• Technical

Relationship of Structure to Properties in Surfactants: III. Adsorption at the Solid-Liquid Interface from Aqueous Solution

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ABSTRACT

Surfactants adsorb onto solid substrates from aqueous solution by a number of different mechanisms: ion exchange, ion pairing, hydrogen bonding, physical adsorption by polarization or dispersion forces. The relationship of the mechanism of adsorption to such factors as the nature of the solid substrate, the molecular structure of the surface active adsorbate, and the pH, electrolyte content, or other additive content of the aqueous phase is discussed. The effect of structural groups in the surfactant molecule on the efficiency, effectiveness, and rate of adsorption onto various types of solid substrates, charged, polar, and nonpolar, is reviewed and explained, and typical adsorption isotherms are presented. Adsorption of surfactant affects the properties of the solid substrate, such as hydrophilic or hydrophobic character, dispersibility, and reactivity towards reagents and dyes. These effects are discussed and explained.

INTRODUCTION

A number of factors strongly influence the adsorption of surfactants at the solid-liquid interface: 1) the nature of the structural groups on the surface; does the surface contain highly charged sites or are they essentially nonpolar groupings, and of what atoms are these sites or groupings constituted; 2) the molecular structure of the surfactant being adsorbed, the adsorbate; is it ionic or nonionic, is the hydrophobic group long or short, straight chain or branched, aliphatic or aromatic; 3) the environment of the aqueous phase, its pH, electrolyte content, the presence of any additives such as short chain polar solutes, e.g., alcohol and urea, and its temperature. Together, these factors determine the mechanism by which adsorption occurs, and the efficiency and effectiveness of adsorption.

These last two terms require definition. For the purpose of this discussion, efficiency is defined as the log of the reciprocal of the equilibrium bulk concentration of surfactant in the aqueous phase when adsorption on the adsorbent has reached half its saturation value. This is analogous to the definition of efficiency in surface or interfacial tension reduction (1). Efficiency of adsorption is related to the free energy change involved in the transfer of surfactant from the bulk phase to the substrate; the larger the free energy decrease resulting from this transfer, the greater the efficiency of adsorption.

The term effectiveness of adsorption, is defined as the amount of surfactant adsorbed per unit area of substrate surface when the surface has become saturated with one or two layers of surfactant. Effectiveness of adsorption is related to the effective cross section of the adsorbate molecule on the substrate; the smaller the effective cross sectional area of the adsorbate on the substrate, the greater the effectiveness of adsorption.

Mechanisms of adsorption

There are a number of mechanisms by which surface active solutes may adsorb onto solid substrates from aqueous solution. In general, adsorption of surfactants involves single ions rather than micelles (2,3).

Ion exchange (4,5,6). This involves replacement of counter-ions adsorbed onto the substrate from the solution by similarly charged surfactant ions (Fig. 1).

Ion pairing (5,6). Adsorption of surfactant ions from solution onto oppositely charged sites unoccupied by counter-ions (Fig. 2).

Hydrogen bonding (5,6,7,8). Adsorption by hydrogen bond formation between substrate and adsorbate (Fig. 3).

Adsorption by polarization of π electrons (7). This type of adsorption occurs when the adsorbate contains electron rich aromatic nuclei and the solid substrate has strongly positive sites. Attraction between electron rich aromatic

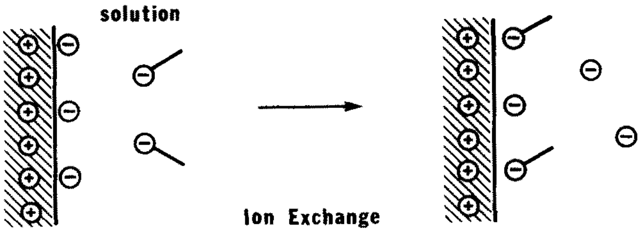

FIG. 1. Ion exchange.

