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Technical Bulletin:
**Surfactants – The Unsung Heroes
of Emulsion Polymerization**

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Scope

The talk is designed to be a primer on the utilization of surfactants in emulsion polymerization systems and the wide range of materials available.

Introduction

The majority of synthetic latexes produced by emulsion polymerization employ surfactants both as emulsifiers during the synthesis stage and later as particle stabilizers in the latex itself. Many surfactants are available to industry to accomplish these tasks. Much of the scientific literature, however, is based on experiments using sodium dodecyl sulfate, which is not necessarily a good model for real life situations.

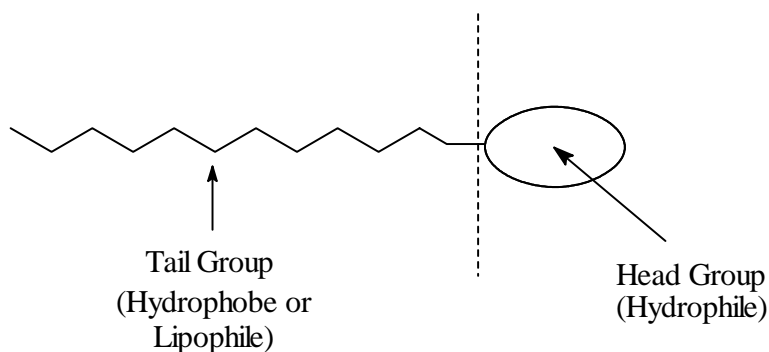
The talk will open with brief reviews of the properties of surfactants, and the adaptation of those properties to the field of emulsion polymerization. This introduction will be followed by detailed chemical descriptions of the surfactants utilized in emulsion polymerization processes. Particular emphasis will be placed on the complex nature of some of these industrial materials and the resulting potential variations in performance faced by formulators.

A) Surfactants

What is a surfactant?

The word “surfactant” is a contraction of the term “surface active agent.” Thus, a material defined as a surfactant is one that possesses the ability to alter radically the free energy of a liquid surface or interface (more commonly referred to as surface or interfacial tension) when present in the system at low concentrations.

A surfactant molecule comprises two distinct portions: a polar, water-loving (hydrophilic) head group which can be compact (anionic e.g. sulfate or cationic e.g. quaternary ammonium) or diffuse (some nonionics e.g. ethoxylates) and a diffuse, non-polar, oil-loving (lipophilic or hydrophobic) tail group – usually a C₁₂ – C₁₈ hydrocarbon chain. Because of this bipolar attribute, surfactants are sometimes referred to as “amphiphiles.” In the literature, a generic surfactant molecule is often represented as a “tadpole.”



There are four classes of surfactant based on the nature of the hydrophilic group: anionic, nonionic, amphoteric and cationic.

a) Anionics: Anionic surfactants are characterized by having a negatively charged head group. Examples are sulfates such as sodium lauryl sulfate, sulfonates, for example sodium dodecylbenzene sulfonate, phosphates, carboxylates (stearates or oleates) and sulfosuccinates.

b) Nonionics: Nonionics are characterized by having an uncharged head group. The most common examples of this type are the alkylphenol ethoxylates and ethoxylated alcohols.

c) Amphoteric (or Zwitterionics): Amphoteric exhibit a head group that possesses both a positive and a negative charge i.e. a “Zwitterionic” head group. Examples of this group are betaines and amine oxides.

d) Cationics: Cationic surfactants contain a positively charged head group. The most common examples of these are the quaternary ammonium salts.

Two subsets of these families are also worth mentioning briefly – water-soluble polymers and polymerizable surfactants. Water-soluble polymers such as polyvinyl alcohol and hydroxymethyl cellulose are used in some specialized applications of high electrolyte concentration.

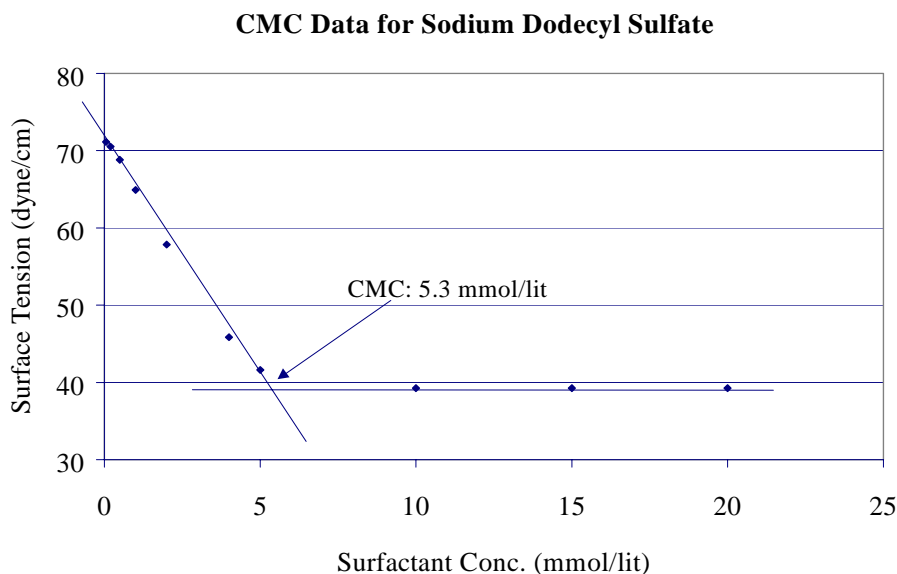
Polymerizable surfactants are a growing area. The group includes vinyl-based monomers such as sulfoethyl methacrylate or sodium styrene sulfonate. These compounds are actually polymerized into the latex polymer backbone, essentially rendering the polymer self-stabilizing. Such latexes have an advantage over standard surfactant-stabilized products because the surfactant cannot be leached out of coating prepared from the latex.

How does a surfactant affect surface or interfacial tension?

