SP MORELL
ELEMENTS TO SOLUTIONS
back$_2$basics

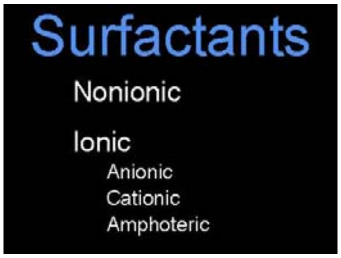
Surfactants – Chemistry and Theory

A major challenge within the coating and ink industries is to formulate more environmentally acceptable end products that comply with increasingly restrictive governmental regulations on volatile organic compounds. However, the technological switch from a dependence on hydrocarbon systems will not be an easy one since there are inherent problems associated with potential waterborne alternatives. Application, performance, and formulating challenges include wetting over low energy surfaces, foam, water sensitivity, rheology, and flow and leveling.

This paper will review the chemistry and theoretical behavior of surfactants in waterborne applications. Topics covered will compare the structures of both nonionic and ionic surfactants. An understanding of how surfactants function with respect to surface tension reduction, wetting, foam stabilization and control, as well as VOC implications will be covered.

It is our hope that you will find this and other issues of **back$_2$basics** sufficiently informative and in-depth to save to your electronic library. A PDF format is available by e-mailing us at Solutions@SPMorell.com.

Chemistry



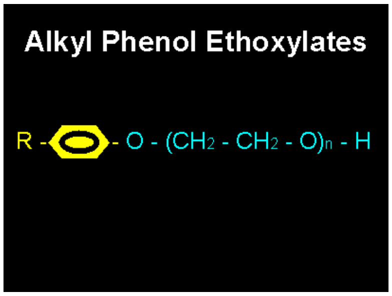
Surfactants
- Nonionic
- Ionic
  - Anionic
  - Cationic
  - Amphoteric

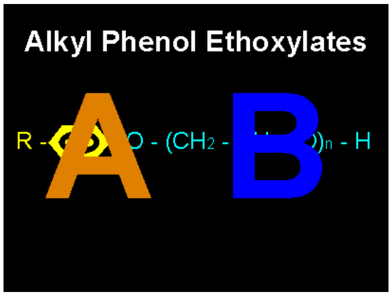
The world of surfactants can be broken down into two distinct groups – ionic (those that have a charge associated with them) or nonionic (those that do not carry any associated charge). Within the ionic group, there are negatively charged species (anionic), positively charged species (cationic), and those that can be either negative or positive (amphoteric) depending upon the pH of the environment. Generally, most waterborne coating and ink formulations are produced with either nonionic or anionic surfactants.

The chemistry and structure of surfactants vary greatly and include, but not limited to, the following: alkyl phenol ethoxylates, dioctyl sulfosuccinates (DOSS), block copolymers of ethylene and propylene oxides, acetylenic diols, silicone surfactants, and fluorosurfactants.

In order to exhibit surface or interfacial active properties, a surfactant molecule is generally constructed with both hydrophilic (water loving) and hydrophobic (water fearing) moieties. As such, a wide array of properties and performance characteristics can be achieved depending upon the chemistry, amount, and arrangement of these hydrophilic and hydrophobic components.

Most surfactants are based on the arrangement of the hydrophobe on one end of the molecule (component A) and the hydrophile on the opposite end (component B). Alkyl phenol ethoxylates (nonyl phenol or octyl phenol) are good examples. The alkyl phenol is hydrophobic (A) and the units of ethylene oxide are hydrophilic (B). This conventional arrangement (AB) accounts for the majority of surfactants commercially produced and is graphically illustrated below.


Alkyl Phenol Ethoxylates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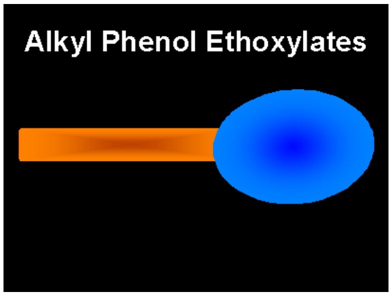
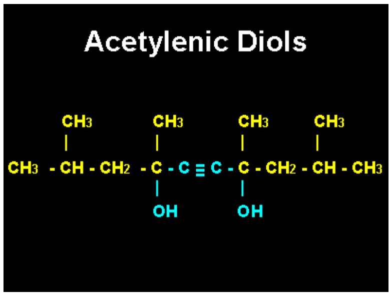

Alkyl Phenol Ethoxylates

While alkyl phenol ethoxylates are examples of nonionic AB structures, fluorosurfactants add yet another degree of surface activity by contributing a negatively charged hydrophile. The most common type for waterborne systems were based on metal salts (potassium) of perfluoro octyl (C_8) sulfonate (PFOS). However, EPA concerns over bioaccumulation of the raw materials used to produce these products have forced the industry to consider alternative fluoro technologies including those based on fluorinated C_1, C_2, and C_4 carbons.