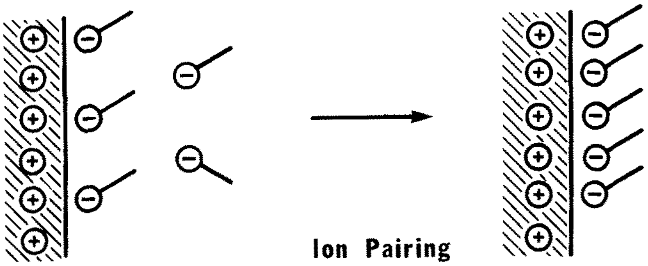

FIG. 2. Ion pairing.

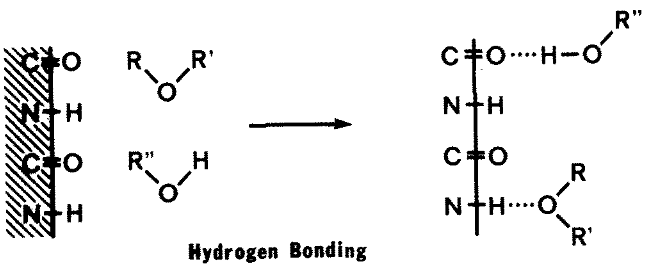

FIG. 3. Hydrogen bonding.

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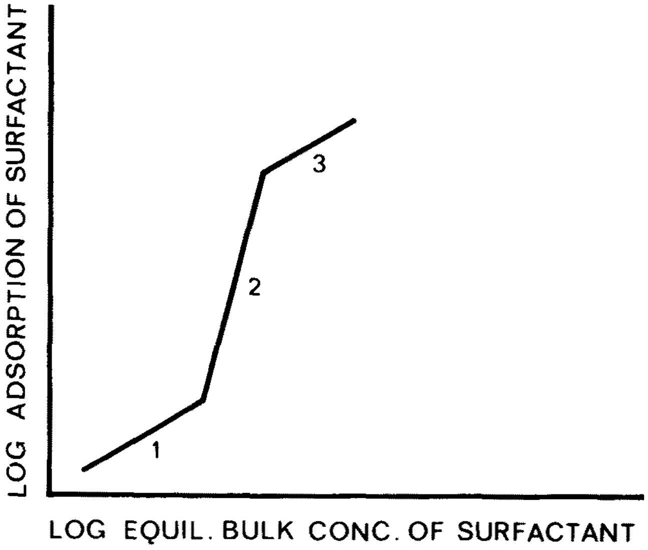

FIG. 4. Adsorption isotherm for an ionic surfactant onto an oppositely charged substrate (4).

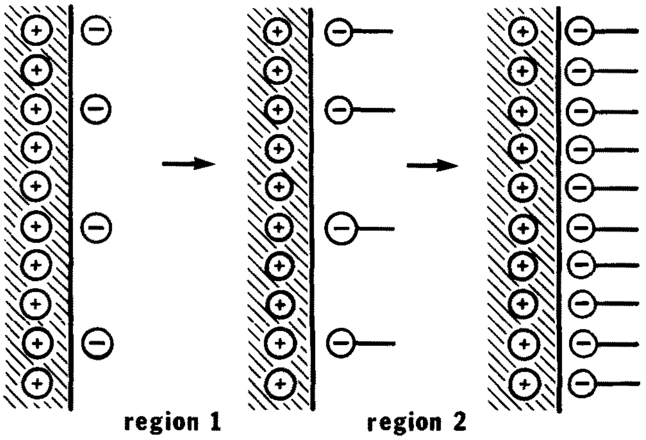

FIG. 5. Adsorption of an ionic surfactant onto an oppositely charged substrate by ion exchange (region 1) and ion pairing (region 2).

nuclei of the adsorbate and positive sites on the substrate results in adsorption.

