Reference Guide for Structural Classifications of Surfactants for Use in Determining if a New Chemical Substance is a Surfactant

Summary

Surfactants (surface active agents) are chemical substances that can modify the surface properties of a liquid. The purpose of this document is to provide a concise reference guide for the structural assessment of a new chemical substance (NCS) to determine if it is a surfactant. This reference document provides a summary of the properties and basic structural features of surfactants, which will enable users to determine if an NCS should be screened as a surfactant.

1. PROPERTIES OF SURFACTANTS

1.1 General Structural Properties

Structurally, all surfactants are amphiphilic compounds. Thus, for an NCS to be classified as a surfactant, it must be an amphiphilic chemical substance, meaning its chemical structure has both a hydrophilic "head" group and a hydrophobic "tail" region. The hydrophilic head is polar and water-soluble, while the hydrophobic "tail" is nonpolar and water-insoluble, and has an affinity for fats/oils (lipophilic). This is the main common structural feature of all surfactants. It determines their properties in solution and, therefore, their uses.[1, 2]

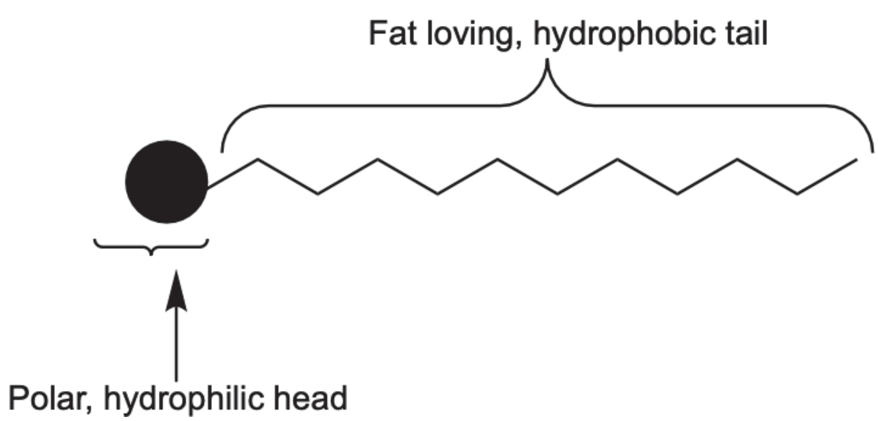

Figure 1. Amphiphilic nature of surfactants

The amphiphilic structure, shown in Figure 1, enables surfactant chemical substances to preferentially adsorb at the interfaces between liquid-gas, liquid-liquid, or liquid-solid. Surfactants reduce the surface (interfacial) tension between two immiscible phases, such as oil and water. This change in interfacial tension subsequently improves the dispersion or solubilization of one phase into the other immiscible phase.

1.2 Physico-Chemical Properties of Surfactants

The amphiphilic structure of surfactants results in certain physico-chemical properties that can be experimentally measured or theoretically estimated. Therefore, the following properties can be used to determine if an NCS can be classified as a surfactant:

a. **Surface tension.** This is the force or tension existing at the interface between a liquid (e.g., water) and gas (e.g., air). It is a measure of internal cohesive force within the liquid, which indicates how much the molecules interact with neighboring molecules (of either liquid or gas or both).[3] Surface tension is measured as the force (in millinewton) acting along the surface per unit length (meter), usually expressed as millinewton/meter (mN/m). Addition of a surfactant to a liquid will lower the surface tension. For example, the surface tension of water at room temperature is 72.8 mN/m. Addition of a surfactant to water will lower the surface tension below 72.8 mN/m. The effect of a surfactant on the surface tension is directly dependent on the concentration of the surfactant up to the critical micelle concentration (CMC), the minimum concentration of the surfactant at which micelle formation takes place.

   If an NCS lowers the surface tension of water below 72.8 mN/m, it is an indication that the NCS may be a surfactant. However, this is not the exclusive property of a surfactant: while all surfactants lower the surface tension of water, not all chemical substances that lower the surface tension are surfactants.

   The greater the strength of the surfactant, the more it can lower the surface tension of water. Examples of some common types of surfactants and the range to which they lower the surface tension of water are shown in Table 1.[4] The "strength of a surfactant" as used here refers to an intrinsic chemical property based on the chemical structure of the surfactant. It does not refer to concentration.