Acetylenic Diols

Acetylenic diols are examples of nonionic surfactants that exhibit ABA structures. The combination of the triple bond and the two adjacent hydroxyl groups creates a domain of high electron density giving polarity to the molecule. The central portion of the surfactant is hydrophilic whereas the highly branched methyl groups, along with the backbone, supplies the hydrophobic parts.

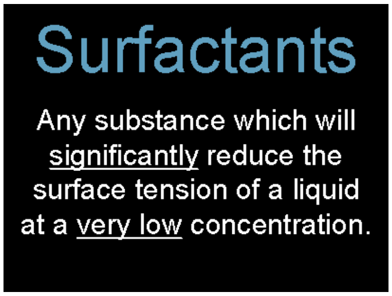
Poly dimethyl siloxanes are another example of ABA surfactants. The central ethylene oxide units offers hydrophilicity whereas the surrounding dimethyl siloxanes contribute to it's hydrophobic nature. The reverse can be achieved when block copolymers of ethylene and propylene oxides are employed to produce BAB structures. Here the central hydrophobic component is made of units of propylene oxide and the end blocks are based on ethylene oxide units.

An anionic version of the ABA structure is exemplified by dialkyl sulfosuccinates. Dioctyl sulfosuccinates (DOSS), for example, have central, yet negatively charged, hydrophiles along with end blocking hydrophobic components (dioctyls).

Theory

The relevance of AB, ABA, BAB, and their charged counterparts, with respect to properties and their contribution to waterborne formulations will be reviewed next. However, due to the complexity of this subject matter, it may be best to begin with the basics and a good place to start is with a definition of the word "surfactant."

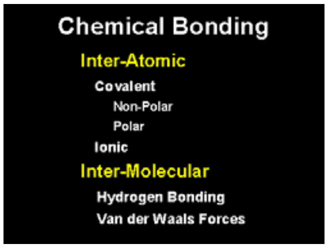
The word "surfactant" is an acronym formed by combining the words "surface active agent". A surfactant can be defined as any substance which will significantly reduce the surface tension of a liquid at a very low concentration.


Surfactants

Any substance which will significantly reduce the surface tension of a liquid at a very low concentration.

The words "significantly" and "very low" are purposely underscored to highlight the fact that many products can reduce the surface tension of liquids but may require amounts significantly higher than surfactants as we define them. For example, alcohols can reduce the surface tension of water but due to their solubility will not concentrate at the surface or interface and, therefore, higher concentrations are needed to achieve the same result. The addition of organic solvents to achieve surface tension reduction will also negatively impact VOCs, safety (flammability), and health.

Returning to our definition of surfactants, there may be other terms that are not fully understood. For example, what is meant by the words “surface tension?” What tension is the surface under? To better appreciate this concept, one must return to Chemistry 101 and review the nature of chemical bonding.



Chemical Bonding

- Inter-Atomic
  - Covalent
    - Non-Polar
    - Polar
  - Ionic
- Inter-Molecular
  - Hydrogen Bonding
  - Van der Waals Forces

Chemical bonding can be grouped into two categories – inter-atomic and inter-molecular. Inter-atomic bonding (attractive forces between atoms) can either be covalent (sharing of electrons between atoms) or ionic (attraction of oppositely charged atoms). Examples of inter-molecular bonding (attractive forces between molecules) include hydrogen bonding and Van der Waals forces. Let’s review inter-atomic bonding first as it will lead to a better understanding of inter-molecular attractive forces.

The goal of each atom is to migrate towards equilibrium and, thus, achieve a more stable energy state. To achieve this, atoms would prefer to have their outer most shell filled with orbiting electrons. The shells around the nucleus (a total of 7), and the maximum number of electrons orbiting around within each shell, are as follows: 2, 8, 8, 18, 18, 32, and 32.

