

The Relationship of Structure to Properties in Surfactants¹

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ABSTRACT

Changes in the various structural units present in surfactants strongly affect the interfacial properties shown by these materials. Such properties as surface tension reduction, micelle formation, wetting, foaming and defoaming, detergency, and dispersion of solids all show marked changes with variations in both the hydrophilic and hydrophobic portions of the surfactant molecule, reflecting the processes occurring on a molecular level. Changes in these properties caused by such factors as the length and nature of the hydrophobic group, branching or unsaturation in the hydrophobic group, the nature of the hydrophilic group and its position in the molecule, and the presence or absence of an ionic charge are described and explained in terms of the molecular processes involved.

INTRODUCTION AND DEFINITION OF TERMS

A surface-active agent is a substance which, when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and of altering to a marked degree the surface or interfacial free energies of those surfaces (or interfaces). The term "interfaces" indicates a boundary between any two immiscible phases; the term "surface" denotes an interface where one phase is a gas, usually air.

The interfacial free energy is the minimum amount of work required to create that interface. The interfacial free energy *per unit area* is what we measure when we determine the interfacial *tension* between two phases. It is the minimum amount of work required to create unit area of the interface or to expand it by unit area. When we measure the surface tension of a liquid, we are measuring the interfacial free energy per unit area of the boundary between the liquid and the air above it. When we expand an interface, therefore, the minimum work required to create the additional amount of that interface is the product of the interfacial tension times the increase in area of the interface; $W_{\min} = \gamma_1 \times A$. A surface-active agent, therefore, is a substance which, at low concentrations, will adsorb at some or all of the interfaces in the system and significantly change the amount of work required to expand those interfaces. A common example of the action of a surface-active agent is the lowering of the surface tension of water when a detergent is added to it. In this case the detergent molecules are adsorbed at the liquid-air interface and reduce the work required to expand that surface.

Since in many processes surfaces or interfaces are expanded greatly, sometimes by many orders of magnitude, i.e., in wetting, emulsification, foaming or in the dispersion of solids, the presence of a surface-active agent which can reduce the amount of work needed to expand the appropriate interface in these systems greatly facilitates the process.

GENERAL STRUCTURES AND MECHANISM OF ACTION

An understanding of why surface-active agents have the property of being adsorbed at interfaces, and how they accomplish this lowering of the interfacial free energy, can

be obtained by an examination of their molecular structure.

The characteristic structural feature of surface-active agents is a molecular structure containing a group which has a strong attraction for the solvent (called the lyophilic group) together with a group which has very little attraction for the solvent (the lyophobic group). When used in water the terms are hydrophilic and hydrophobic, respectively. The hydrophobic group is usually a long chain hydrocarbon residue, occasionally an halogenated or oxygenated hydrocarbon residue; the hydrophilic group is an ionic or highly polar group. Molecules containing both lyophilic and lyophobic groupings are called amphipathic molecules; a surfactant, therefore, is an amphipathic molecule. When an amphipathic molecule is dissolved in water, its hydrophobic group distorts the water structure in such fashion as to decrease the entropy of the system, with the result that some of the molecules are expelled from the bulk of the solvent and are adsorbed at the interfaces surrounding the solution; the hydrophilic group, however, keeps them in solution and prevents them from separating out as another phase. In addition their amphipathic nature causes the molecules adsorbed at the interfaces to be oriented, usually with the hydrophilic portions turned *towards* the water and the hydrophobic portions oriented *away* from the water. This orientation is a very important factor in determining the change in the properties of the interface produced by the surfactant upon adsorption there. The properties of an interface with adsorbed molecules may vary greatly, depending upon the particular orientation of these molecules with respect to it.

As in all molecules, changes in the structural characteristics of the various groupings in the amphipathic molecule (in this case the hydrophilic and hydrophobic portions), particularly their relative size, shape, and position with respect to each other, result in changes in the properties of the molecule. This discussion will be confined to the effect of structural changes on certain interfacial phenomena in aqueous media—surface tension reduction, wetting, foaming and defoaming, detergency, and dispersion of solids.