Adsorption by dispersion forces (2,6). Adsorption occurs via London-Van der Waals dispersion forces acting between substrate and adsorbate molecules. Adsorption by this mechanism generally increases with increase in the mol wt of the adsorbate, and is important not only as an independent mechanism, but also as a supplementary mechanism in all other types. For example, it accounts in part for the pronounced ability of surfactant ions to displace equally charged simple inorganic ions from solid substrates by an ion exchange mechanism (9).

Hydrophobic bonding (4,10,11). Adsorption by this mechanism occurs when the combination of mutual attraction between hydrophobic groups of the surfactant molecules and their tendency to escape from an aqueous environment becomes large enough to permit them to adsorb onto the solid adsorbent by aggregating their chains. Adsorption of surfactant molecules from the liquid phase onto or adjacent to other surfactant molecules already adsorbed on the solid adsorbent also may occur by this mechanism.

Effects of Molecular Structure of the Surfactant and the Environment of the Aqueous Phase

Surfaces with strongly charged sites. Surfaces with strongly charged sites include such substrates as wool and other polyamides at pH above and below their isoelectric points, oxides such as alumina above and below their points of zero charge, and cellulosic and silicate surfaces at high pH. Adsorption onto these surfaces is a complex process, during which adsorption of the solute may occur successively by ion exchange, ion pairing, and hydrophobic bonding mechanisms.

If we start at very low concentrations of surfactant, the adsorption isotherm for an ionic surfactant onto an oppositely charged substrate, e.g., sodium alkanesulfonates (4) and alkylbenzenesulfonates (10) on positively charged Al_2O_3, is S-shaped. The shape of the isotherm (Fig. 4) is be believed (4) to reflect 3 distinct modes of adsorption. In region 1, the surfactant adsorbs by ion exchange. The surface charge density, or surface potential, on the solid remains essentially constant. In region 2, there is a marked increase in adsorption, due to interaction of the hydrophobic chains of oncoming surfactant ions with those of previously adsorbed surfactant and with themselves. This aggregation of the hydrophobic groups, which may occur at concentrations well below the critical micelle concentration of the surfactant, has been called hemimicelle formation (4) or cooperative adsorption (11). In this adsorption region, the original surface charge of the solid is neutralized by the adsorption of oppositely charged surfactant ions and eventually reversed, so that at the end of region 2, the surface has acquired a charge of the same sign as the surfactant ion. The processes in regions 1 and 2 are diagrammed in Figure 5. In region 3, the slope of the isotherm is reduced, because adsorption now must overcome electrostatic repulsion between the oncoming ions and the similarly charged surface. Adsorption in this fashion is usually complete when the surface is covered with a monolayer of the surfactant (12). In many cases, this occurs in the neighborhood of the critical micelle concentration (3,13,14), since adsorption involves single ions rather than micelles.

An increase in the length of the hydrophobic group increases the efficiency of adsorption in all 3 regions, because the free energy decrease associated with the removal of the hydrophobic chain from contact with the water, and the tendency to aggregate or adsorb via dispersion forces all increase with increase in the length of the chain (4,10,15,16,17). For this purpose, the phenyl ring may be considered to have an effective length of ca. 3.5 carbon atoms in a straight carbon chain. Carbon atoms on short branches on an alkyl hydrophobic group, or on the shorter portion of a hydrophobic group when the hydrophilic group is not terminally located, have ca. one-half the effective length of a carbon atom on a straight alkyl chain with terminal hydrophilic groups. An increase in the size of the hydrophilic group also increases the efficiency of adsorption by ion exchange or ion pairing (18), in contrast to its almost negligible effect upon the critical micelle concentration.