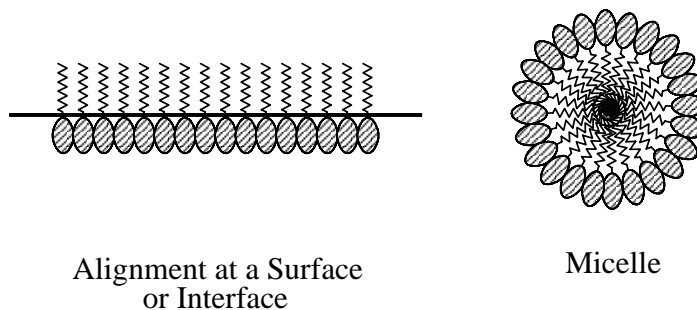
The surface tension of any liquid depends on the strength of intermolecular interactions within that liquid. For example; water, having strong intermolecular interactions (hydrogen bonds), has a surface tension of 73 mN m^{-1} ; heptane, on the other hand, with much weaker intermolecular interactions (van der Waal’s forces), has a surface tension of only 20 mN m^{-1} .

When a surfactant is dissolved in water, the presence of the hydrophobic portion in solution disrupts the balance of the intermolecular forces in the bulk liquid. This leads to a rise in the free energy of the system. This means that it is easier (requires less work) to promote a surfactant molecule than a water molecule to the surface. The surfactant molecules therefore congregate at the surface with their hydrophobic tails aligned along the surface plane minimizing contact with water molecules. This effectively makes the surface less “expensive” so the surface tension drops.

In extremely dilute solutions, the drop in surface tension is proportional to the surfactant concentration. However, at a certain concentration, the surface tension drop stops and from then on, as the concentration increases, the surface tension remains almost constant. The point at which this behavior change is observed is called the *Critical Micelle Concentration*.



Physically, what is happening here is the following; surfactant molecules congregating at the surface gradually cover more and more of that surface as their concentration in the solution increases - surface tension drops proportionally. At the point where the surface becomes saturated, micellization occurs in the bulk liquid. The number of surfactant molecules at the surface reaches a maximum - the surface tension remains constant.



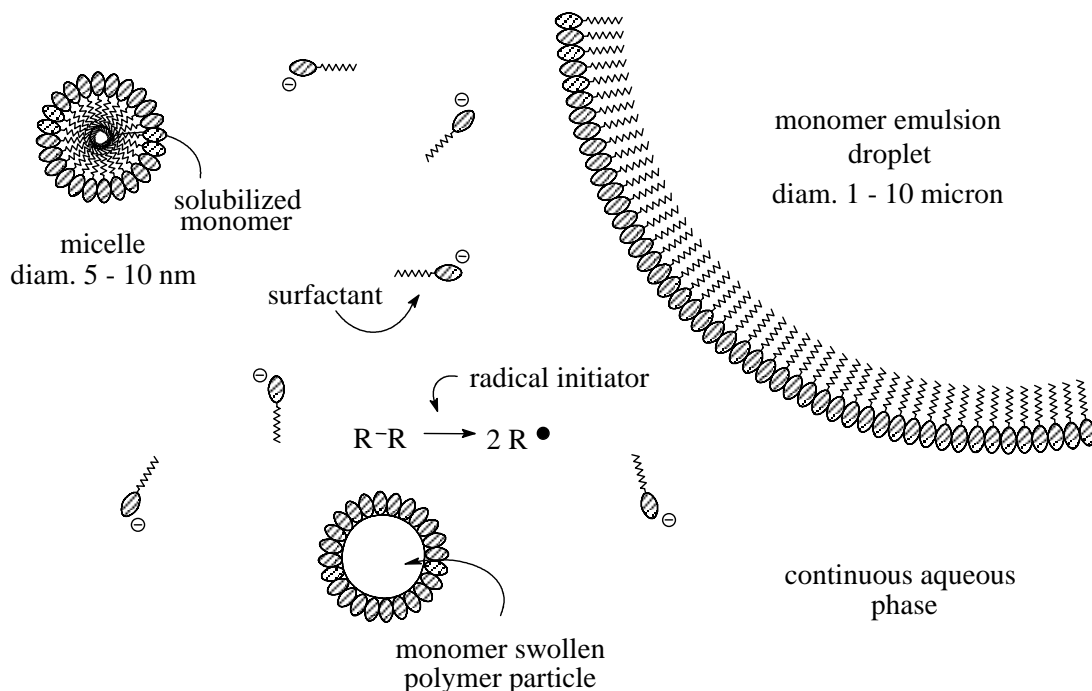
There are types of micelles other than the spherical form shown in the diagram above; cylindrical or lamellar, for example. These structures, however, only exist in conditions of high surfactant or electrolyte concentrations and thus are unimportant in emulsion polymerization.

B) Emulsion Polymerization

Emulsion polymerization (EP) refers to a process whereby water-insoluble monomers are polymerized in an aqueous medium. The resultant stable suspension of polymer particles in water is called a LATEX.

EP is used in the preparation of a wide variety of polymers used in an ever-growing number of consumer and industrial applications. The technology represents one of the main industrial uses of surfactants in the world today. EP offers a number of advantages over other radical initiated polymerization processes including better heat transfer capabilities, lower reaction mixture viscosities, better particle size control and easier copolymer composition control. EP also offers the ability to achieve high polymerization rates and high polymer molecular weights - two factors that have an inverse relationship in “normal” polymerizations. EP reactions are run in one of three ways; batch processes, where all the constituents are present at the beginning of the reaction; semi-batch processes, where one constituent (usually a monomer) is metered in over time; and continuous processes where all the constituents are metered in. All three offer advantages and disadvantages, however, the last two are the most commonly used.

There are four main chemical components in most EP processes. These are; water, an oil soluble monomer or monomers (vinyl monomers such as styrene, vinyl acetate and acrylic acid derivatives are the main components), an emulsifier (e.g. sodium lauryl sulfate) and a radical initiator. Initiators are generally one of two types; water-soluble peroxide salts such potassium persulfate, or more oil-soluble, organic compounds such as azobisisobutyronitrile (AIBN). In both cases, the parent molecule dissociates into a pair of radicals, the dissociation being forced by heat or catalysis. A latex solids content of 50 - 60% is the norm. A schematic representation of the basic EP system is shown below.