SURFACE TENSION REDUCTION IN AQUEOUS MEDIA

Surface tension reduction in aqueous media depends upon the replacement of water molecules at the surface by surface-active molecules from the interior of the solution; the adsorption at the surface of surfactant molecules results in a lowering of the surface tension of the water. For our purposes it is necessary to distinguish between the *efficiency* of a surfactant, measured by the concentration of surfactant required to produce some significant reduction in the surface tension of the water, and its *effectiveness*,

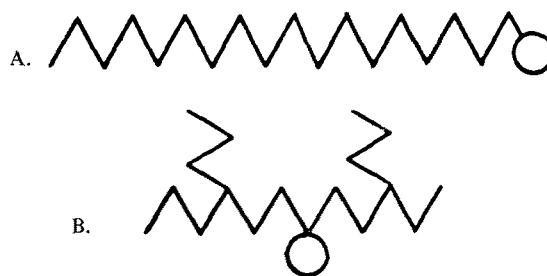


FIG. 1. A. Efficient γ reducer. B. Effective γ reducer.

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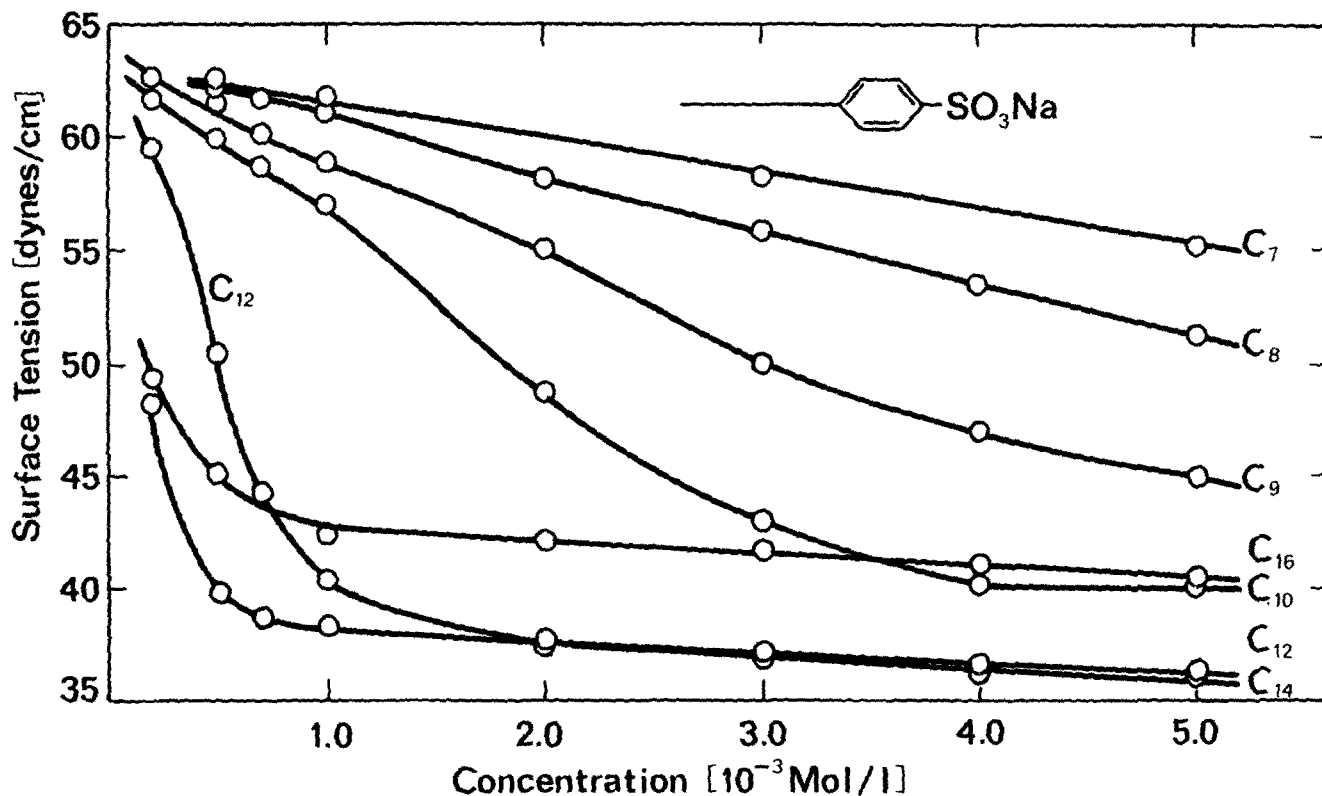


FIG. 2. Surface tension of aqueous solutions of sodium p-(n-alkyl)benzenesulfonates at 75 C as a function of their concentration.

measured by the *minimum* value to which it can lower the surface tension, since these two often run counter to each other.