Table 1. Surfactants and Their Effects of Surface Tension of Water.[4]

Types of Surfactants	Surface Tension (mN/m) of Water upon Addition of Surfactant
Silicone surfactant	20-30
Hydrocarbon surfactant	30-40
Perfluoro-surfactant	15-20

b. **Critical Micelle Concentration (CMC).** The CMC of a surfactant is the minimum concentration of the surfactant at which it forms micelles. Micelles are self-assembling molecular aggregates consisting of hydrophobic cores and hydrophilic capsules. They are formed by amphiphilic molecules. Formation of micelles is one of the most important physico-chemical parameters of a surfactant and the CMC is the common physico-chemical property that scientists routinely measure for surfactants. It provides the thermodynamic threshold at which the chemical substances self-assemble into micelles. The lower the CMC value, the stronger the surfactant property. If a CMC value is reported for an NCS, then it is a surfactant.[5]

The comparison in Table 1 assumes that the concentrations are kept constant at a constant temperature. However, it should be noted that a very high concentration of a weak or poor surfactant will not drastically change the surface tension of water. The concentration at which the optimum surface tension is measured is around the CMC. Once the CMC is reached, the surface tension of water remains relatively constant.

c. **Hydrophilic/Lipophilic Balance (HLB).** Surfactants possess a property referred to as "hydrophilic power," which is related to their solubility in water and oil and is reported as the Hydrophilic/Lipophilic Balance (HLB). The Griffin's method for determining HLB gives a dimensionless quantity with values ranging from 0-20. For an NCS to be classified as a surfactant, the reported or estimated HLB value must fall between 1 and 19. Table 2 shows classification of surfactants based on HLB values.[6]

Table 2. HLB Values for Classifying Surfactants.[6]

HLB Range	Surfactant Properties/Use	Solubility Range
1.5-3	Defoamer	↑ Lipophilicity
4-6	Water-in-oil emulsifier	
7-9	Wetting agents	
8-18	Oil-in-water emulsifier	↓ Hydrophilicity
13-15	Detergents	
15-18	Solubilizing agent and peptizer	

1.3 Specific Uses of Chemical Substances that May Signify that They are Surfactants

If an NCS is reported to have any of the properties described in Section 1.2 and/or uses described here in Section 1.3, there is a high probability that it is a surfactant. Some common uses of surfactants are:

a. Wetting agent
b. Foaming agent
c. Emulsifying or dispersing agent
d. Suspending or stabilizing agent
e. Solubilizing property or agent
f. Antifogging
g. Antifoaming and/or defoaming agent
h. Deinking property or agents
i. Detergent

However, it is notable that not all chemicals with these uses are surfactants. Specifically, there are chemical substances that are designed to perform some of these functions and do not have the physical properties of a surfactant. As such, use pattern cannot be used solely as a determinant of a surfactant.

2. CLASSIFICATION OF SURFACTANTS BASED ON FUNCTIONAL GROUPS AND CHEMICAL STRUCTURES

Section 1.2 describes the physico-chemical properties that can be used to determine whether an NCS is a surfactant. However, for some NCSs, this information is not available. If experimental or theoretical (estimated) physico-chemical properties are unavailable for identifying an NCS as a surfactant, the chemical structure can be assessed.

A simple process for this structural assessment is shown in Figure 2 and is described in greater detail in the following sections. In summary:

- The first step in the structural assessment is to determine if the NCS has distinct hydrophilic and hydrophobic parts.
- Without clear hydrophilic and hydrophobic structural moieties, the NCS is not a surfactant.
- If the NCS has distinct hydrophilic and hydrophobic moieties, then the chemical substance should be assessed for ability to dissolve in a liquid (such as water) and move to its surface. This is a unique structural feature of surfactants which will enable the NCS to lower the surface tension of a liquid and ultimately form micelles in the liquid as concentration goes up.
- If the NCS meets these criteria, it should be categorized as a surfactant.
- If it does not meet them, it is not a surfactant.
- If the hydrophobic part (tail) is too short (less than 8 carbons) and the hydrophilic part (head) is too large (cluster of polar and ionic species), the chemical substance will dissolve in water, but it will not be a surfactant. It would likely be categorized as a salt or an acid.
- If the hydrophobic part (tail) is too long or big (longer than 20 carbons or several aromatic rings) and the hydrophilic part (head) is too small, it will not dissolve or mix with water. It will likely act like oil or wax.