The EP reaction itself occurs in three “intervals” – I, II and III. Initially in interval I there are monomer droplets and free surfactant present. Surfactant both stabilizes the monomer droplets and forms micelles in the aqueous phase. Number densities for the two surfactant-stabilized species are $10^9 - 10^{11} \text{ ml}^{-1}$ for droplets and $10^{17} - 10^{18} \text{ ml}^{-1}$ for micelles. From these densities

one can calculate that the total micelle surface area is $10^2 - 10^3$ times that of the droplets. Monomer diffuses from the droplets into the micelles where polymer chain initiation is begun by a penetrating radical resulting in the nucleation of a polymer particle. The end of interval I is defined as the moment at which all the available surfactant is involved in supporting either monomer droplets or monomer swollen polymer particles. No new particles are nucleated after this point. This leads to the relationship between amount of surfactant present and the ultimate particle size - the more surfactant, the higher number of particles, the smaller the particle size.

Interval II usually begins at $\sim 5 - 15\%$ conversion and is characterized by the diffusion of monomer at a steady rate from the droplets into the growing polymer particles. (If one is running a so-called “seeded” polymerization where polymer particles prepared elsewhere are added to the mixture prior to initiation, interval I is avoided altogether). At the end of interval II all the remaining monomer is contained in the swollen polymer particles, there are no monomer droplets left. During interval III the remaining monomer in the particles polymerizes. The surfactant from this point is used to stabilize the colloidal polymer particles that form the product latex.

The basic kinetics of this process (especially interval II) is covered by Smith-Ewart theory which assumes that all nucleation occurs in the micelles. There are two main sources of deviations from this theory. Homogeneous nucleation (chain growth in the aqueous phase - especially important in the more water-soluble monomers such as vinyl acetate) and monomer drop nucleation. Since the total surface area of the micelles is 2 – 3 orders of magnitude greater than that of the droplets, the radicals in solution are much more likely to encounter a micelle than a droplet. Thus, this latter mechanism is generally relatively insignificant.

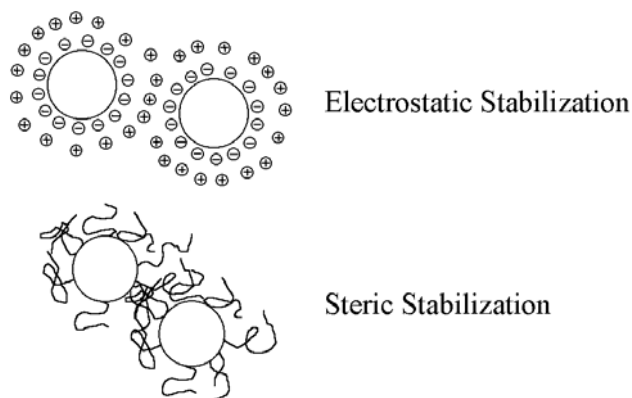
It can be seen, therefore, that the surfactant, although only present in low concentration, affects many aspects of an EP reaction. The surfactant:

- solubilizes highly water-insoluble monomers,
- determines the particle nucleation mechanism by forming a high concentration of micelles,
- determines the total particle number in the system because of the limited period available for the formation of micelles,
- determines the rate of polymerization and
- the final particle size and distribution,
- is responsible for particle stability during interval III and in the final latex product.

What surfactants are available?

Of the four different types of surfactant outlined in the introduction, anionics and nonionics are those usually chosen for EP reactions. Cationics can be used; however, their positively charged head groups will interact with the common negatively charged initiators such as persulfate, so their utility is limited.

Particle stabilization in a latex is by one of two means; electrostatic (as with anionics) or steric (as with nonionics).



For the most part anionics are preferred; however, nonionics offer advantages in systems unsuited to electrostatic stabilization, such as high electrolyte content or high shear situations. Often it is advantageous to have both mechanisms present, so an anionic/nonionic mixture is used. Amphoteric, having a zwitterionic, compact head group allow for neither of these stabilization mechanisms and are thus not used in EP.

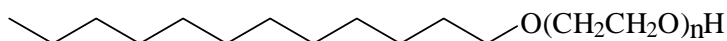
The table below details the main nonionic and anionic surfactants used in EP today.

Nonionics	Anionics
Alcohol ethoxylates	Fatty acid salts
Alkylphenol ethoxylates	Lauryl and lauryl ether sulfates
	Alkylbenzene sulfonates
	α -Olefin sulfonates
	Alkyldiphenyl oxide disulfonates
	Phosphate esters
	Sulfosuccinates

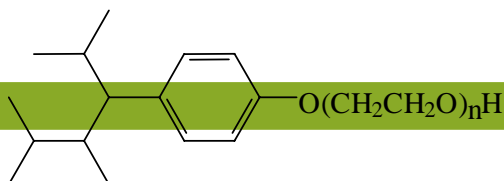
A more detailed description of the main surfactant families follows.

A) NONIONICS

The two main types of nonionics used in EP are alcohol and alkylphenol ethoxylates. These are prepared by catalytic ethoxylation of the corresponding alcohol or phenol with ethylene oxide (EO).



Alcohol Ethoxylate



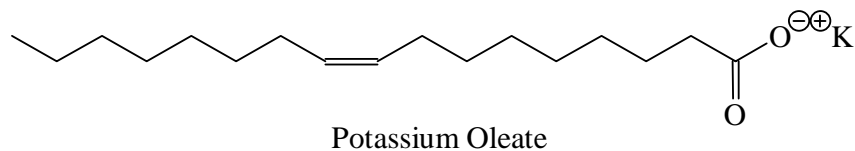
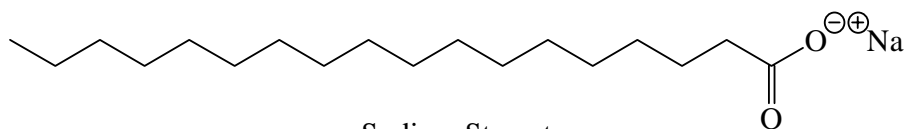
Nonyl Phenol Ethoxylate

In the case of the alcohol ethoxylates, the basic alcohol is usually lauryl or dodecyl alcohol as shown. With the alkylphenol ethoxylates two alkylphenols are generally used, branched nonyl (NPE; shown) and octyl derivatives. It is important to note that the chain branching in the phenol ethoxylates render them not biodegradable by usual definitions, thus they are losing favor in many quarters. There are also similar structural complications as those described in detail below for sulfates.