Efficiency increases with increase in the length of the hydrophobic portion; effectiveness usually decreases (1,2). Efficiency decreases with increased branching or unsaturation of the hydrophobic portion and with movement of the hydrophilic group from a terminal to an increasingly central position in the hydrophobic chain; effectiveness increases with these changes (2). Therefore a surfactant with a long, straight hydrophobic group and with a terminally located hydrophilic group will lower the surface tension of water more efficiently, but much less effectively, than a shorter chain homologue, or one with a branched chain, or one with a centrally located hydrophilic group (Fig. 1).

Efficiency is also decreased by electrostatic repulsion between ionized hydrophilic groups, with the result that ionic surfactants are usually much less efficient than nonionics, although not necessarily more effective. When counter-ions are strongly associated with the surfactant ions, however, especially where the counter-ion is itself a surface-active ion, efficiency is greatly improved (3).

The explanation for all these effects is that efficiency is a reflection of the concentration of surfactant at the surface relative to that in the bulk of the solution, and this is determined by the free energy change involved in the transfer of a surfactant molecule from the interior to the surface. Since for each additional carbon atom in the hydrophobic chain of the dissolved surfactant there is a corresponding decrease in the entropy of the molecule, and thus an increase in its free energy in the bulk phase relative to that at the surface, the proportion of molecules of surfactant at the surface, and hence its efficiency, increases with increased length of the hydrophobic chain. Branching of the hydrocarbon chain, on the other hand, or positioning of the hydrophilic group in a more central location in the molecule, reduces the effective length of the chain and its entropic effect in solution with a consequent decrease in its efficiency.

The lower efficiency of ionic surfactants compared to nonionics can be explained in similar fashion. Since the surfactant molecules are adsorbed at the surface in oriented fashion, there is greater repulsion between the similarly charged ionic heads there than when the molecules are dissolved in random fashion in the bulk phase. The presence of an ionic hydrophilic group therefore increases the free energy of the molecule at the surface relative to that in the interior with a consequent decrease in the proportion of molecules at the surface.

On the other hand the *effectiveness* of a surfactant—the minimum value to which it can depress surface tension of the water—depends to a large extent upon the cohesiveness of the hydrophobic groups in the surface-active molecules. The lower their cohesiveness, the lower the attainable surface tension. The minimum value to which a surfactant can depress the surface tension of water appears to approach that of the parent hydrophobe (4). Since branched chain hydrocarbons have lower cohesive forces than straight chain hydrocarbons with the same number of carbons, surfactants having branched chain hydrophobic groups can reduce the surface tension of water to lower values than their straight chain analogs. For the same reason surfactants with dimethylsilicone hydrophobic groups can depress the surface tension of water to lower values than those with hydrocarbon chains and those with fluorocarbon chains can depress it to even lower values.

The effectiveness of a particular surfactant in reducing the surface tension of water depends also upon another phenomenon characteristic of amphipathic molecules in aqueous solution—micellization.

Surface-active agents, when dissolved in water at very low concentrations, are present as individual molecules. However as the amount of surface-active agent in solution is increased, a critical concentration is reached, the value of which is dependent upon the structure of the surfactant, at which point an increase in the amount of dissolved surfactant causes no significant increase in the amount of molecularly dispersed material. Instead the additional mate-