The effectiveness of adsorption, i.e., the amount adsorbed at surface saturation, however, may increase, decrease, or show no change with increase in the length of the hydrophobic group, depending upon the orientation of the adsorbate at the substrate solution interface. If adsorption is perpendicular to the substrate surface in a close packed arrangement, then an increase in the length of a straight chain hydrophobic group will cause no significant change in the number of moles of surfactant adsorbed per unit area of surface at surface saturation (16), because the cross sectional area occupied by the chain oriented perpendicular to the interface does not change with increase in the number of units in the chain. In perpendicular orientation, moreover, the effectiveness of adsorption may be determined by the size of the hydrophilic group, when the cross sectional area of that group is greater than that of the hydrophobic chain; the larger the hydrophilic group, the smaller the amount adsorbed at surface saturation (16). If the arrangement is predominantly perpendicular but not close packed, or if it is somewhat tilted away from the perpendicular, then there may be some increase in effectiveness of adsorption with increase in the length of the hydrophobic group, due to greater Van der Waals attraction and consequent closer packing of longer chains (17).

However, if the orientation of the adsorbate is parallel to the interface, as may occur when the surfactant has two ionic groups of charge opposite to that of the substrate at opposite ends of the surfactant molecule, or when the hydrophobic chain interacts strongly with the surfact, e.g., electron rich aromatic nuclei in the adsorbate and positively charged sites on the substrate (7), then effectiveness of adsorption will decrease with increase in chain length, because this will increase the cross sectional area of the molecule on the surface, and thus saturation of the surface will be accomplished by a smaller number of molecules (2).

Nonionic surfactants may adsorb onto charged surfaces by an entirely different mechanism than ionic surfactants. For example, on negatively charged silica, cationics are adsorbed by ion exchange and ion pairing mechanisms, while polyoxyethylated nonionics are adsorbed by hydrogen bonding between -SiOH groups on the surface and the oxygens of the oxyethylene groups (5).

Changes in the pH of the aqueous phase usually cause marked changes in the adsorption of ionic surfactants onto charged solid substrates. As the pH of the aqueous phase is lowered, a solid surface will become more positive, or less negative, because of adsorption onto charged sites of protons from the solution, with consequent increase in the adsorption of anionic surfactants and decrease in the adsorption of cationics (17,19). The reverse is true when the pH of the aqueous phase is raised. These effects are shown markedly by wool and other polyamides (2,14,20). The adsorption of sodium dodecyl sulfate on Nylon 6, for example, increases markedly with decrease in pH at constant ionic strength, due to ion pairing with positively charged amido and terminal amino groups.

Change in the pH also may affect the surfactant molecule, notably those containing carboxylate groups (soaps) or nonquaternary ammonium groups. In these cases, change in the pH may convert the surfactant from one containing an ionic group capable of strong adsorption onto oppositely charged sites on the substrate to a neutral molecule capable of adsorption only through hydrogen bonding or dispersion forces. Changes in pH also may affect nonionic surfactants, notably those having polyoxyethylene chains, because the ether linkages in these chains can be protonated at low pHs, yielding positively charged groupings which may adsorb onto negatively charged substrates.

An increase in the ionic strength of the aqueous phase due to the addition of neutral electrolyte, such as NaCl or KBr, causes an increase in both the efficiency and effectiveness of adsorption of ionic surfactants unto similarly charged substrates (14,17,21). These effects are probably due to decreased repulsion between the ionic heads of the surfactant ions and the similarly charged substrates at the higher ionic strength.

The presence of polyvalent cations, especially Ca^{++}, in the solution will cause an increase in the absorption of anionics. This may be due to the adsorption of Ca^{++} unto the substrate yielding $\oplus$-charged sites unto which negatively charged surfactant can adsorb (19).

Temperature increase generally causes a decrease in the efficiency and effectiveness of adsorption of ionic surfactants (16). However, a rise in temperature usually results in an increase in the adsorption of nonionic surfactants containing a polyoxyethylene chain as the hydrophilic group. This is due to the decreased solute-solvent interaction, i.e., dehydration of the polyoxyethylene group, as the temperature is raised (22).