Helium, for example, with an atomic number of 2, has one shell and two electrons orbiting within that shell. Since it’s outermost shell (there’s only one to begin with) is complete with it’s two electrons, there would be no need for helium to congregate with other atoms to achieve a lower energy state. For that reason, helium (or any other atom who’s shells are replete with the maximum allowed electrons) are considered inert.

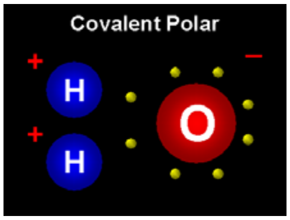
On the other hand hydrogen, with an atomic number of 1, also has one shell but only 1 electron orbiting within it’s shell. To be complete, it would prefer to gain an additional electron. One option would be for this atom to congregate with another hydrogen atom and share each of its respective electrons to achieve what appears to be 2 electrons orbiting around it’s outer shell. This would result in a more stable state and for that reason hydrogen gas always exists as H_2 as opposed to H. Note that Helium gas exists simply as He – no need to tag up with another helium atom to form He_2.

Since each hydrogen atom, in hydrogen gas (H_2), has the same exact desire to complete it’s outer shell, there is an equal sharing of the electrons between the two atoms. Thus we say H_2 is a covalent (sharing of electrons), non-polar (equal sharing), molecule.

Now let’s examine oxygen. With an atomic number of 8 it has two shells and a total electron count of 8. There are two electrons in the first shell and that leaves six in it’s second, or outermost, shell. However, the outermost shell would be complete with 8 electrons and, thus, oxygen would prefer to find two additional electrons.

One option would be to congregate with two hydrogen atoms (each has one to share) and again achieve what appears to be a more stable state. However, since the oxygen atom has about ¾ of it’s outer shell already complete (6 electrons out of 8) compared to the hydrogen atom with half of it’s outer shell complete (1 electron out of 2), there would be a tendency for the oxygen atom to “draw in” or disproportionately share the hydrogen electrons.

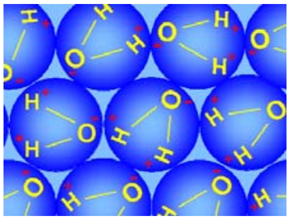
The propensity for atoms to either evenly share, “draw in”, or even grab electrons from other atoms is directly related to the atom’s outermost shell state with respect to electron completion. Dr. Linus Pauling developed an electronegativity scale (ranging from 1 to 4) which better predicts this behavior. Hydrogen has an electronegativity of 2.1 whereas oxygen has an electronegativity of 3.5.



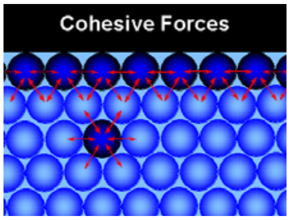
Because of it's higher electronegativity, oxygen will pull the hydrogen electrons closer to it's nucleus and, as a result, create a covalent (sharing of electrons), polar (disproportionate sharing), molecule of water. This "hogging" of electrons by the oxygen atom leads to a slight negative charge on the oxygen's atom and a corresponding slight positive charge on the hydrogen atoms. Therefore, think of this water molecule as molecular sized magnet.

There is yet one more inter-atomic attractive force to review beyond covalent non-polar (even sharing of electrons) and covalent polar (disproportionate sharing of electrons). With ionic attractive forces there is no sharing . . . . there's simply grabbing of electrons!

Chlorine, with an atomic number of 17, has 3 shells with a total of 17 electrons. Thus, the first 2 shells are replete with 2 and 8 electrons respectively. The third and outermost shell has the remaining 7 electrons and, therefore, chlorine only needs to capture 1 to complete this shell. Sodium, with an atomic number of 11, also has 3 shells with a total of 11 electrons – 2 in the first shell, 8 in the second, and the remaining 1 in it's outermost shell. Because of the relatively higher electronegativity of chlorine (7/8 of it's outer shell is complete) compared to sodium's electronegativity (1/8 of it's outer shell is complete), the chlorine atom will take (and the sodium atom will gladly donate) the needed electron. Now both atoms have filled outer shells but the taking and corresponding giving of the electron has resulted in a negative charge on the chlorine atom and a positive charge on the sodium atom. Since opposites attract, we have ionic bonding, thus, $Na^+ Cl^-$.



