Sorting Out Surfactants

The Modular Cleaning Program (MCP) incorporates a number of surfactants that can be used in the aqueous cleaning of painted surfaces. There are both major and subtle differences in the properties and behaviors of these surfactants. The following are my thoughts/insights on these surfactants.

But first, a bit of background. A surfactant is a chemical entity that has both polar (hydrophilic) and non-polar (hydrophobic) areas on the same molecule. The polar, hydrophilic end dissolves in water while the non-polar, hydrophobic end dislikes water and does its best to get away from the aqueous environment. As these dual personality molecules are added to water, the hydrophobic ends, repelled by the water molecules, pull the rest of the molecule to the surface of the water. (Hence the term surface active agent or surfactant for short.)

The polar, hydrophilic end of the molecule can be created via an acid or base group which can disassociate in water (anionic and cationic surfactants) or by having a group with sufficient polar quality in the molecule that it is soluble in water through hydrogen bonding and/or dipole interactions. The hydrophobic end of the molecule can be anything that is not soluble in water. In fact the nature of the hydrophobic end of the molecule determines the specificity of the attraction of the surfactant to the "dirt."

This specificity of the surfactant's interaction with the "dirt" is key to the exploitation of surfactants in conservation. Just as "like dissolves like" in the world of solvents, "like attracts like" when considering how a surfactant's hydrophobic end interacts with "dirt. "

We can exploit this "like attracts like" idea by matching our hydrophobic end of the surfactant to that which we wish to pull up into an aqueous cleaning system. The most obvious use of this approach is soap. If we want to get something greasy off of our hands, we take fat, react it with a base to saponify the fat (adding the hydrophilic end onto the molecule), and use the resulting soap to clean our hands. If we want to remove aged natural resin, we take an acidic resin, react it with a base, and use the resulting resin soap to assist pulling the aged resin coating into our aqueous cleaning system. Properly, when a surfactant is used this way, it is referred to as an affinity surfactant, which is the term Richard Wolbers, uses in his presentations and publications.

As surfactant is added to water, the molecules first are pushed to the surfaces by the repulsion of the hydrophobic ends by the water. The surfactant molecules will collect at the surfaces of the water (air/water interface, water/glass interface, etc) until all of the surface space is taken. At this point, additional surfactant must go somewhere, so it forms little spherical blobs with the hydrophobic parts of the molecule towards the inside of the sphere and the hydrophilic parts on the outside of the sphere, a micelle. This point where micelles begin to form as more surfactant is added is called the critical micelle concentration or cmc for short.

Prior to the formation of micelles, the surfactant only reduces the surface tension of the water. When micelles begin to form, the solution can begin acting as a detergent. A detergent "cleans" by incorporating dirt into the micelles that allows the dirt to be suspended in the water and float away.

If we wish to exploit surfactants to "clean" something, we need to have sufficient surfactant in solution to not only exceed the cmc but to form sufficient micelles to allow the "dirt" to be suspended in our cleaning system. However, we want to avoid having a huge excess of surfactant in solution to reduce the effort in removing (rinsing) the excess surfactant from the surface. Typically, we use a surfactant at 5 to as much as 10 times its cmc. (See the graphs, Figures 4.2 and 4.3, on pages 59 and 60 in Wolbers*.)

Consider the micelle. These form into spherical blobs with the hydrophobic ends of the surfactant in the middle, surrounded by a skin of hydrophilic groups. On average, a certain number of surfactant molecules will make a micelle. This number is called the Aggregation Number. If the aggregation number is known, we can calculate the concentration of the actual micelles in our cleaning solution. The micelle concentration would be the concentration of surfactant in the cleaning solution, less the cmc, all divided by the Aggregation Number. If the Aggregation Number is low, we would use our surfactant at closer to 5 times the cmc, while if it were very large, we might work at closer to 10 times the cmc.

Perhaps the most common metric for the "cleaning power" of surfactants is the HLB or Hydrophile Lipophile Balance number. (Lipophilic is the same as hydrophobic … unless one is discussing rabies.) The HLB system is an empirical method of evaluating the comparative strength of surfactants. It was developed for classifying nonionic surfactants by William C. Griffin of the Atlas Powder Company nearly 60 years ago.

