids with 12 to 18 ethylene oxide units.

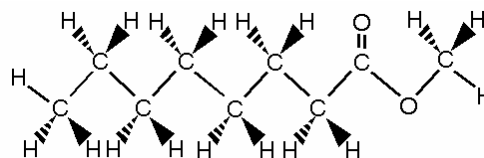
Example: Alkaril's Alkasurf™ CO series, Emery's 5340

FATTY ESTERS R(CO)OR'

Esters hydrolyze in either hot acid or hot base. Example: ICI's Atlas EM-17

Lanolin is the product of the sebaceous glands of sheep. It is a complex mixture of esters formed from over thirty fatty acids and over thirty long-chain fatty alcohols.

Example: Amerchol's series, ICI's Atlas G-1441



Polyethoxylated esters have increased water-solubility.

Example: GAF's Emulphor™ EL series

GLYCEROL ESTERS H(CHOZ)(CHOZ')(CHOZ'')H

A glycerol has three -OH groups on adjacent carbons. The kinetics of the organic acid-glycerol reaction are such that commercial glycerol esters are mixtures that contain mostly monoesters (monoglycerides) substituted at one end (Z is (CO)R, Z' is H, Z'' is H). Most of the diesters (diglycerides) in the mixture are substituted at the two end positions (1,3 or Z,Z'', so that Z' is H) rather than at the 1,2 positions (so that Z'' is H). Many glycerol esters are edible and also act as anti-foam agents.

Examples: Loders Croklaan's Dur-Em™ series and Santone™ series, Gillco's Myverol™ series, Witco's Witconol™ RHT

Menhaden oil and other fish oils are mixtures of triglycerides of unsaturated fatty acids up to C₂₂ with about 10 % lecithin(a phospholipid surfactant). They have a characteristic, strong, fishy smell.

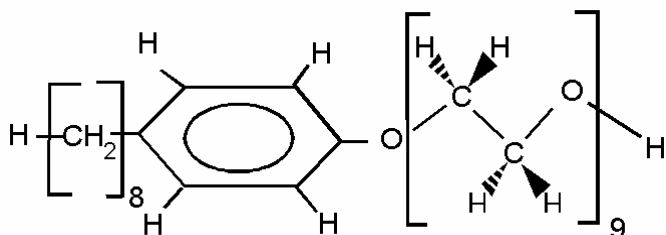
GLYCOL ESTERS R(CHOZ)(CHOZ')H

A glycol has two -OH groups on adjacent carbons. The first -OH reacts more readily than the second, so commercial glycol esters are mixtures containing about twice as much monoester (Z is (CO)R, Z' is H) as diester. Many of these are edible. Propylene glycol esters (R is CH₃) are more soluble in oil than the corresponding glycerol esters would be.

Example: Loders Croklaan's Dur-Pro™ series, Witco's Witconol™ RDC-D

ALKYL PHENOLS R-Ph-O-PEO-H

The non-ethoxylated forms are not sold as commercial surfactants. The C₈ and C₉ alkyl phenols carbon are oil-soluble dispersants if they contain 1 to 5 ethylene oxide units and water-soluble dispersants if they contain 9 or 10 ethylene oxide units. Since the alkane is usually synthetic and branched, these surfactants



are relatively resistant to biological degradation. The alkane is usually located para- (4-position) to the ethylene oxide (1-position) on the benzene ring, but can also be ortho- (2-position). There may be a considerable amount of dialkylated material present. The water-soluble members of this group are used to disperse carbon and other organics in aqueous systems, even at high ionic strength.

Example: Rohm & Haas's Triton™ X-100, Stepan's Merpol™ 100

ACETYLENIC GLYCOLS R[(COH)CH₃]C≡C[(COH)CH₃]R

These are unstable at low pH and have a low tendency to foam. Because they are highly volatile, they may be driven out of a slurry by heating. The parent compound is not very soluble in any liquid, but water solubility increases (and volatility decreases) when 4 to 9 units of ethylene oxide are added at each of the two -OH groups.