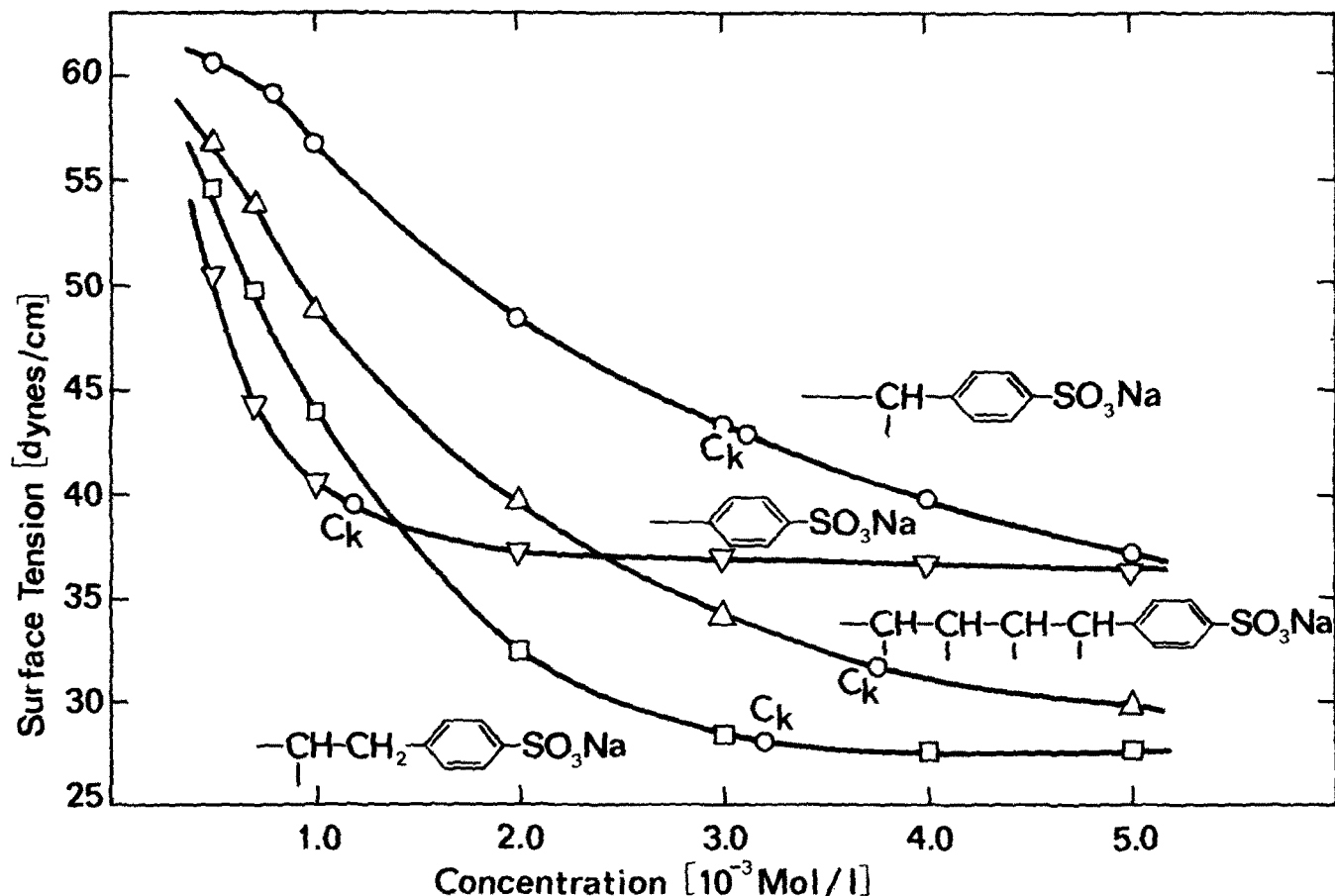


FIG. 3. Surface tension of aqueous solutions of sodium p-dodecylbenzenesulfonates at 75 C as a function of their concentration.

rial dissolves to form a polymeric form of the surfactant known as a micelle. This concentration is known as the critical concentration for micelle formation (cmc). Micellization provides a mechanism alternative to expulsion to the interfaces for removing hydrophobic groups from contact with water molecules and thereby reducing the free energy of the system.

Since the amount of molecularly dispersed surfactant does not increase significantly above the cmc, those interfacial properties which depend upon molecularly dispersed surfactant reach their ultimate value and do not change significantly above the cmc. On the other hand, since micelles appear in significant numbers only at the cmc, those properties which depend upon the presence of micelles in the solution first become significant at the cmc. Since reduction in surface tension depends upon the presence at the surface of molecularly dispersed molecules, this property shows no significant change once micellization starts. Since the micelles compete with the interfaces for the surfactant molecules, structural factors in surfactant molecules which cause micellization before the interfacial properties have reached their maximum possible values will prevent those maximum values from being attained, i.e., decrease the effectiveness of the molecule. On the other hand structural factors which inhibit micellization will increase the probability of interfacial properties reaching their maximum potential values and increase the effectiveness of the molecule.