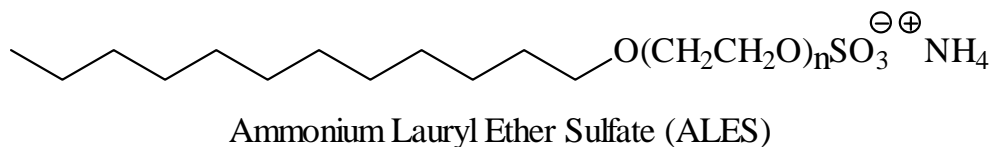
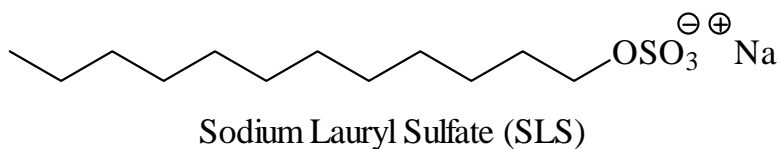
B) ANIONICS

1) Fatty Acid Salts

These fatty acid salts or soaps are included more from a historical point of view than as examples of surfactants currently used in EP. The range of hydrophobe carbon chain lengths was generally from 12 (laurate) to 18 (stearate), salts with less than 12 carbons being too water soluble, those over 18 being too insoluble. These materials have a number of disadvantages over more modern anionic surfactants including a narrow effective pH range and poor hard water tolerance. Additionally, the carboxylate anion is not as effective a particle stabilizer as, for example, sulfate or phosphate.



2) Lauryl and Lauryl Ether (Laureth) Sulfates



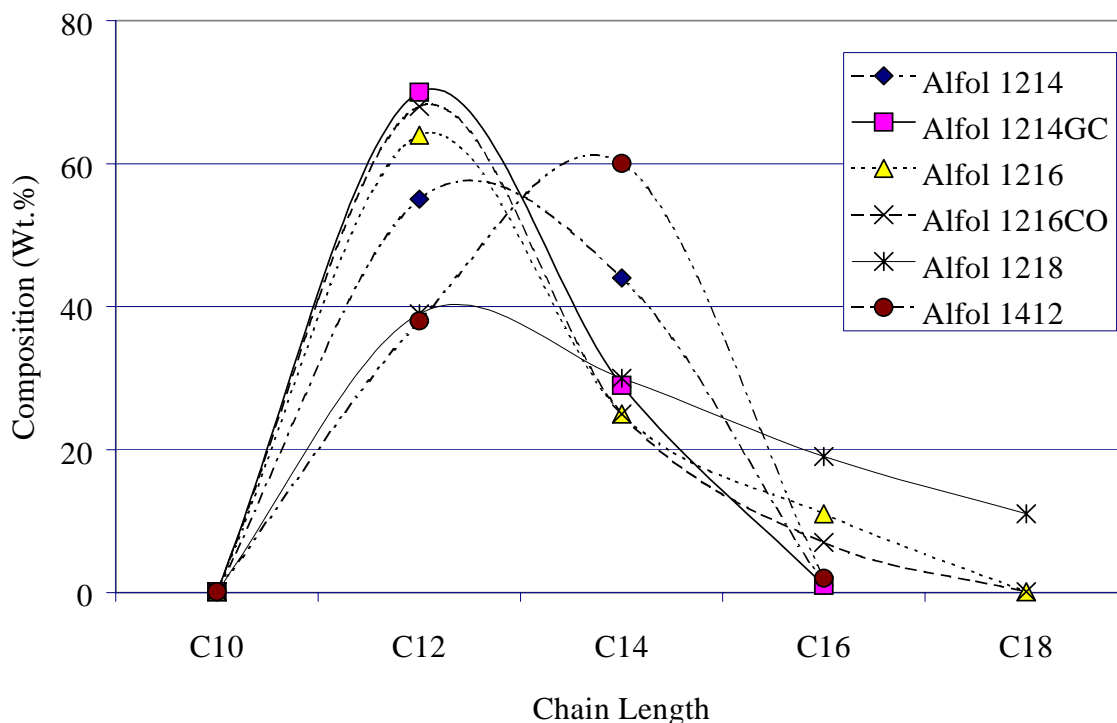
Sodium lauryl or dodecyl sulfate (SLS or SDS) is a true workhorse of the industry. A large portion of academic research into EP is undertaken using SDS as the surfactant. This material is

available as a crystalline solid from the usual special chemical suppliers, and affords the academic researcher the reproducibility required due to its high purity.

For industrial applications, SLS is the sulfate of choice and the situation is somewhat different. SLS is manufactured by reaction of a feedstock lauryl alcohol with either sulfur trioxide (SO₃) or chlorosulfonic acid (ClSO₃H) followed by neutralization with usually sodium or ammonium hydroxide. SLS is usually supplied as an approximately 30% aqueous solution. The feedstock and manufacturing conditions, while generally under excellent control at any one manufacturer, allow for a wide range of product variations from one supplier to the next for two main reasons.

Firstly, while the dodecyl alcohol used to produce SDS is essentially a pure, C₁₂ alcohol; natural lauryl alcohol is a variable mixture of C₁₂ – C₁₆ alcohols as shown in the table below. Additionally, commercial lauryl alcohol, while less variable than its natural counterpart is available in a large number of grades depending on the mix of these, and in some cases, higher chain lengths. The table and graph below detail the range of lauryl alcohol blends manufactured by Condea Vista. Obviously, each blend will produce an SLS with significantly different properties with respect to EP systems. For example, information presented later will show that a C12-14 SLS has a CMC approximately one quarter that of SDS.