Example: Air Product's Surfynol™ 104 series is polyethoxylated and R is CH₃(CCH₃)CH₂

ALKANOLAMINES AND ALKANOLAMIDES

The most common alkanolamines used as surfactants are ethanolamine (HOCH₂CH₂NH₂), triethanolamine ([HOCH₂CH₂]₃N) and 2-amino-2-methylpropanol (CH₃[(CNH₂)CH₃]CH₂OH). They are stable in hot basic solutions.

Alkanolamides, HOCH₂CH₂(NR)(CO)R' are the condensation products of fatty acids and ethanolamine. They are more polar than the alkanolamines. The monoalkanolamides (R is H) are waxes, insoluble in water. The dialkanolamides (R is HOCH₂CH₂- often called superamides when fairly pure) are soluble in polar organic liquids and are used to stabilize foams. The superamides may be heated to decompose about a third of the dialkanolamide to the alkanolamine, the monoethanolamide, and some free acid. This mixture has low viscosity and is a good dispersant. All the alkanolamides are stable in hot basic solutions.

Example: ICI America's Atlas EM-16, Mona's Monamine™ series, Witco's Witcamide™ series

Polyethoxylated alkanolamides are made by adding 3 to 50 ethylene oxide units at the OH group (or 3 to 50 total for both groups in dialkanolamides).

Example: Akzo Nobel's Ethomid™ series

POLYETHOXYLATED MERCAPTANS RS-PEO-H

These are stable in hot alkali and are insensitive to divalent ions, but they decompose in acid, oxidize readily, and may have an unpleasant odor. They are useful for dispersing proteinaceous materials in water.

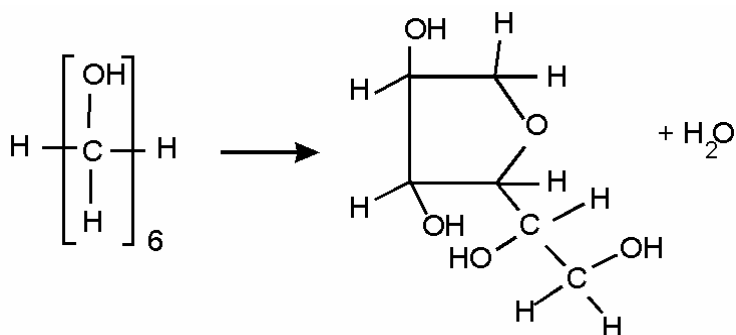
Example: Alcolac's SiponicTM-260

SORBITOL AND SORBITAN DERIVATIVES

Sorbitol, a hexose (C₆) sugar, can be cyclized by dehydration to form the 1:4 sorbitan structure. Many such compounds are edible.

Esterification occurs mainly at the side-chain OH group, but some occurs at the ring OH's.

Commercial mixtures are mainly mono-substituted, but contain some di- and tri-esters.



The high pH reaction conditions used when adding ethylene oxide to sorbitan monostearate (R is the C₁₆ fatty alcohol) cause further exchange of -OH and -OR groups (inter-esterification).

A typical detergent made in this way will have an average of 20 ethylene oxide units.

Polyethoxylated sorbitans enhance the biological activity of pharmaceuticals by increasing their dispersibility in biological systems.

Example: ICI America's SpanTM series and TweenTM series (PEO), Loders Crokiaan's DurtanTM series

4.7 Cationics

Since many biological surfaces are negatively charged, cationic surfactants adsorb strongly on them. While cationics can be very effective in dispersing natural products, they tend to be more expensive than anionic or nonionic surfactants. See Jungermann [ref list] for further discussion of synthesis and application.

ALKYLAMINES R(NR')R''

These are derived from natural oils and acids and may be primary (both R' and R'' are H), secondary (R'' is H), or tertiary amines. The R chain for a typical surfactant is C₈ to C₁₂. Primary amines pick up a hydrogen ion at pH < 10 to become positively charged and soluble. Secondary amines become charged at pH < 4. Tertiary amines may have an unpleasant (fishy) odor. All amines are stable in strongly acidic solutions. The unshared pair of electrons on nitrogen interacts well with metal surfaces, so they are good for dispersing metals in organic liquids.