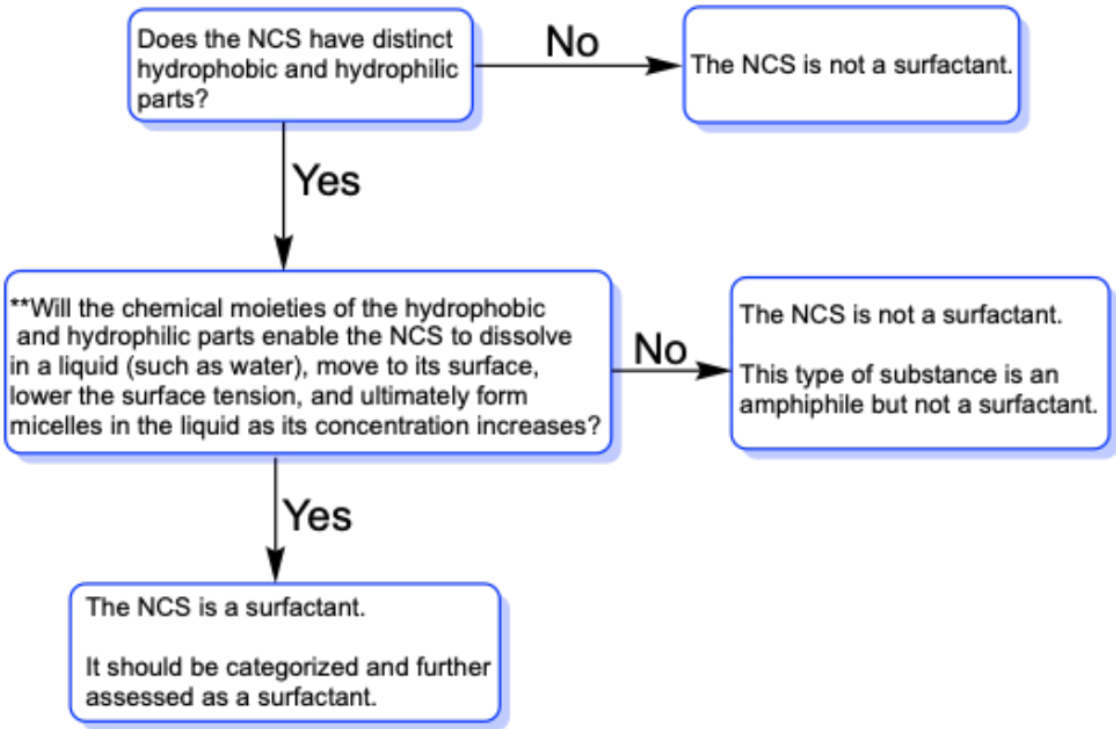

Figure 2. Flowchart showing how to assess if an NCS is a surfactant based on chemical structure

***Whether an NCS will dissolve in water and lower its surface tension can be determined by visual inspection of its hydrophobic and hydrophilic chemical moieties. For surfactants, the hydrophobic part (tail) should be about 8 to 20 carbons (Figure 3). The hydrophilic part (head) should be polar and/or ionic species (shown in Figures 4 to 7) large enough to pull the entire chemical substance into water.*

2.1 Distinct Hydrophobic and Hydrophilic Regions of a Surfactant

The hydrophobic region of a surfactant typically has at least 8 carbons (C8), which may be a straight chain aliphatic, alicyclic, or aromatic hydrocarbon. A surfactant may also contain halogens. Representative structures are shown in Figure 3.