Now that we understand the behavior of inter-atomic attractive forces, we can easily extrapolate to inter-molecular attractive forces such as hydrogen bonding. Since H_2O, for example, is considered polar (a molecular sized magnet), imagine the arrangement and networking of many water molecules with themselves by aligning the slightly negative charge of one end of the molecule to the slightly positive charge of another end of another water molecule.

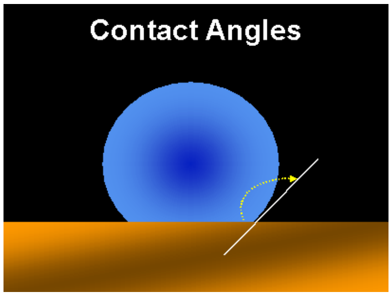


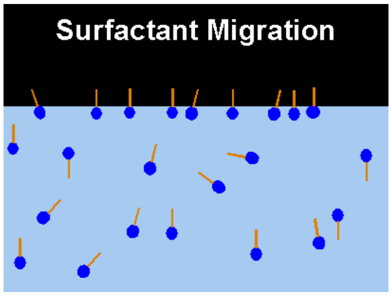
With the absence of external forces, we can imagine that a water molecule in the bulk would be at equilibrium as inter-molecular attractive forces above, below, in front, behind, and to the sides are all even. However, the water molecules on the surface behave differently as there are attractive forces below and to the sides but nothing above. Thus, water molecules at the surface posses a net attractive force into the bulk and, thus, surface tension is created.

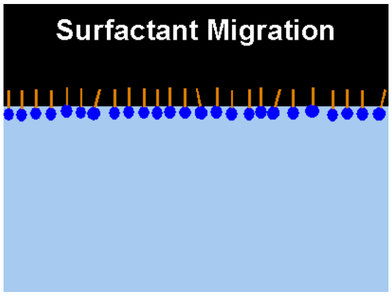
Because of surface tension, liquids (particularly water with its very high surface tension) will bead up since surface molecules will be "pulled" towards the bulk and, thus, expose the least amount of surface area. Given the same volume of liquid, the geometrical configuration that exposes the least amount of surface area is a sphere. Notice what happens to liquids that escape astronaut pouches in a gravity free environment.

Therefore, think of liquids with internal cohesive forces. When a drop of water is placed on a substrate (a metal panel for example) there is a natural tendency to bead up because of cohesive forces. Yet, there are also other attractive forces in play that allows water to adhere to the same substrate. For example, turning the metal panel over will demonstrate that the water bead still clings to the substrate in spite of gravitational pull.

The phenomenon of wetting, or lack thereof, is determined by the net balance of both cohesive forces within liquids and attractive forces between liquids and other materials. If the liquid has extremely high cohesive forces and low attractive forces (i.e. mercury) there will be no association with the substrate and, in this case, the spherical mercury bead would easily run off the panel.

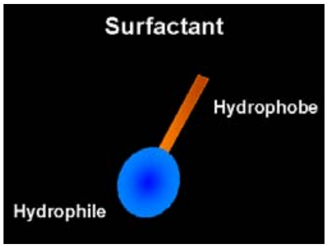






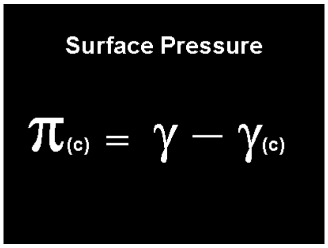
One measure of wetting is to record contact angles - a line tangent to the bead's contact with the substrate. The higher the angle the less wetting and, therefore, the understanding of higher cohesive forces at work compared to attractive forces. The converse is true with lower contact angles – less cohesiveness compared to attractive forces and, thus, improved wetting.

However, if we can alter the surfaces of liquids to either reduce it's surface tension and/or enhance it's attractive forces to other materials, we will be able to achieve lower contact angles and, thus, improve wetting. Enter surfactants!



The ability of a surfactant to reduce the surface tension of water results from the combined hydrophilic and hydrophobic parts of its structure.