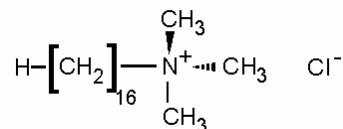
Example: Witko's KemamineTM T series, Lion Akzo's ArmeenTM, Pennwalt series

Alkylamines with few ethylene oxide units and a long alkane chain for R are oil-soluble. As the number of ethylene oxide units substituted at the active H's increases from 3 to 50 (total for both H's), the alkylamines become less cationic and more nonionic, water-soluble above pH 7, and useful for dispersing waxes and other organics in water.

Example: Lion Akzo's Ethomeen™ series, Exxon Mobil's E series, Witco's Witcamine™ RAD series

QUATERNARY AMINES $R[(N^+R')R'']R''' X^-$

These are also called quaternized amines or quaternary ammonium salts. Often all three of the R's are $-CH_3$ and X^- is Cl^- . Unlike the alkylamines, these are ionized and water-soluble at all pH values. They may be desorbed from a surface by excess washing of a filtercake or by high dilution in the final application. Quaternary pyridinium amines are unstable in basic solutions.



Many quaternary amines are toxic and can be adsorbed through the skin, so they must be handled with care in the laboratory or in the plant, and they cannot be used for food or cosmetic products. They are useful as biocides in dispersions which are good growth media for bacteria and which must be stored for long periods.

Adding ethylene oxide to the two active hydrogens in $CH_3(N^+H_2)R X^-$ produces surfactants that will disperse inorganics in oils or organics in water.

Example: Lion Akzo's Arquad™ series, Witco's Variquat™ K300, Exxon Mobil's Q series

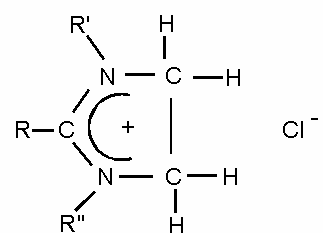
Adding propylene oxide to the active hydrogens produces a good antistatic agent.

Example: Witco's Emcol™ CC series, Lion Akzo's Ethoquad™ series

IMIDAZOLINES

If R' is H these behave as cationics at low pH, anionics at high pH, and zwitterions in between. The specific ranges depend on the specific structures. They remain good surfactants in solutions of high ionic strength.

Example: Alkaryl's Alkaquat™ O, Mona's Monateric™m LF-100



Imidazolines in which R' is an alkyl group are zwitterionic above the isoelectric pH and cationic below that pH. They are used to disperse hydrophilic powders in oils.

Example: Alkaryl's Alkaquat™ series, Witco's Witcamine™ AL42-12

DIALKYLAMINE OXIDES $R-[(NO)R']R''$

These are used in mixtures with anionic surfactant acids to form zwitterionic 1:1 salts that are more surface active than either component alone. (The acid's hydrogen ion moves onto the NO group.) The mixtures have a high tendency to foam and are antistatic agents.

Example: Witco's Emcol™ L, Witco's Varox™ 3657, Exxon Mobil's AO series

4.8 Anionics

See Linfield [ref list] for further discussion of synthesis and applications.

4.8a Carboxylates

SALTS OF FATTY ACIDS $R(CO)O^- M^+$

The sodium or potassium salts of C_{10} to C_{20} fatty acids are used as surfactants in aqueous systems; salts of longer-chain acids are used as surfactants in oils. The pK_a is the pH at which half the acid is ionized, about 4 for many organic acids. If $pH < (pK_a + 2)$, the carboxylate ion reacts with the H^+ ion to form a relatively insoluble neutral compound. Divalent cations will precipitate with the acid, and high salt concentrations strongly reduce the effective charge on the anion.

Example: American Ingredients 's Pationic™ series

The triethanolamine salts of fatty acids (M^+ is $HN^+(OCH_2CH_3)_2$) are soluble in nonaqueous solvents.