Some of the structural factors which inhibit micellization (increase the cmc) are: (a) Decrease in the overall length of the hydrophobic group; (b) branching in the hydrophobic group; (c) unsaturation in the hydrophobic group; (d) moving the hydrophilic group towards the center of the hydrophobic group; (e) substitution of two short hydrophobic groups for one long one with the same

number of carbon atoms; and (f) ionized hydrophilic group. These are all structural factors which prevent the close packing of hydrophobic groups.

The decreased effectiveness of longer chain surfactants in reducing the surface tension of water, compared to shorter chain or branched chain homologs, is therefore a reflection of the increased micellization tendency of the former. Figure 2 illustrates this and, in addition, the increase in efficiency with increased chain length. Figure 3 illustrates the greater efficiency of a straight chain (C_{12}) surfactant over isomeric branched chain surfactants at low concentrations and its lower effectiveness compared to the latter.

WETTING

Good wetting agents characteristically have either a branched chain structure with a centrally located hydrophilic group or a shorter chain hydrophobic group with a terminally located hydrophilic group (Fig. 4).

Wetting depends upon effective reduction of the surface tension under dynamic conditions, i.e., as the wetting liquid spreads over the substrate, the surface-active molecules

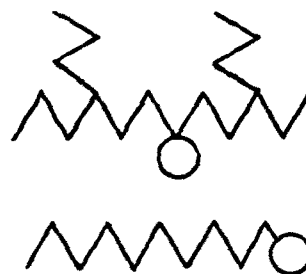


FIG. 4. Wetting agents.

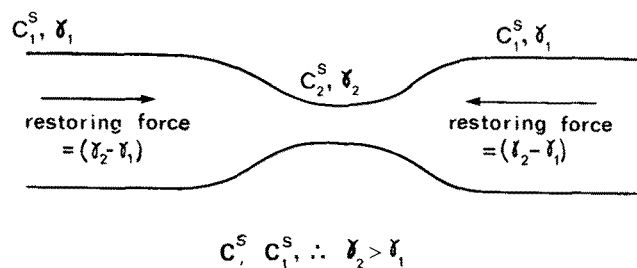


FIG. 5. Elasticity mechanism in a stretched foam film.

must diffuse rapidly to the moving boundary between liquid and substrate and reduce the surface tension (and ideally, also the substrate-liquid interfacial tension) in that region to a low value. Therefore the structural requirements for a good wetting agent are those for an effective reduction of surface tension coupled with mobility and rapid adsorption at a new surface. Short chain or branched chain structures, as mentioned above, yield effective surface tension reducers; in addition these structures are believed to be rapidly adsorbed at interfaces (5,6). The length of the hydrophobic group should therefore be no longer than that required to cause efficient adsorption or the surfactant at the surface, under the conditions of use; the hydrophilic group should have only sufficient interaction with the solvent to prevent the molecule from becoming insoluble, since interaction with the solvent reduces the tendency of the molecule to migrate to the interface.

The hydrophilic group may be ionic or a nonionic polar grouping such as two or more hydroxyl groups or a short polyoxyethylene chain.

FOAMING

Some wetting agents, especially those of low solubility in water, also function as antifoaming agents. The reason for this is not difficult to understand. In contrast to the requirements for wetting, which depends upon almost instantaneous reduction of the surface tension as the interface is extended, foaming depends upon the existence, when the interface is extended, of an appreciable period of time before the surface tension is reduced to its equilibrium value.

The production of foam is facilitated by the lowering of the surface tension, since that reduces the work ($W = \gamma A$, where A = the total surface area of the bubbles in the foam) required to produce the foam. Thus initial foam height correlates well with surface tension of the foaming solution (7). The lower the surface tension, the higher the initial foam.

However for foam to have any stability, the foam film produced must have some elasticity, i.e., as the film thins and stretches, there must be some restoring force generated by the stretching process which opposes this effect and prevents the stretching from continuing with eventual rupture of the film. It is for this reason that pure liquids, even with low surface tension, do not foam. In solutions of surface-active agents, this restoring force is believed to be due to the higher surface tension which a newly increased surface shows. According to this mechanism (Fig. 5) when a portion of a foam film is stretched, the local concentration of surfactant decreases momentarily and the surface tension at the stretched spot becomes momentarily greater than the tension in the surrounding areas. This causes a surface tension gradient, radiating out from the stretched spot, which draws liquid in from the surrounding areas counteracting the stretching of the film and thickening it (8).