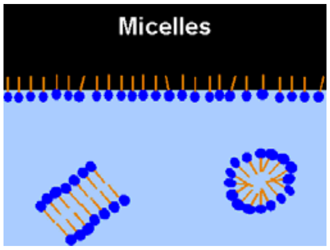
As a result of its hydrophobic component, surfactant molecules are forced to migrate to the water/air interface when added to an aqueous medium. The presence of surfactant molecules at this interface, results in a compressive force acting on the surface. A force that is known as surface pressure. A simple experiment which demonstrates surface pressure occurs with a limp loop of thread on water. It will snap into a circle when the water inside is touched by soap. It is this surface compressive force, or surface pressure, that reduces the surface energy or surface tension.



Surface Pressure

$$\pi_{(c)} = \gamma - \gamma_{(c)}$$

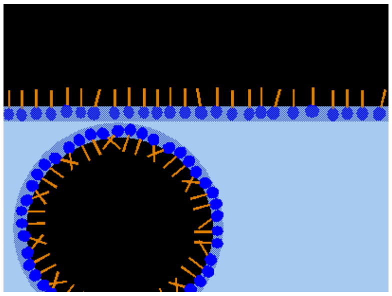
It is often difficult to relate to the concept of surface tension. It's much easier to think in terms of surface pressure and there is a relationship between the two terms and it is shown in this equation. The surface pressure of a surfactant solution at a certain concentration is equal to the surface tension of the pure solvent minus the surface tension of the surfactant solution at the same concentration. Therefore, as the surfactant concentration is increased, there is an increase in surface pressure and, conversely, a reduction in surface tension.

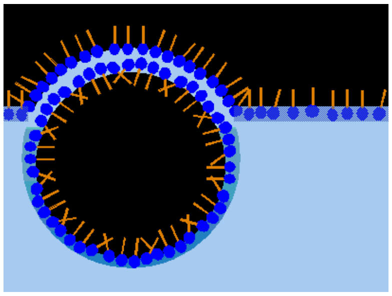


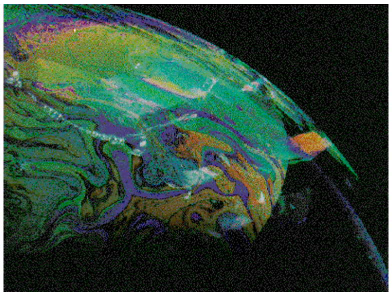
When the surface is completely saturated with surfactant molecules and surface pressure approaches its greatest value, the incremental addition of most surfactants will result in the formation of micelles. This is known as the critical micelle concentration. Micelles are a prerequisite for emulsion polymerization as the hydrophobic monomer droplets work their way into the micelle domain where polymerization takes place. These micelles can take on different forms including spherical or cylindrical shapes.

At high concentrations, most surfactants condense into a structured elastic film as a result of the molecular attraction between the chains of methylene groups in neighboring molecules. This structured film determines the surface property of the surfactant solution. How this mechanism contributes to foam generation can be easily explained by examining how foam bubbles are created and stabilized.

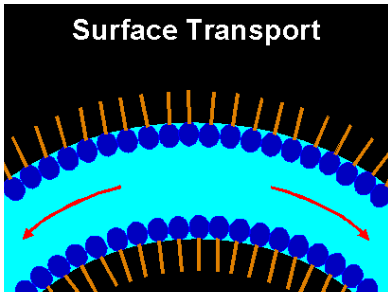
In pure water, an air bubble rises attempting to achieve the same equilibrium state with the denser fluid on the bottom. It should be noted that sustained foam, that is foam in which air or gas is firmly entrapped in a liquid for a considerable interval of time, only occurs in a complicated colloidal system. Therefore, it is not possible for foam to exist in a pure liquid.

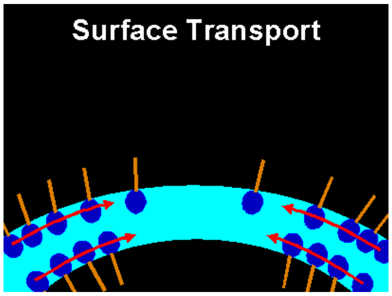


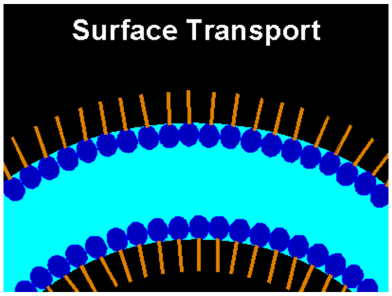




The colloids in a foamy system are surfactants with varying degrees of hydrophillic/hydrophobic balance. Here, the hydrophobic hydrocarbon tails protrude from the water, both at the top surface and within the bubble, with the circular polar hydrophilic heads engaged in the water phase. As mentioned earlier, most surfactants that congregate at this gas/liquid interface are capable of forming a structured elastic film. Therefore, gases which rise in these systems expand these elastic films without rupturing them. The result is entrapped air gradually rising to the surface as froth or bubbles.







