

# A Study of Chemical Properties of Some Surfactant Solutions

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## Abstract

Surfactants form a unique class of chemical compounds. This review provides to the nature and physical properties of surfactants, emphasizing their ability to radically alter surface and interfacial properties and to self-associate and solubilize themselves in micelles. These properties provide the means to apply surfactants in wettability modification, detergency, and the displacement of liquid phases through porous media on one hand, and to stabilize dispersions (including foams, froths and emulsions), or to destabilize dispersions (again including foams and emulsions) on the other hand. These in turn lead to a vast array of practical application areas which are illustrated in terms of mineral and petroleum processing, biological systems, health and personal care products, foods, and crop protection.

**Keywords:** *Chemical Properties, Surfactant Solutions, chemical compounds, crop protection*

## 1. INTRODUCTION

The widespread importance of surfactants in practical applications, and scientific interest in their nature and properties, have precipitated a wealth of published literature on the subject. Good starting points for further basic information are classic books like those of Rosen, Myers, and Mittal. There are many other books on surfactants 5–18 including Karsa's Industrial Applications of Surfactants series and the volume Surfactant Science Series. There are also glossaries and dictionaries covering terminology in surfactant science and technology. Most good colloid chemistry texts contain introductory chapters on surfactants; good starting points are references. For more detailed treatment of advances in specific surfactant related areas the reader is referred to some of the chapters available in specialist books.30–35 For example, four recent books describe the principles and occurrences of surfactants, emulsions, foams, and suspensions in the petroleum industry. The most comprehensive source for surfactant information on the internet is probably Huibers' The Surfactants Virtual Library, which contains over 1000 links to surfactant and detergent related web sites.

The surfactant industry is dominated by several types: alkyl benzene sulfonates, alcohol ethoxylates, sulfates and ethersulfates. These are the major components of laundry detergents, household, and personal care products and account for over half of all use of surfactants. Interest in increasing performance in these areas has also led to research into mixed surfactant systems. Other commercial interests have also influenced the developments in surfactant science. For example in the 1970s, during the oil crisis, new methods of enhanced oil recovery, such as microemulsions, were heavily investigated. Scientific curiosity has also driven surfactant research into areas such as organization of surfactant molecules into interesting shapes and structures, all with unique properties. Surfactants have even been the subject of investigation into the origins of life, meteorites containing lipid-like compounds have been found to assemble into boundary membranes and may be an interstellar prebiotic earth source of cell-membrane material. Over the past ten years, new surfactant molecules have been appearing at a relatively rapid pace. This growth in surfactant synthesis has, not surprisingly, paralleled the emphasis on increasing the basic performance of surfactant formulations and the provision of new surfactant technologies to a diverse range of disciplines. Although surfactant science is now a reasonably mature discipline, there is still room for new molecules designed for specific purposes and new applications (such as nanoparticle synthesis and more diverse and environmentally friendly consumer products). These new materials have spurred on the quest for improved molecular models, computer simulations, and improved structure–activity relationships. New functionalized surfactants depend critically on the nature and placement of additional functional groups. Slight modifications of the

molecular structure with respect to conventional surfactants lead to a rich morphology of structures that are being explored by increasingly more sophisticated techniques and, in turn, enhancing our understanding of their properties at a molecular level.

One of the original and predominant reasons for the ubiquitous deployment of surfactants is their remarkable ability to influence the properties of surfaces and interfaces, and to thereby have an impact on industrial processes and products, as will be discussed below. The applications of surfactants in industry area are quite diverse and have a great practical importance. Surfactants may be applied to advantage in the production and processing of foods, agrochemicals, pharmaceuticals, personal care and laundry products, petroleum (see Table 1), mineral ores, fuel additives and lubricants, paints, coatings and adhesives, and in photographic films. They can also be found throughout a wide spectrum of biological systems and medical applications, soil remediation techniques, and other environmental, health, and safety applications