Example: Naxel's AAS-60S, Stepan's Stepanol™ WAT

SALTS OF MULTIPLE ACIDS $HO(CO)(CHOH)(CO)O^- M^+$

Monosodium citrate (shown above) and other multiple organic acid salts can adsorb on highly polar surfaces more strongly than acids with a single hydrogen-bonding group. They can adsorb on a slightly negatively charged surface and cause a positive or uncharged surface to become negative. This extends to lower pH's the pH range over which the dispersion can be stabilized by charge repulsion.

SARCOSINE DERIVATIVES $R(CO)(NCH_3)CH_2(CO)O^- Na^+$

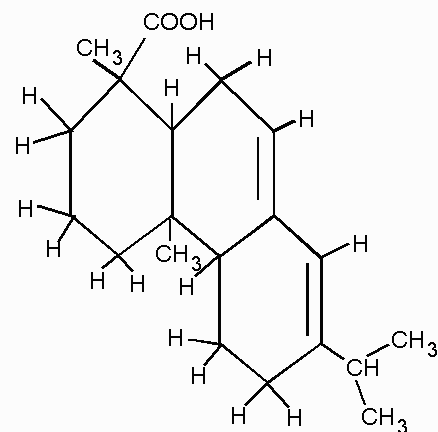
These are nontoxic, can serve as antistatic agents, and are used to generate foams. They are less likely to precipitate with divalent cations than fatty acids are.

Example: Ciba's Sarkosyl™ series

SALTS OF TALL OIL ACIDS

These byproducts of papermaking are complex mixtures of wood pulp derivatives. One-third to one-half of the mixture is fatty acids; the balance is rosin acids (polycyclic terpene carboxylic acids related to abietic acid). The rosin acids are more resistant to precipitation or complexation by divalent cations than the straight chain acid salts alone would be, and their solutions have lower viscosity.

Example: Westvaco's Indulin™ series



4.8b Sulfonates

Sulfonates have the structure $R-(SO_2)-O^- M^+$, with sulfur bonded directly to carbon. Do NOT confuse them with sulfates. Many commercial sulfonates are mixtures, so the chemical categories below overlap somewhat.

SODIUM ALKYL SULFONATES (SAS) $RSO_3^- Na^+$

The sulfonate group is attached to a mid-chain carbon of a C_{13} to C_{24} chain. They have a high tendency to foam, are soluble at low pH, and are not precipitated by divalent cations. They are better than fatty acids in systems with high salt concentration, and they resist hydrolysis in hot acid or base.

Example: Colonial AOS, Witco's Witconate™ AOK

ALPHA-OLEFIN SULFONATES (AOS)

These are mixtures of the salts of alkenesulfonates and hydroxyalkanesulfonates, with properties similar to SAS. The sub-class called petroleum sulfonates are mixtures of polyunsaturated hydrocarbons; these tend to add considerable color to a formulation. The sodium salts of a roughly C_{20} AOS can be used to emulsify oil in water for tertiary oil recovery, to form froth for ore floatation, or to disperse pigments in organic liquids. The ammonia or divalent metal salts are used as sludge dispersants for fuel oil.

Example: Stepan's Petrostep™ series, Alcolac's Siponate™ A series

LINEAR ALKYL BENZENE SULFONATES $R(CH_2)_n-Ph-SO_3^- Na^+$

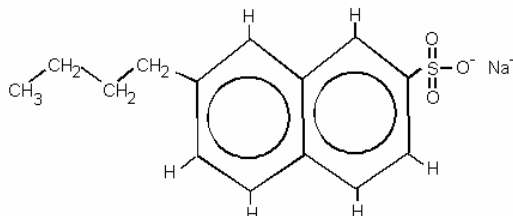
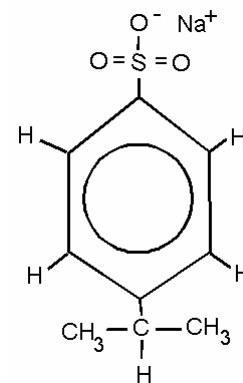
Linear alkylbenzene sulfonates (LAS) have a benzene ring substituted at random positions along a C_{10} to C_{14} chain. They have properties similar to SAS, but the benzene ring makes them less susceptible to biodegradation. A second alkylation of LAS adds a second alkane chain to the benzene ring and produces an oil-soluble surfactant. The sodium salts are commonly used for aqueous systems. The isopropylamine salts are soluble in hydrocarbons.