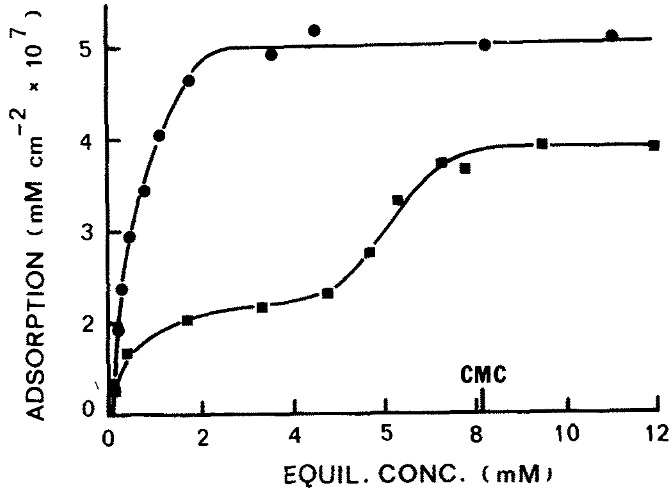

FIG. 6. Adsorption of sodium dodecyl sulfate onto Graphon at 25 C from aqueous solution (13). CMC = Critical micelle concentrations.

Polar substrates without strongly charged sites. These include such substrates as cotton, polyesters, and polyamides in neutral solution. Adsorption of surfactants onto these substrates is mainly by a combination of hydrogen bonding and adsorption via Van der Waals forces. For adsorption to occur by hydrogen bonding, the hydrophilic head of the surfactant must contain a grouping capable of hydrogen bonding. Thus, quaternary ammonium, and sulfate or sulfonate hydrophilic groups would not be expected to adsorb by this mechanism. On the other hand, free fatty acids from the hydrolysis of soaps are adsorbed, probably by H-bonding, for example, unto polyester and nylon 66 (23). Where the substrate has groups, such as -OH or -NH, capable of donating the hydrogen for bonding to the adsorbate, surfactants containing a polyoxyethylene chain will be adsorbed. Thus, under laundering conditions, adsorption on nylon and cotton has been reported (24) to be much greater for nonionics than anionics by a factor of 2:1. Polyoxyethylenated n-dodecanol adsorbs onto cotton from aqueous solutions, at 25 C to form a close packed monolayer with the molecules lying flat on the substrate (25). An increase in the number of units in the polyoxyethylene chain causes a decrease in the efficiency, the effectiveness, and the rate (24) of the adsorption. Increase in the length of the hydrophobic chain, on the other hand, will increase the efficiency of the adsorption.

When the substrate is not capable of donating a hydrogen for bonding of the adsorbate (polyesters, polyacrylonitrile), adsorption is often mainly by dispersion forces (2); the character of the adsorption will be similar to that on nonpolar, hydrophobic surfaces.

Nonpolar, hydrophobic surfaces. Common substrates in this class are carbon and polyethylene or polypropylene. Adsorption onto these substrates is mainly by dispersion forces. Orientation of the adsorbate is initially parallel to the surface of the solid or slightly tilted or L-shaped with the hydrophobic group close to the surface and the hydrophilic group oriented towards the aqueous phase. As adsorption continues, the adsorbed molecules become oriented more and more perpendicular to the surface with hydrophilic heads oriented towards the water.

Adsorption isotherms for monofunctional anionic and cationic surfactants are similar on these substances (Fig. 6 and 7), and show surface saturation in the vicinity of the critical micelle concentration of the adsorbate with an orientation of the adsorbate perpendicular to the substrate. In some cases, the adsorption isotherm shows an inflection point (fig. 6) indicative of a change in orientation of the surfactant from parallel to perpendicular. An increase in the length of the hydrophobic group increases efficiency and