Compositions of Lauryl Alcohols



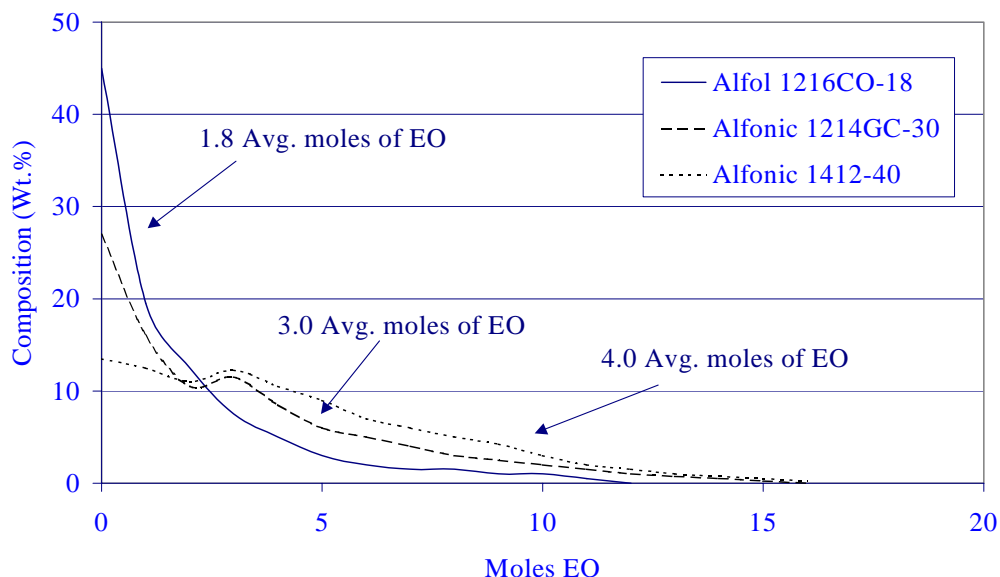
Chain Length	Natural	Alfol 1214	Alfol 1214GC	Alfol 1216	Alfol 1216CO	Alfol 1218	Alfol 1412	Dodecanol
C10	<1%	<1%	<1%	<1%	<1%	<1%	<1%	

C12	65-70%	55%	70%	64%	68%	39%	38%	100%
C14	21-28%	44%	29%	25%	25%	30%	60%	0%
C16	4-8%	1%	1%	11%	7%	19%	2%	0%
C18	<1%	<1%	<1%	<1%	<1%	11%	<1%	
MW		198.0	193.9	197.5	195.5	213.3	203.0	186.3
Avg. Chain		12.9	12.6	12.9	12.7	14.0	13.3	12.0

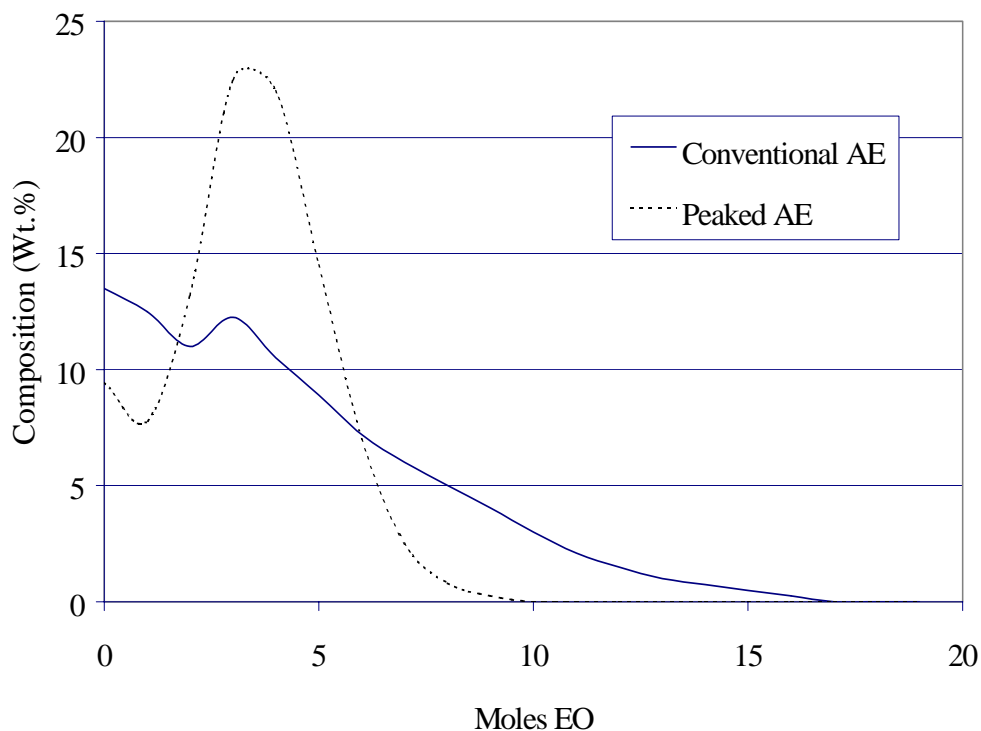
Secondly, SLS prepared using ClSO₃H as the sulfating agent can have a markedly higher and more variable sodium chloride content than SO₃ sulfated material. Again, given the sensitivity of EP reactions to the electrolyte content of the system, switching from SO₃-prepared SLS to ClSO₃H-prepared SLS can greatly affect the latex product characteristics.

There is a further complication involved with the lauryl ether or laureth sulfates. These compounds are the products of sulfonation of ethoxylated alcohols. They are designated, for

Ethoxylated Alcohol Compositions

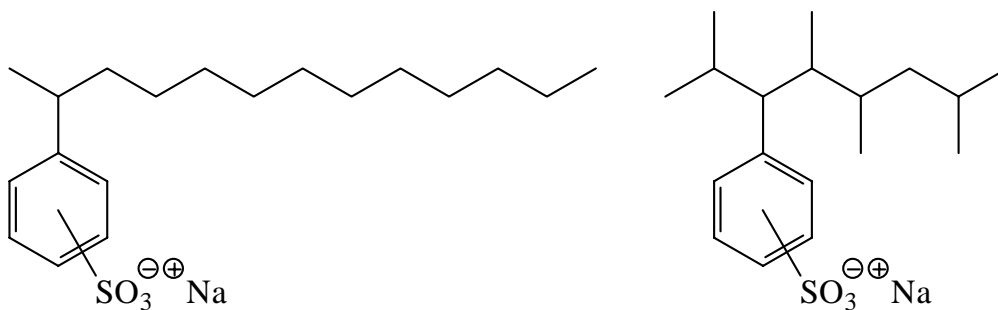


example, 2 or 3-mole ethoxylates, however, the ethoxylation reaction does not produce a single 2 or 3-mole product, instead a range of ethoxylation is achieved as shown in the graphs on the next page. A normal, 2-mole ethoxylate distribution will average out at 2 moles of EO; however, it will contain a range from zero (lauryl alcohol) to sometimes greater than 15 moles of EO. A so-called peaked ethoxylate will have a much narrower distribution. These materials tend to be significantly more expensive than the normal products and so have received marginal attention. Nonionic surfactant ethoxylates similarly have a wide range of compositions; however, the EO content is generally much higher, averaging out at 4 – 50 moles of EO rather than 1 – 3 moles.