**Table 1 Some examples of surfactant applications in the petroleum industry**

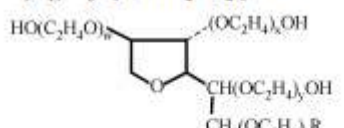
Gas/liquid systems	Producing oil well and well-head foams Oil flotation process froth Distillation and fractionation tower foams Fuel oil and jet fuel tank (truck) foams Foam drilling fluid Foam fracturing fluid Foam acidizing fluid Blocking and diverting foams Gas-mobility control foams
Liquid/liquid systems	Emulsion drilling fluids Enhanced oil recovery in situ emulsions Oil sand flotation process slurry Oil sand flotation process froths Well-head emulsions Heavy oil pipeline emulsion Fuel oil emulsions Asphalt emulsion Oil spill emulsions Tanker bilge emulsions
Liquid/solid systems	Reservoir wettability modifiers Reservoir fines stabilizers Tank/vessel sludge dispersants Drilling mud dispersants

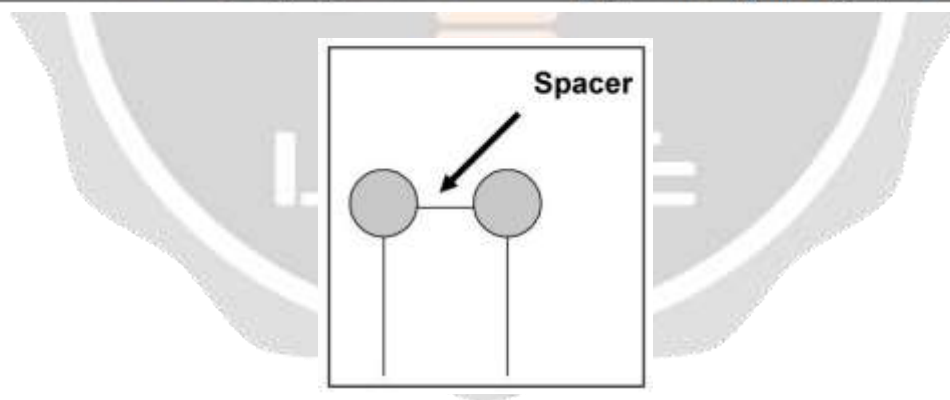
## 2. SURFACTANTS AND THEIR SOLUTIONS

Some compounds, like short-chain fatty acids, are amphiphilic or amphipathic, i.e., they have one part that has an affinity for nonpolar media and one part that has an affinity for polar media. These molecules form oriented monolayers at interfaces and show surface activity (i.e., they lower the surface or interfacial tension of the medium in which they are dissolved). In some usage surfactants are defined as molecules capable of associating to form micelles. These compounds are termed surfactants, amphiphiles, surface-active agents, tensides, or, in the very old literature, paraffinchain salts. The most commonly used term, surfactant, was originally registered as a trademark for selected surface-active products and later released to the public domain. Soaps (fatty acid salts containing at least eight carbon atoms) are surfactants. Detergents are surfactants, or surfactant mixtures, whose solutions have cleaning properties. That is, detergents alter interfacial properties so as to promote removal of a phase from solid surfaces. The unusual properties of aqueous surfactant solutions can be ascribed to the presence of a hydrophilic head group and a hydrophobic chain (or tail) in the molecule. The polar or ionic head group usually interacts strongly with an aqueous environment, in which case it is solvated via dipole–dipole or ion–dipole interactions. In fact, it is the nature of the polar head group which is used to divide surfactants into different categories, as illustrated in Table 2. Compared with the commonly encountered hydrocarbon-based surfactants, substituting fluorocarbon into the structure creates a molecule that is resistant to oxidation, and, because of the smaller size of fluorine over

hydrogen atoms, the surfactants are more rigid in structure thus having a strong surface tension lowering action, water and oil repellency, thermal resistance, chemical resistance and lubricating ability. An application of hybrid fluoride–hydrogen containing surfactants is in water-based paints. Adding silicone into fluorine-containing surfactants creates quality lubricants, good defoamers, and even molecules with a high anti-HIV activity. There is also an entire class of surfactants known as microbial, or biosurfactants, which have some very interesting and complicated structures, although being expensive to produce compared to chemically synthesized surfactants.