The original definition was 20 x molecular weight of the hydrophilic end of the molecule divided by the total molecular weight of the surfactant giving an HLB range of 0-20. Since that initial proposition, the HLB has been redefined and extended numerous times and now includes anionic and cationic surfactants as well. There is even an elaborate experimental HLB measurement based on how quickly a mixture of mineral oil, water, and the surfactant will separate after shaking. When cationic and anionic surfactants are added, the HLB scale is extended from 0 to 40. Perhaps the best summary of the HLB system is a quote from an unnamed tech director at a major consumer products company: "We're disappointed by the lack of science behind the HLB System, we just use it because it works." †

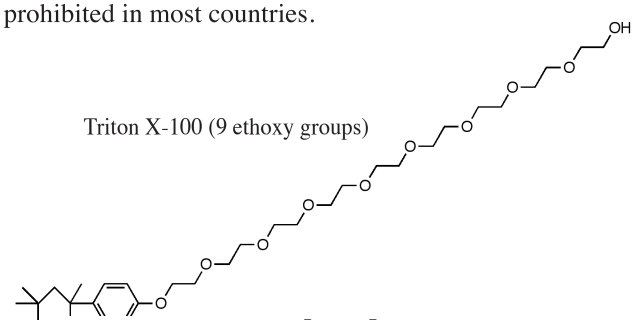
The table on page 13 summarizes the various properties of the surfactants. I've also written a bit about each surfactant as a guide as to when and under what circumstances it might be found to be effective.

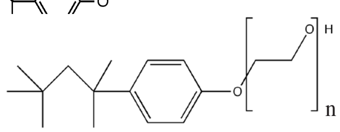
by Chris Stavroudis

Nonionic Surfactants (These can be used at any pH.)

Triton X-100

Triton X-100 was once our favorite surfactant. Its structure incorporates a linear carbon chain and a benzene ring on the hydrophobic side and a long chain of polyoxyethylene (POE) for the hydrophilic side of the molecule. While it is of moderate HLB, the molecular diversity of the hydrophobic portion of the molecule allows it to snuggle up to a wide variety of dirts. Unfortunately, the hydrophobic component, octylphenol, is an estrogen mimic and plays havoc with fishes reproductive systems (and likely peoples' too). Ocytlphenol and nonylphenol cause feminization of male fish rendering them nearly sterile. (Coincidentally, the most common spermacide nonoxynol-9 is polyethoxylated nonylphenol.) So the long and short of it is, these products are on their way out. Their discharge into the ecosystem is, or is going to be, prohibited in most countries.





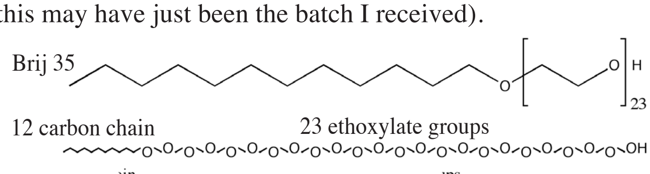
Triton X series
Triton X-114: n = 7.5
Triton X-100: n = 9.5
Triton X-405: n = 35

Triton XL-80N or Surfonic JL-80X

Triton XL-80N was originally formulated to work as a replacement for Triton X-100 when the environmental concerns about X-100 became clear. XL-80N has been discontinued, but the Surfonic JL-80X is chemically very similar and appears to have comparable properties to XL-80N and, so by extension, to X-100. Many of the physical properties of the JL-80X are not know (or I haven't been able to find them) so I've used those of XL-80N in the MCP.

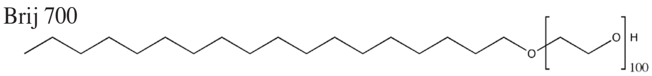
Brij 35

Brij 35 is a polyethoxylated lauryl alcohol (yielding a lauryl ether). Lauryl is code for a fatty mess obtained from coconut oil consisting of mostly a 12 carbon, straight chain, primary alcohol, dodecanol. The ethyxolate chain averages 23 repeating units. In my practice, I've been using Brij 700 which is similar but has both a longer hydrophobic chain and a longer hydrophilic chain. I also found that the bottle of Brij 35, while a nonionic, had a very low pH (although this may have just been the batch I received).