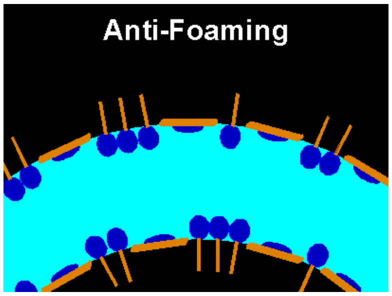
A closer view of the foam bubble wall (the lamella) would reveal the continuous motions caused by concentration gradients along the surface. Drainage of the bulk liquid, due to gravitational forces, results in surface pressure variations. This pressure differential is alleviated by the movement of surfactant molecules from concentrated high pressure areas to lower concentrated areas. Along with this movement is surface transport of water molecules associated with the surfactant's hydrophilic end which, in turn, drags along other bounding water molecules.

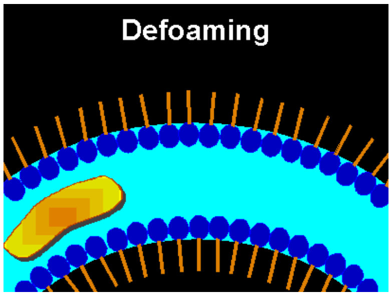
This counter drainage movement is known as the Plateau Maringoni Gibbs effect and is responsible for restoring the bubble wall and giving it its surface elasticity and stability.

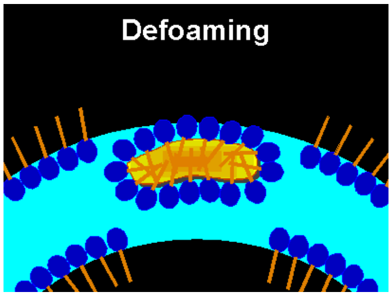
A good example demonstrating surface transport occurs in cocktail glasses. A water alcohol mixture swirled around in a glass leads to a phenomenon called "wine tears", drops that move up and down the side of the glass. Alcohol evaporation of the liquid film on the glass increases its surface tension and, conversely, lowers its surface pressure. The surface is, therefore, continuously pulled from the bulk liquid up the side of the glass. Liquid pumped up in this fashion accumulates to form wine tears.

Let us now examine how non-foaming, anti-foaming, and defoaming agents function to help mitigate this problem.

Because of their hydrophobic nature, some ABA surfactants are capable of diffusing rapidly to the interface and, thus, alleviate any surface pressure differential caused by drainage. If there is no pressure differential, there is no surface transport and, thus, no reconstitution of the lamella. At the final moment, these molecules slip away from each other, due to low intermolecular attraction, and the wall collapses. Thus, non-foaming agents are products that do not sustain foam on their own.







Anti-foaming agents are materials that help control foamy systems generated by other surfactants. Their presence at the surface interferes with the close packing of foam stabilizing species thereby reducing surface monolayer rigidity.

Like anti-foaming agents, defoamers also function by interfering with the stability of the foam bubble's elastic film. They migrate to the interface and capture the hydrophobic ends of the surfactant molecules, rupturing the bubble wall and, thus, causing the foam to collapse.

Conclusion

Surfactants play a key role in transitioning conventional solvenborne formulations to waterborne alternatives. Properly formulated, surfactants will aid in the wetting and coverage of difficult to wet surfaces as well as contribute to the wetting and dispersion of pigments. Because of their interfacial activity, surfactants have been engineered to mitigate surface transport and, thus, contribute to improved flow and leveling. However, the side affects of foam, water sensitivity, and the potential impact on rheology need to be considered when choosing surfactants for specific purposes. These issues, along with the practical application of surfactants, will be addressed in a future **back$_2$bacics** issue.

back$_2$back Issues

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