**Table 2 Surfactant classifications**

Class	Examples	Structures
Anionic	Na stearate Na dodecyl sulfate Na dodecyl benzene sulfonate	$\text{CH}_3(\text{CH}_2)_{16}\text{COO}^- \text{Na}^+$ $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4^- \text{Na}^+$ $\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{SO}_3^- \text{Na}^+$
Cationic	Laurylamine hydrochloride Trimethyl dodecylammonium chloride Cetyl trimethylammonium bromide	$\text{CH}_3(\text{CH}_2)_{11}\text{NH}_3^+ \text{Cl}^-$ $\text{C}_{12}\text{H}_{25}\text{N}^+(\text{CH}_3)_3\text{Cl}^-$ $\text{CH}_3(\text{CH}_2)_{13}\text{N}^+(\text{CH}_3)_3\text{Br}^-$
Non-ionic	Polyoxyethylene alcohol Alkylphenol ethoxylate  Polysorbate 80 $w + x + y + z = 20$ $\text{R} = (\text{C}_{17}\text{H}_{33})\text{COO}$  Propylene oxide-modified polymethylsiloxane (EO = ethyleneoxy, PO = propyleneoxy)	$\text{C}_w\text{H}_{2w+1}(\text{OCH}_2\text{CH}_2)_m\text{OH}$ $\text{C}_9\text{H}_{19}-\text{C}_6\text{H}_4-(\text{OCH}_2\text{CH}_2)_n\text{OH}$  $(\text{CH}_3)_3\text{SiO}((\text{CH}_2)_2\text{SiO})_x((\text{CH}_2)_3\text{SiO})_y\text{Si}(\text{CH}_3)_3$ $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}(\text{EO})_m(\text{PO})_n\text{H}$
Zwitterionic	Dodecyl betaine Lauramidopropyl betaine Cocoamido-2-hydroxypropyl sulfobetaine	$\text{C}_{12}\text{H}_{25}\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$ $\text{C}_{11}\text{H}_{23}\text{CONH}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$ $\text{C}_w\text{H}_{2w+1}\text{CONH}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{SO}_3^-$