Example: Lion Akzo's Lipon F, Witco's Witconate™ 9OF

OTHER AROMATIC SULFONATES

Benzene (no substitution on the Ph), toluene (one CH_3), xylene (two CH_3 's), and cumene (three CH_3 's) sulfonates are used to help solubilize linear alkylbenzene sulfonates or other water-insoluble polar organics in aqueous systems. Example: Norman, Fox & Co.'s NORFOX® SXS-40

Alkyl naphthalene sulfonates adsorb on hygroscopic materials and make them nonhygroscopic. They may be added to humidity-sensitive powders to inhibit caking in humid environments or to increase the ability to wet into organic liquids. Example: Witco's Petro™ series



ISETHIONATES $R(CO)OCH_2CH_2SO_3^- M^+$

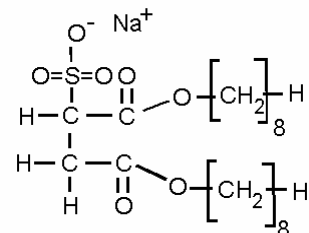
These can be used in the presence of divalent cations. They are hydrolyzed in hot, high pH solutions and have a high tendency to foam.

Example: Elfan AT 84

SULFOSUCCINATES $RO(CO)CH_2CH(SO_3^- M^+)(CO)OR$

If R is big and branched, the compound may be soluble in both water and organic solvents. They hydrolyze in hot acid or hot base.

Example: Cytec's AerosolTM OT series, Crompton's EmcolTM 4000 series



TAURATES $R(CO)(NR')CH_2CH_2SO_3^- M^+$

The charge on taurates are not sensitive to low pH, high ionic strength, or divalent cations. They are good wetting agents for organic powders.

Example: Rhodia's IgeponTM T series, Clariant's HostaponTM T series

4.8d Sulfates

Sulfates have the structure $R-O-(SO_2)-O^- M^+$, with sulfur bonded only to oxygens. Do NOT confuse them with sulfonates.

ALCOHOL SULFATES $R-O-SO_3^- M^+$

These are usually sodium salt of C_8 to C_{18} alcohol sulfates. The sulfate may be on a primary (terminal) carbon or on a secondary (mid-chain) carbon. Alcohol sulfates are readily biodegradable, have a high tendency to foam, hydrolyze in hot acid solutions, and are stable in alkali. The magnesium salts are less hygroscopic and even less affected by divalent ions than the sodium salts are. Sodium dodecyl sulfate (SDS, also called sodium lauryl sulfate, SLS) is commonly used as a low-temperature detergent.

Example: DuPont's DuPonolTM series, Shell's TeepolTM

The polyethoxylated alcohol sulfates are less affected by divalent ions than the alcohol sulfates are.

Example: Stepan's StepanolTM series

ALKYL PHENOL SULFATES $R-Ph-O-PEO-SO_3^- M^+$

See Alkyl Phenols (under Nonionics) for a discussion of the structure. The polyethoxylated alkyl phenol sulfates are similar to polyethoxylated alcohol sulfates.

Example: Union Carbide's TritonTM 770, Witco's WitcolateTM series

SULFATED TRIGLYCERIDES

These are complex products of the action of sulfuric acid on natural oils (glycerol esters). They hydrolyze in hot acid or hot base and have a low tendency to foam.

Example: Proctor's SulfonatedTM GTO

4.8e Phosphates

ALCOHOL PHOSPHATES $\text{RO}[(\text{PO})\text{OZ}]\text{O}^- \text{M}^+$

The organic esters of phosphoric acid are colorless, stable in hot base, and have a low tendency to foam. The free acid forms are skin irritants and are soluble in some organic solvents. The alcohol phosphates are sold as the free acid (M is H) or as a mixture of the monobasic (Z is H) and dibasic (Z is R) salts with sodium (M^+ is Na^+) or a protonated primary amine (M^+ is RNH_3^+). They are relatively insensitive to the presence of divalent cations.