Brij 700

Brij 700 is a polyetholylated stearyl alcohol, stearyl being largely an 18 carbon linear chain predominant in animal fat. The polyethoxylate chain is a whopping 100 repeating units. This yields a very large molecule with one of the highest HLBs for a nonionic surfactant. Both Brij 35 and 700 are good at solubilizing straight chain fats and oils, making them very effective detergents. Again, using the "like attracts like" these would be good candidates for greasy surface dirt. You might also want to avoid detergents with long, linear carbon chains if you are working with very young oil.



Ethofat 242/25

This Ethofat is an ethoxylated tall oil. Tall oil, it turns out, is some sort of yuck derived from processing of trees into paper and consists in large part of rosin. So, Ethofat 242/25 is sort of a nonionic resin soap. It is certainly not as effective as anionic resin soaps (abietates and deoxycholates) but because it is nonionic, it can be used at any pH.

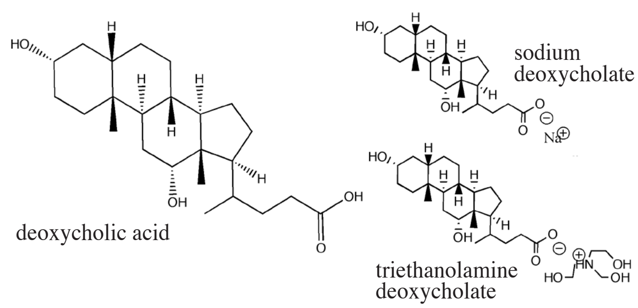
Anionic Surfactants

The solubility of anionic surfactants relies on the acid group on the hydrophilic end of the molecule to be disassociated when in solution. Therefore, there is a pH below which any anionic surfactant will separate into a greasy oil floating on top of the water or a precipitate in the water.

The "resin soaps"

Deoxycholic acid

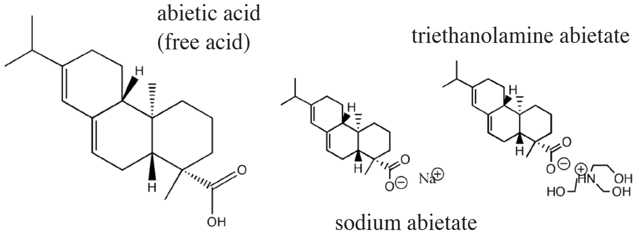
Deoxycholic acid is a bile acid. It has a structure that is similar to the structure of dammar's major component. Different soaps can be made using sodium hydroxide, ammonium hydroxide, or triethanolamine to deprotonate the deoxycholic acid. Deoxycholic acid is virtually insoluble in water. That and its high pKa mean that a dexoycholate solution will not be stable below a pH of 8.0 to 8.3. The choice of the counter ion has some bearing on the solubility of the resin soap, too. Also, since ammonium hydroxide is volatile, ammonium dexoycholate solutions' pH can drop over time, which can cause the deoxycholate to begin to precipitate. Another odd quirk of deoxychloate is that at a certain pH it can form dimers and self emulsify the free acid, at this point the solution becomes a mucous-like slimy mess. Increasing the pH slightly will bring the deoxycholate into complete solution.