3) Dodecylbenzene Sulfonates

The next family of anionic surfactants of note in EP is the dodecylbenzene sulfonates. Linear or branched isomers are available, the sodium salt of the linear variety, NaLAS, being the most common. Catalytic alkylation of benzene with either olefins or chloroparaffins gives linear or



Sodium Dodecylbenzene Sulfonate

branched alkylbenzenes (LAB or BAB's). Detergent alkylates are distilled overhead so heavy fractions are not a problem with these materials. These alkylates are then sulfonated, either in air/SO₃ or liquid SO₂/SO₃ systems and neutralized with the desired base, usually sodium hydroxide, although potassium hydroxide or amines such as isopropylamine or triethanolamine are sometimes used.

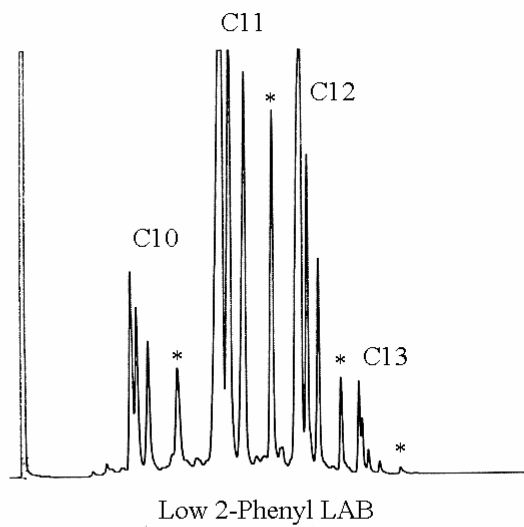
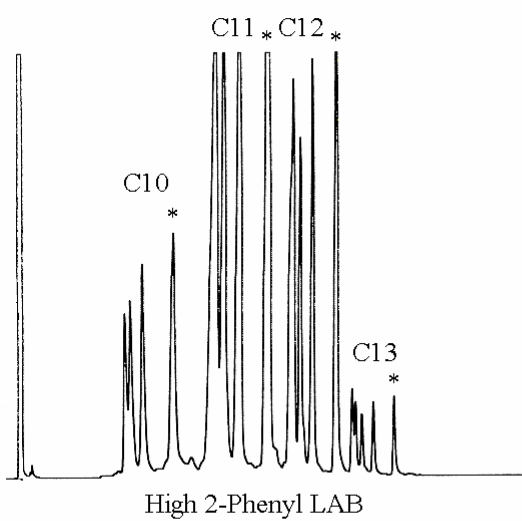
There are two main factors associated with LAB's that can produce performance differences between sources of alkylbenzene sulfonates, alkylate chain length distribution, chain substitution position. For simplicity's sake the following discussion will address linear isomers only.

Firstly, as was the case with lauryl sulfates above, the feedstock olefins or chloroparaffins a mixture of different chain lengths, generally, C₁₀ to C₁₃. Obviously, the chain distribution affects the molecular weight of the alkylate, and LAB's are usually sold by the average chain number such as C_{11.3} or C_{11.8}. Again mimicking SLS, properties vary along with the average chain length; for example, longer chains give lower CMC sulfonates.

The second factor, chain substitution position, is a result of the alkylation reaction mechanism. Intermediate rearrangement during the reaction allows the phenyl group to attach at any carbon on the chain except the 1- position. Thus, with a C₁₁ chain, five positional isomers are found due to substitution at the 2-, 3-, 4-, 5- and 6- positions. The amounts of these isomers found in an alkylate, is a factor of the catalyst used in production. This is particularly true with the 2-phenyl isomer. In fact LAB's are marketed as "high" or "low 2-phenyl" depending on whether the total 2-phenyl content is 30% or more or in the 10 - 20% range.

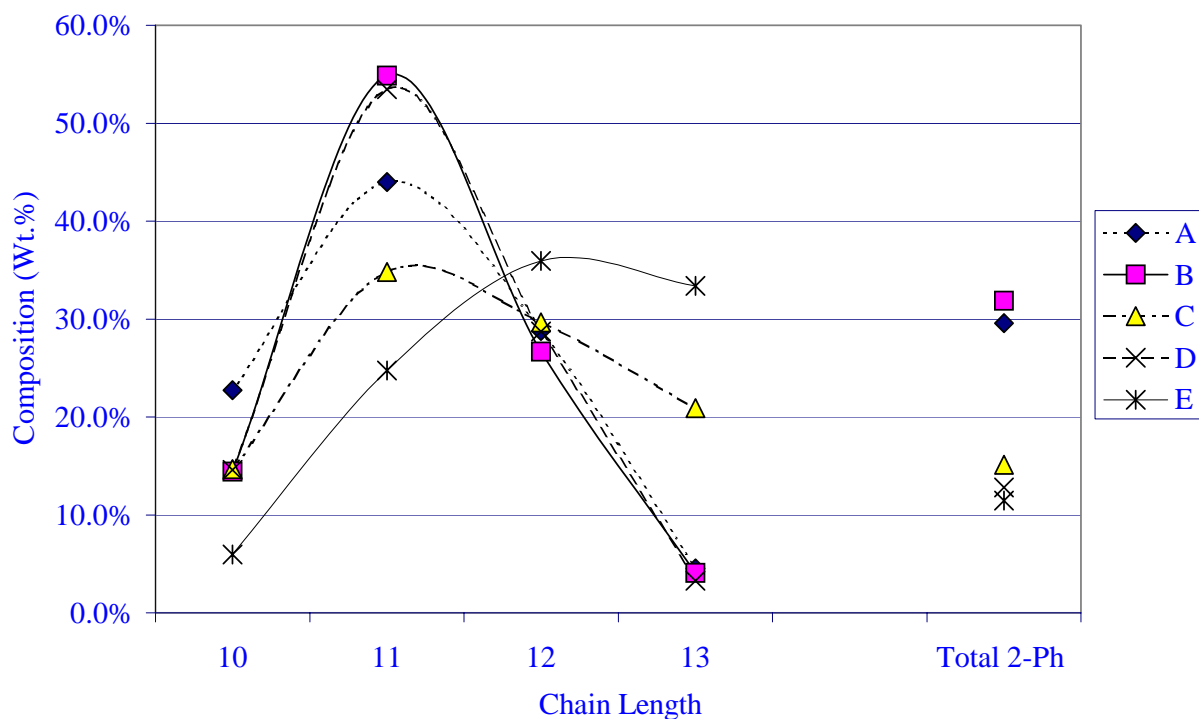
The data on the next two pages detail some of these differences with reference to alkylates from different sources, domestic and overseas. The gas chromatographs presented below clearly show