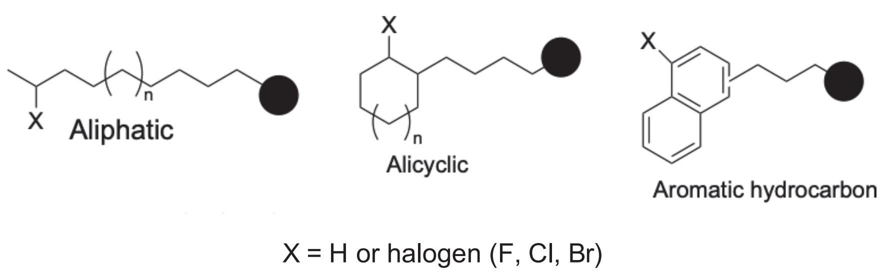

Figure 3. Representative hydrophobic region of a surfactant

The hydrophilic region of a surfactant contains heteroatoms, such as oxygen, sulfur, nitrogen, and phosphorus. Heteroatoms are non-carbon atoms that replace carbon in the backbone of the molecular structures. These are seen in functional groups like alcohol, thiol, ether, ester, acid, sulfate, sulfonate, phosphate, amine, amide, and so on.

The polar hydrophilic head can be classified as anionic, cationic, non-ionic, or amphoteric or zwitterionic. The type of hydrophilic head can also be used to describe (or classify) a surfactant.

Anionic hydrophiles (for anionic surfactant). These surfactants have functional groups that ionize in the aqueous phase to liberate negatively charged ions and contain cations that can be alkali metal-like (Na^+, K^+) or quaternary ammonium ions (NR_4). Examples of anionic groups in anionic surfactants are shown in Figure 4.

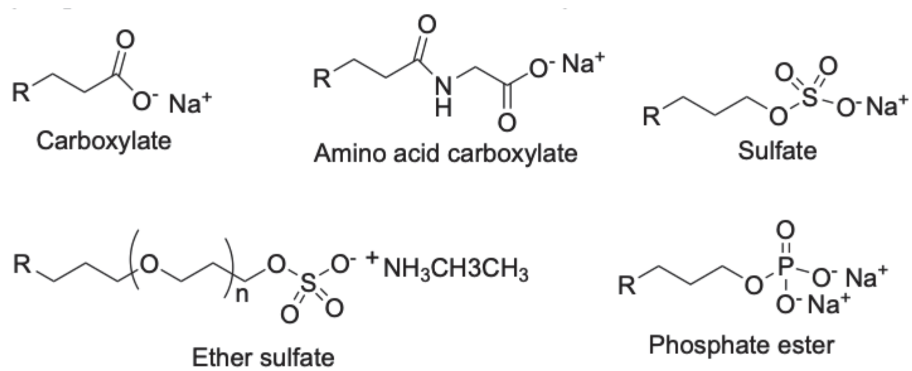

Figure 4. Representative anionic moieties of an anionic surfactant

Cationic hydrophiles (for cationic surfactants). These surfactants have functional groups that ionize in the aqueous phase to liberate positive ions. The hydrophilic (polar) head is positive, and this enables the surfactant to adsorb easily onto negatively charged substrates. Examples of chemical functional groups in this category include quaternary ammonium and phosphonium cations. Representative examples are shown in Figure 5.