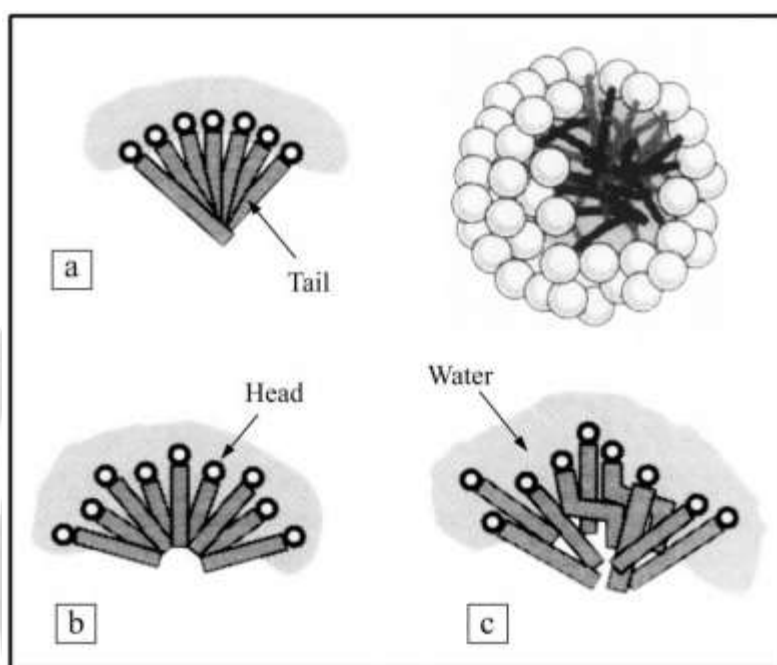


**Fig. 1 Illustration of a Gemini surfactant**

A number of reviews cover the properties of cationic and anionic Gemini surfactants. Gemini surfactants possess a number of superior properties when compared to conventional single-headed, single-tailed surfactants, the Geminis tending to exhibit lower cmc values (by about an order of magnitude), increased surface activity (C20) and lower surface tension at the cmc, enhanced solution properties such as hard-water tolerance, superior wetting times, and lower Krafft points. Given these performance advantages of Gemini surfactants one can anticipate their use in a myriad of surfactant applications (e.g., soil remediation, oil recovery, and commercial detergents), given a favourable cost/performance ratio.

### 3. THE HYDROPHOBIC EFFECT AND MICELLE FORMATION

In aqueous solution dilute concentrations of surfactant act much as normal electrolytes, but at higher concentrations very different behaviour results. This behaviour is explained in terms of the formation of organized aggregates of large numbers of molecules called micelles, in which the lipophilic parts of the surfactants associate in the interior of the aggregate leaving hydrophilic parts to face the aqueous medium. An illustration presented by Hiemenz and Rajagopalan<sup>28</sup> is given in Fig. 2. The formation of micelles in aqueous solution is generally viewed as a compromise between the tendency for alkyl chains to avoid energetically unfavourable contacts with water, and the desire for the polar parts to maintain contact with the aqueous environment.



**Fig. 2 Organization of surfactant molecules in a micelle**

A thermodynamic description of the process of micelle formation will include a description of both electrostatic and hydrophobic contributions to the overall Gibbs energy of the system. Hydrocarbons (e.g., dodecane) and water are not miscible; the limited solubility of hydrophobic species in water can be attributed to the hydrophobic effect. The hydrophobic Gibbs energy (or the transfer Gibbs energy) can be defined as the Gibbs energy for the process of transferring the hydrocarbon solute from the hydrocarbon solvent to water. In considering the transfer Gibbs energy in terms of its entropic and enthalpic contributions, a significant characteristic of the hydrophobic effect is that the entropy term is dominant, i.e., the transfer of the hydrocarbon solute from the hydrocarbon solvent to water is accompanied by an increase in the Gibbs transfer energy. The decrease in entropy is thought to be the result of the breakdown of the normal hydrogen-bonded structure of water accompanied by the formation of differently structured water, often termed icebergs, around the hydrocarbon chain. The presence of the hydrophobic species promotes an ordering of water molecules in the vicinity of the hydrocarbon chain. To minimize the large entropy effect, the “icebergs” tend to cluster, in order to reduce the number of water molecules involved; the “clustering” is enthalpically favoured, but entropically unfavourable. The overall process has the tendency to bring the hydrocarbon molecules together, which is known as the hydrophobic interaction. Molecular interactions, arising from the tendency for the water molecules to regain their normal tetrahedral structure, and the attractive dispersion forces between hydrocarbon chains, act cooperatively to remove the hydrocarbon chain from the water “icebergs”, leading to an association of hydrophobic chains.

### 4. CONCLUSION

As with all chemicals, the use of surfactants brings with it the need to understand the environmental fate and effects of these chemicals, both in normal applications and in accidental releases. An obvious constraint for surfactant-



based soil and aquifer remediation, for example, is that any surfactants left behind must not impose an environmental threat, and the environmental issues concerned with the transport of surfactants through the subsurface must be addressed as part of the advancement of this technology. The regulatory environment for surfactant usage has evolved considerably over the past several decades, and environmental risk assessment requires knowledge of biodegradation and toxicity of these chemicals. There are some common themes in surfactant biodegradation, such as mechanisms for degrading the alkyl chains that form the hydrophobic groups of all commercial surfactants, and toxicity of surfactants is also reasonably predictable, so that it is possible to arrive at reasonably sound judgments on the environmental safety of surfactants. As with other colloidal species, continued research is needed to understand the health hazards linked to surfactants.

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