the presence of different chain lengths and of positional isomers on those chains. The peaks marked with asterisks correspond to the 2-phenyl isomers.



LAB Analyses

C Chain	A	B	C	D	E
10	22.7%	14.4%	14.7%	14.6%	6.0%
11	44.0%	54.8%	34.8%	53.5%	24.7%
12	28.8%	26.6%	29.7%	28.7%	35.9%
13	4.5%	4.1%	20.9%	3.2%	33.4%
Total 2-Ph	29.6%	31.9%	15.1%	12.8%	11.5%
MW	234.0	234.8	239.6	234.6	245.3
Avg. C Chain	11.2	11.2	11.6	11.2	12.0

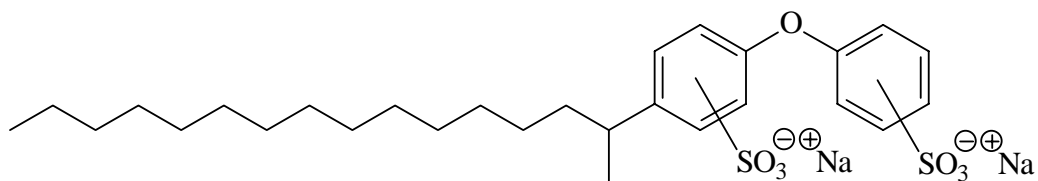


Notes: Alkylates C and E are from Asian and European sources respectively. Materials imported from the Far East or Europe is almost exclusively of the low 2-phenyl variety. A, B and D are all from domestic suppliers.

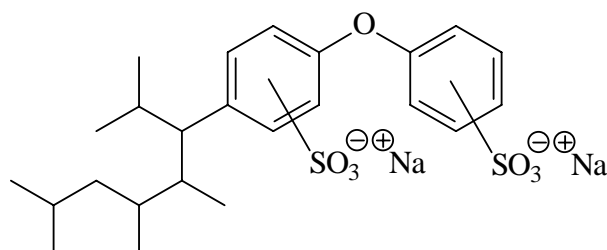
One final point; in addition to these LAB variables, air/SO₃ sulfonation produces sulfonates that contain markedly higher amounts of organic extractable oils than the SO₂/SO₃ methodology.

4) Alkyldiphenyl Oxide Disulfonates.

The last family of anionic surfactants of note in EP that will be discussed in detail are the Alkyldiphenyl Oxide Disulfonates. Again both linear and branched isomers are available. The two products most commonly used in EP are the disodium salts of the linear C₁₆ and branched C₁₂ based sulfonic acids, although the linear C₁₀ variety has been used also. A similar three-step process as was described for NaLAS above is used to prepare these materials. Catalytic alkylation of diphenyl oxide (DPO) with olefins gives linear or branched alkyl DPO's. These alkylates are then sulfonated and neutralized with sodium hydroxide.



Disodium Hexadecyldiphenyl Oxide Disulfonate



Disodium br-Dodecyldiphenyl Oxide Disulfonate

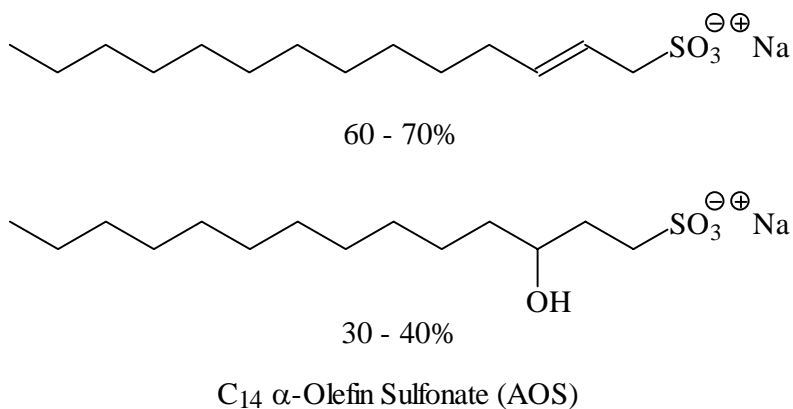
The composition of the DPO alkylates is somewhat simpler than with LAB's because relatively pure olefins are used. Thus, for example, in the C₁₆ alkylate, there are < 5% total of other chain lengths. The chain positional isomers still occur (seven in the case of C₁₆), and, since the alkylation is now on a substituted phenyl ring, ortho and para isomers are possible.

In alkyl DPO's there will always be a certain amount of di and even trialkylated products. Processing controls, however, keep the levels of these higher molecular weight species constant.