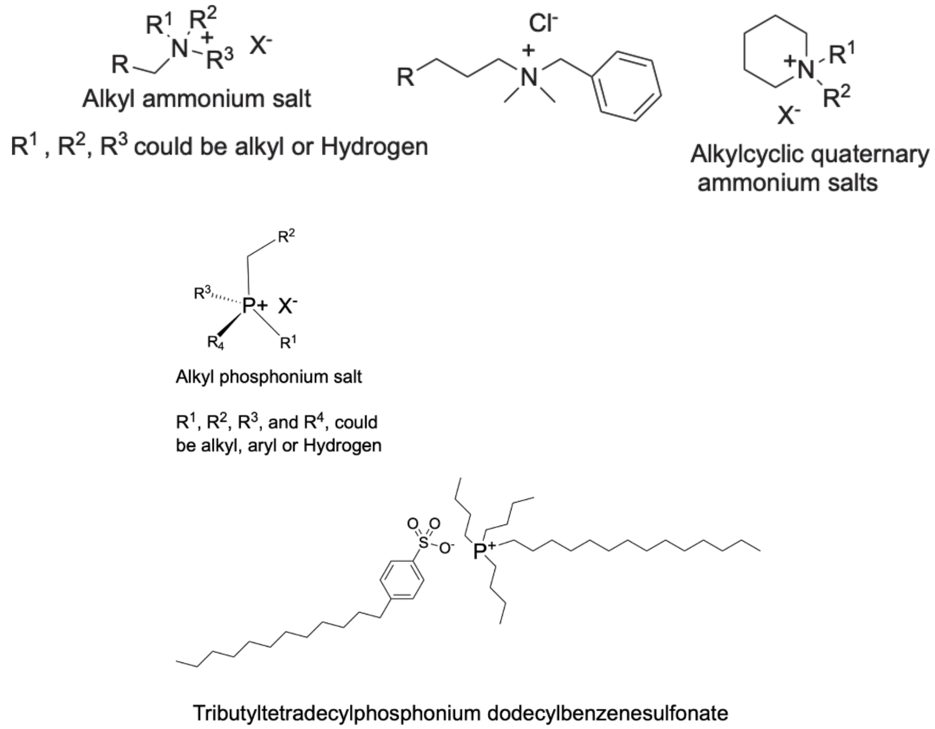

Figure 5. Representative cationic moieties for a cationic surfactant

Non-ionic hydrophiles (for non-ionic surfactants). These surfactants contain an uncharged polar chemical moiety as the hydrophilic head. In these types of surfactants, several polar groups are bonded to a saturated or slightly unsaturated hydrocarbon (represented as R in the examples in Figure 6). Polar groups may include ether, alcohol, carbonyl, and/or amine moieties, with different combinations of carbon and electronegative heteroatoms like oxygen, nitrogen, or sulfur or may be a polymeric chain such as polyoxyethylene chain. Examples are shown in Figure 6.