For this mechanism to act effectively, it is essential that the surface tension at the stretched portion not be reduced too rapidly, i.e., that the reduction of the tension to its equilibrium value by surfactant molecules migrating to the



FIG. 6. Foaming agent.



FIG. 7. Detergent.

surface from the interior not take place before sufficient material from the perimeter has been moved in to thicken the film under the influence of the surface tension gradient. Therefore a surfactant which is a good wetting agent, i.e., rapidly reduces the surface tension at an extended interface, can act as a defoamer by preventing the operation of this film-healing mechanism.

For practical purposes, however, foam must not only be produced but must also show appreciable stability-resistance against mechanical and thermal shock. This requires the presence at the surface of molecules which can pack closely to form a film with mechanical strength. For this purpose the hydrophobic groups should be long and straight. This type of hydrophobic group also shows slow adsorption at the surface and thus promotes film elasticity. However since increased length of the hydrophobic group decreases the effectiveness of the molecule for reducing the surface tension of the system, foaming capacity goes through a maximum with increase in length of the hydrophobic chain (9), and good foaming agents have structures of *intermediate* chain length (Fig. 6).

Other structural factors which increase foaming capacity are: (a) increased association of the counter-ion with the surfactant ion in ionic surfactants. This makes for decreased electrostatic repulsion between similarly charged ionic hydrophilic groups in the film with consequent closer packing; (b) functional groups in the surfactant molecules, such as a few ether linkages between hydrophobic and hydrophilic portions (10), which increase the interaction of the surfactant molecules with the water without changing the packing of the hydrophobic tails significantly. These hydratable functional groups decrease the rate of migration of the surfactant to the surface and also cause the surface film to include bound water molecules which increase its stability.

DETERGENCY

Detergency is a very complex phenomenon which depends on many factors and the mechanisms of which vary with the nature of the soil to be removed and the substrate upon which the soil is held (11). However despite this complexity, good detergents generally have a very long, straight hydrophobic group and a terminally located hydrophilic group (Fig. 7). Almost all studies indicate that detergency is increased with increase in the length of the hydrophobic chain, subject to solubility limits (2,12,13), and with movement of the hydrophilic group to a terminal position in the molecule (2,14,15). These are structural factors which promote micellization and correlate well with studies which indicate that detergency becomes significant only when the cmc is reached (16,17). For oily soil and nonionic surfactants, detergency has been correlated with solubilizing power of the surfactant (17), and solubilization is well known to be a property shown only by micelles. For carbonaceous soil, the increase in detergency with chain length may reflect the increased adsorption of the longer chain materials onto carbon particles (12) with resulting increased dispersion or solubilization, or both, of this type of soil.

DISPERSION OF SOLIDS

The dispersion of solids in aqueous media depends upon

the formation of energy barriers around the particles, to aid their dispersion and to prevent their coalescence when dispersed. These energy barriers may be either electrical or steric in nature. The production of an electrical barrier to coalescence involves the adsorption of ionic surfactant molecules onto the solid particles to give all the particles electrical charges of similar sign. The similarly charged particles repel each other and remain suspended. It follows that the more ionic charges a surfactant can impart to a particle, the more effective it will be as a dispersing agent. As a result most good dispersing agents contain multiple ionic groups. In addition dispersing agents for use with polar solids in aqueous media usually have hydrophobic groups with polarizable or slightly polar structures such as aromatic rings or ether linkages, or both, rather than saturated hydrocarbon chains. The purpose of these is to increase the adsorption of the surfactant molecule onto the solid particles and, most importantly, to prevent adsorption from occurring with "reverse orientation," that is, to prevent adsorption with the hydrophilic group oriented towards the solid to be dispersed and the hydrophobic group oriented towards the water. This "reverse orientation" would result in the flocculation of the solid, rather than in its dispersion. Positioning of hydrophilic groups in

both central and terminal positions in the molecule is also believed to inhibit this adverse orientation.

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