Common name	Surfactant type	Other names	Chemical Abstracts Service (CAS) number	Active percent	Physical form	Molecular weight	Aggregation number	CMC (mM)	CMC (%)	Density	HLB
Triton X-100	nonionic	octylphenol ethoxylate polyoxyethylene 9.5-octlphenol	9036-19-5	100	liquid	628	140	0.24	0.015	1.07	13.4
Triton XL-80N	nonionic	alkyl-oxy-polyethylene-oxy-polypropylene-oxy-ethanol		100	liquid	442		0.19	0.0086	0.985	12.5
Surfonic JL-80X	nonionic	C10-C12 alcohols, ethoxylatedpropoxylated	68154-97-2	100	liquid	603		?		1.007	13.1
Brij® 35	nonionic	polyoxyethylene 23-lauryl ether	9002-92-0	100	solid	1225	40	0.068	0.01		16.9
Brij® 700	nonionic	polyoxyethylene 100 stearyl ether	9005-00-9	100	solid	4670		0.02	0.01	1.100	18.8
Ethofat 242/25	nonionic	ethoxylated tall oil	65071-95-6	100	liquid	945		4	0.4	1.081	12.2
Pluronic L64		poloxamer 184	9003-11-6	100	liquid	2900					15
deoxycholic acid	anionic	cholan-24-oic acid, 3,12-dihydroxy	302-95-4	100	solid	392.6	22	5	0.20		17.6
sodium deoxycholate	anionic	sodium salt	302-95-4	100	solid	414.6	22	5	0.21		17.6
triethanolamine deoxycholate	anionic	triethanolammonium salt	302-95-4	100	solid		22	5			17.6
abietic acid	anionic	decahydrophenanthrene-1-carboxylic acid	514-10-3	100	solid	302.5		2	0.061		8.2
sodium abietate	anionic	sodium salt		100	solid	324.4		2	0.07		8.2
triethanolamine abietate	anionic	triethanolammonium salt		100	solid	433.6		2	0.87		8.2
sodium lauryl sulfate	anionic	sodium dodecyl sulfate, SDS, SLS, Orvus WA	151-21-3	100	solid	288.4	62	7.1			40
Maypon 4C	anionic	potassium cocoyl hydrolyzed collagen	689920-65-0	35	solution	?				1.06	

Abietic acid

Abietic acid is another material that has a structure similar to dammar. It is a component of rosin. As with deoxycholic acid, abietic acid can be made into resin soaps with sodium, ammonium, or triethanolammonium counter ions. It also can only be used at a high pH. For a time, finding commercial abietic acid that was indeed abietic acid was a bit of a challenge. However commercial triethanolammonium abietate is available. This material looks something like earwax and requires additional triethanolamine to bring it into solution.



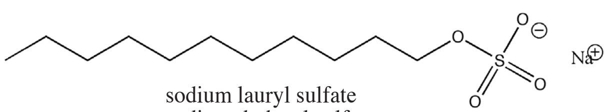
abietic acid (free acid)

sodium abietate

triethanolamine abietate

Sodium lauryl sulfate

Sodium lauryl sulfate (SLS) or sodium dodecyl sulfate (SDS) is a very widely used anionic surfactant. It is the basis for many shampoos and soap systems and is used in textile conservation. (Orvus is a brand name for a 35% solution of SLS.) It has as high an HLB as is possible. It is a very powerful surfactant and again, in terms of “like attracts like” it is very good at bringing fatty materials into solution. Its main disadvantage in cleaning paint surfaces is that it is very prone to foaming. It has a very low pKa and can be used at pHs as low as 4. At a pH of about 3.6, a greasy layer of lauryl sulfonic acid will float to the surface.



sodium lauryl sulfate
sodium dodecyl sulfate

Maypon 4C

Maypon is an anionic surfactant that is based on hydrolyzed collagen. It is used in shampoo to help remove proteinacious yuck from our hair and scalp. Again, applying the idea of “like attracts like” this is a good candidate for trying to solubilize a coating with a component of protein or a very degraded animal glue. While it is certainly no where near as effective as an enzyme at removing animal glue, it can sometimes be just enough to coax a material partly bound with glue to yield or even a very thin or degraded glue film to go into solution. Maypon can be used down to a pH of about 5. At a pH of 4.6, it separates.

There are literally hundreds of thousands of other surfactants available. Plus many surfactants from different manufacturers have the same or very similar composition.

*Wolbers, Richard. *Cleaning Painted Surfaces: Aqueous Methods*. Archetype Publications: 2000.

† “The HLB System,” a PDF of a Power Point presentation ©2005 by Uniqema Ltd. at croda.com/download.aspx?133&doc&id=267.