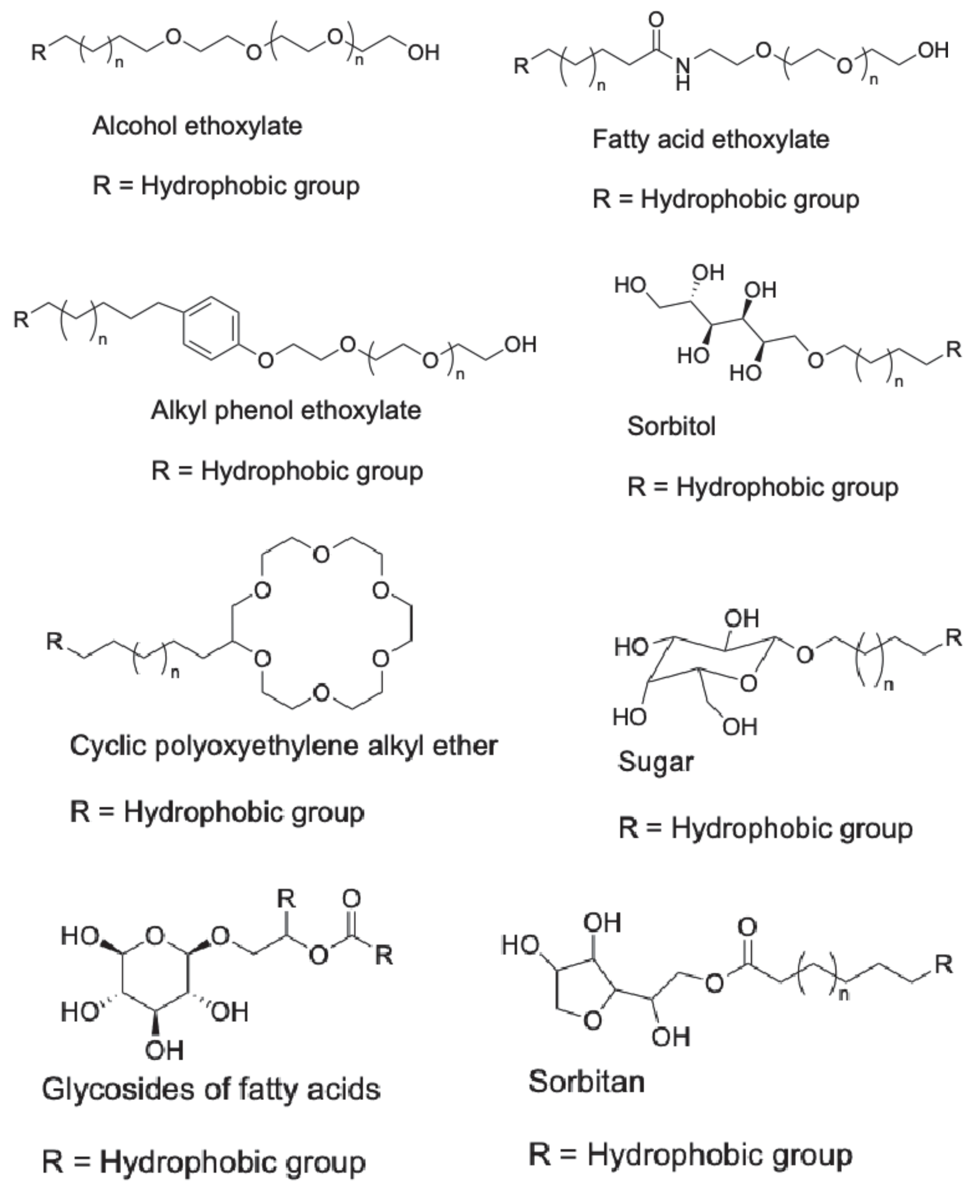

Figure 6. Representative non-ionic moieties for nonionic surfactants

Amphoteric or zwitterionic hydrophiles (for amphoteric surfactants). These surfactants contain a hydrophilic head with two separate functional groups or moieties, one of which is positively charged (cationic) and the other is negatively charged (anionic). For most of these surfactants, the main ionic property displayed by the hydrophilic head at a given point in solution is dependent on the pH of the solution. These hydrophiles are similar to natural phospholipids surfactants.[7, 8] Examples are shown in Figure 7.

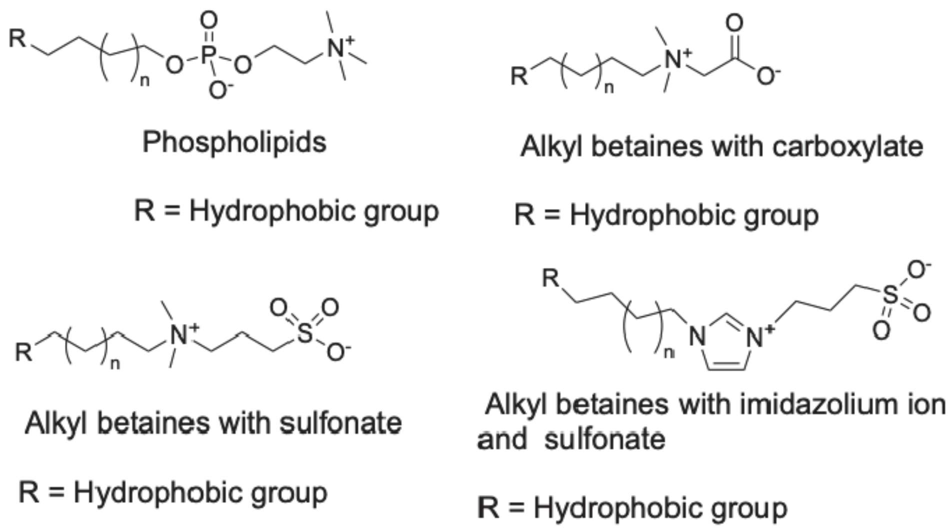

Figure 7. Representative zwitterionic moieties for zwitterionic surfactants

Although the chemicals described in this memorandum are not a complete list of the diverse chemical structures of all the hydrophobic and hydrophilic chemical moieties of surfactants, this memorandum provides a guide for users to determine if an NCS is a surfactant by comparing the chemical structure of the NCS to the structures described herein.

In summary, the distinct presence of a hydrophilic and hydrophobic region in the chemical structure of a chemical substance is the first indication that it may be a surfactant. Physico-chemical properties such as surface tension, CMC, and HLB are important to determine the strength of a surfactant. Certain uses of a chemical substance may also suggest that it is a surfactant, for example, wetting agent, detergent, emulsifier, or foaming agent. Combining the physico-chemical properties of the NCS with its structural information is an effective way to assess its strength as a surfactant.

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