The structural factor that appears to have the largest effect on EP processes is the disulfonate content of the product. Just as LAB sulfonates contain a small amount of unsulfonated material, the DPO disulfonates contain a measurable amount of monosulfonate. Because of their much lower solubility, the CMC of monosulfonated alkyl DPO's is at least an order of magnitude lower than the corresponding disulfonated species, thus variation in the amounts of monosulfonate in these products could affect EP systems. The manufacturers have recognized this situation and therefore the disulfonate content is a closely watched factor during the manufacturing process.

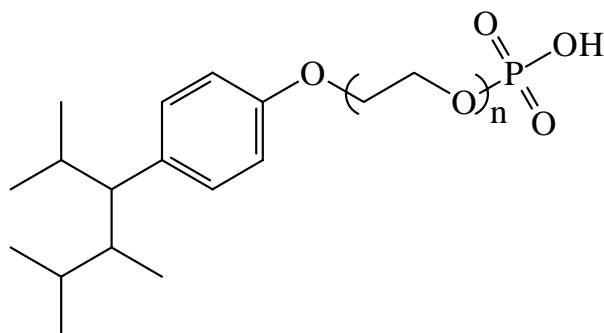
The final three EP surfactants will be mentioned only briefly:

4) α -Olefin Sulfonates.



AOS is prepared by air/SO₃ sulfonation of a blend comprising primarily C₁₄ and C₁₆ α-olefins. Ratios of the two main components vary from around 35: 65 to 65: 35 C₁₄: C₁₆. The AOS sulfonate itself is a mixture of two different materials; a true alkene sulfonate comprising 60 – 70% of the mix and the hydrated form, a 3-hydroxy alkane sulfonate making up the other 30 – 40%. As with the materials discussed previously, these ratios do vary from manufacturer to manufacturer.

5) Ethoxylated Phosphates.

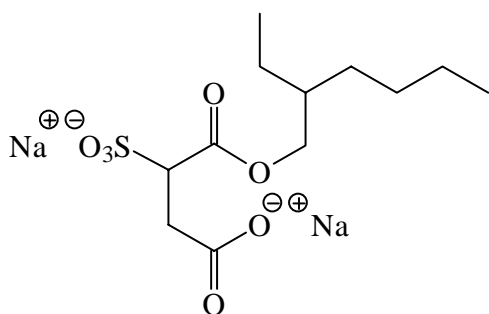


Nonylphenol Ethoxyphosphate
(Acid Form)

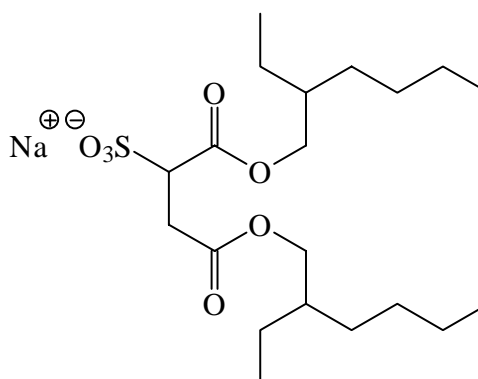
Essentially prepared by the reaction of phosphoric acid or phosphorus pentoxide with the nonylphenol ethoxylate nonionic surfactants described previously.

6) Sulfosuccinates.

Prepared by action of the appropriate alcohol on succinic anhydride to form the mono or diester of maleic acid followed by reaction with aqueous sodium bisulfite.



Disodium Octyl Sulfosuccinate



Dioctyl Sodium Sulfosuccinate

Choice of Surfactants for EP

The choice of which surfactant to use for a particular EP system is a difficult one given the wide range of products available and the variety both of the polymers produced by EP and of the different end uses of the latexes themselves. Some narrowing of the choice can be made based on knowledge of the EP system and the desired properties of the latex.

With nonionics in particular, a hydrophile-lipophile balance (HLB) based assessment can also prove helpful in matching a surfactant to the EP system. The HLB of a surfactant is a measure of the relative simultaneous attraction of that surfactant to both phases of an emulsion.

Since the number of micelles present in the reaction determines latex particle size and the polymerization rate, the CMC of the surfactant is often a consideration. At a given surfactant concentration, a lower CMC will mean a larger number of smaller particles will be formed. Conversely, for a given particle size requirement, the lower the CMC, the less surfactant will be

required. A low surfactant concentration is generally beneficial to most latex end uses. For any particular family of surfactant the main determining factor for the CMC is the size of the hydrophobe – for example, as the hydrocarbon chain length increases in a series, the CMC decreases. CMC's for a number of the surfactants discussed here are given in the table below (Note the substantial difference between the CMC's for SDS and “industrial” SLS).

Product	CMC (mmol/lit)	CMC (g act./lit)	Surf. Tens. at CMC (dyne/cm)
Control; SDS (anly. grade)	5.75	1.66	39.3
“Industrial” SLS	1.51	0.46	27.3
Liquid NaLAS	2.19	0.76	36.8
NaLAS powder	2.00	0.68	36.8
Low 2-phenyl NaLAS	2.00	0.68	35.8
DPOdisulfonate (lin. 10)	3.02	1.59	37.0
DPOdisulfonate (lin. 16)	0.50	0.31	49.8
DPOdisulfonate (br. 12)	0.66	0.37	36.2
α-Olefin Sulfonate	2.04	0.64	36.6

Once these general considerations have been taken into account, the next step in surfactant choice is essentially one of trial and error based on prior experience. A few side-by-side tests of surfactants in specific systems exist in the open literature, for example work carried out at EPI in the early '90's comparing DPOdisulfonates with SDS in the polymerization of styrene, however, these are somewhat limited in scope.

During testing particular attention would be given to coagulum content (a product of particle instability), foaming, latex viscosity and any other specified attributes.

Summary and Conclusions.

Surfactants are very important contributors to most EP systems. They help control

- average particle size
- particle size distribution
- stability of the product latexes

all of which factors directly affect the performance of the product.

Industrial surfactants are not single species materials. Possible supplier to supplier variations include

- Active contents
- Chain length distribution
- Positional isomers
- Electrolyte content
- Oil content

Finally

Choose a surfactant carefully

Understand the sources of product variation

Remember the wide variety of products lead to system control and customization.

Despite the dependence of the latex industry on surfactants, they remain a somewhat understudied group of materials, at least partially due to the complex nature of EP systems, and that of industrial surfactants themselves.