Example: Stepan's ZelecTM series, Rhodia series

Polyethoxylated alcohol phosphates have a PEO between the R and the O. They can be used to prepare dispersions of organics in aqueous dispersions with high salt concentrations.

Example: Stepan's ZelecTM series

Polyethoxylated phenol phosphates, $\text{H-Ph-O}[(\text{PO})\text{O-PEO-Z}]\text{O}^- \text{M}^+$, are a closely related class of surfactants.

INORGANIC PHOSPHATES $\text{M}^{n+} [\text{O}^- (\text{PO})\text{O}^- \text{M}^{n+}]_n \text{O}^- \text{M}^{n+}$

The basic linear phosphate polymers are named ortho- (n is 1), pyro- (n is 2), and tripoly- (n is 3) phosphates. These are often potassium salts (all the M^{n+} 's are K^+). For the acid orthophosphates, most of the M^{n+} 's are H^+ , but one or two may be Na^+ . In sodium hexametaphosphate, six phosphate links form a ring and M^{n+} and $-\text{O}^- \text{M}^{n+}$ are not present.

Phosphates adsorb strongly on metal oxides and hydroxides and may react with the surface to form an insoluble layer of metal phosphate. The multiply charged and strongly complexing or adsorbing pyro-, tripoly-, and metaphosphate anions are even more powerful surfactants than the orthophosphate ion is, but in acid solution they decompose into orthophosphate ions and thus gradually lose their effectiveness.

4.9 Zwitterionics (Amphotherics)

AMINO ACIDS $\text{R}-(\text{N}^+\text{H}_2)\text{CH}_2\text{CH}_2(\text{CO})\text{O}^-$

The β -N-alkylaminopropionic acids are generally derived from fatty acids. They are cationic at $\text{pH} < 4$ and are soluble at both low and high pH. They remain active at high ionic strength and act as biocides. They are useful for dispersing polar organics, biological products, fibers, and metals. Dispersions are best at $\text{pH} > 6$, where the amino acids are completely in the zwitterionic form.

Example: Inolex's LexamineTM series

IMINO ACIDS $\text{R}-[(\text{N}^+\text{H})\text{CH}_2\text{CH}_2(\text{CO})\text{OH}]-\text{CH}_2\text{CH}_2(\text{CO})\text{O}^-$

The N-alkyl- β -iminodipropionic acids have lower isoelectric points ($\text{pH}_{\text{isoelect}} = 1.7$ to 3.5) and higher solubility in water than the corresponding amino acids.

BETAINES $R[N^+(\text{CH}_3)_2](\text{CH}_2)_x(\text{CO})\text{O}^-$

These are quaternized amino acids, with methyl groups in place of the amino H's.

Examples: Cytac's AerosolTM 30, Inolex's LexaineTM series, Mona's MonatericTM LMAB

Sulfobetaines are the sulfonic acid form, with SO_3^- in place of $(\text{CO})\text{O}^-$. The isoelectric points are so low that they are zwitterionic at all pH's.

Example: Witco's VarionTM CAS

IMIDAZOLINES These are listed under Cationics.

PHOSPHOLIPIDS $R(\text{CO})\text{OCH}_2[\text{CHO}(\text{COR}')\text{CH}_2\text{O}(\text{PO}_2^-)\text{X}^+$

Phospholipids are biological surfactants with two hydrocarbon tails (the R groups) and a hydrophilic head (the phosphate salt group). They form bilayer micelles which can solubilize organic compounds. Phospholipids may spontaneously form *vesicles*, also called *liposomes*, when mixed into water. A vesicle is a hollow sphere, composed of an outer bilayer micelle skin surrounding an inner core of water. These are typically about 20 μm in diameter and may shrink (or swell) due to osmosis if the salt concentration inside is less (or greater) than that outside.

Lecithin is an edible surfactant, commonly made from soybean oil. The glycerol base is esterified with two C_{16} to C_{20} fatty acids and the cation is a quaternized ethanolamine (X^+ is $\text{HO}-\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3$).

Example: American Lecithin's AlcolecTM series, Troy's Lecithin