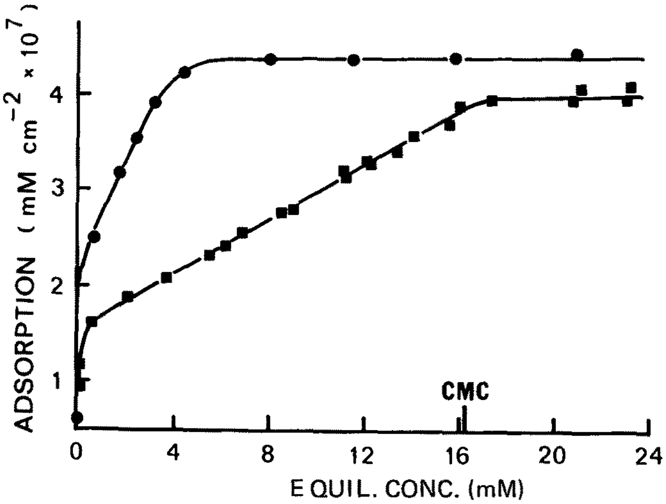

FIG. 7. Adsorption of dodecyltrimethylammonium bromide onto Graphon at 25 C from aqueous solution (13).

slightly increases effectiveness of adsorption. The efficiency is due to the increase in the magnitude of the -Δ G of adsorption with increase in the number of units in the hydrophobic chain, and the effectiveness is due to tighter packing of the hydrophobic chains (27,28). Here, as in the case of adsorption onto surfaces having strongly charged sites, the phenyl ring in a p-benzenesulfonate may be considered to have an effective length of ca. 3.5 carbon atoms in a straight alkyl chain (27). In polyoxyethylenated nonionics, an increase in the length of the polyoxyethylene chain decreases both efficiency of adsorption, because -Δ G of adsorption is decreased in magnitude as the number of oxyethylene units is increased, and effectiveness, because the cross sectional area of the molecule at the interface increases with increase in the number of oxyethylene units (29). Increase in the length of the hydrophobic group, however, increases the efficiency of adsorption (22).

The rate of adsorption has been shown to be a function of the position of the hydrophilic group in the molecule, with surfactants containing the hydrophilic group in a central location in the molecule adsorbing faster than those in which the hydrophilic group is terminally located (28). Although some of the experimental evidence is conflicting, the effect here may be due to the more compact structure in aqueous solution, and hence greater diffusion coefficient of surfactants with a hydrophilic group in a central position (30). The rate of adsorption on carbon also has been shown to be dependent upon the presence in the aqueous phase of additives which affect the structure of water. Additives which are structure breakers, such as urea and N-methylacetamide, increase the rate of adsorption, while those which promote structure, such as xylose and fructose, decrease the rate of adsorption (31).

Neutral electrolyte addition increases both the efficiency of adsorption of ionic surfactants by decreasing the electrical repulsion between the similarly charged adsorbed ions and oncoming ions, and the effectiveness by decreasing the electrical repulsion between the similarly charged adsorbed ions, permitting closer packing (Fig. 6 and 7). The addition of small amounts of cationics to aqueous solutions of anionics (32), or small amounts of metal carboxylates to cationic solutions (33), also increases the adsorption of the predominant ionic surfactant by decreasing the electrical repulsion between the adsorbing ions.

Effects of Adsorption on Surface Properties of Solid Substrate

Substrates with strongly charged sites. As mentioned above, the adsorption of surface active counter ions by an ion exchange mechanism causes no change in the net charge of the substrate. However, if adsorption of surface active counter-ions continues by an ion pairing mechanism, then the net charge on the substrate decreases and eventually is completely neutralized. During this process, the tendency of the substrate to repel other, similarly charged, substrates diminishes and ceases when the charge on the substrate has been eliminated. Thus, solid substrates in the form of finely divided particles, dispersed in the aqueous phase, in part because of their mutual electrical repulsion, will usually flocculate at some point as the surface charge is neutralized by the adsorption of oppositely charged surfactant ions.

Furthermore, because adsorption by an ion-exchange or ion-pairing mechanism results in the orientation of the adsorbed surfactant with its hydrophobic group toward the aqueous phase (Fig. 5), such adsorption causes the surface to become increasingly more hydrophobic (6,12). This is shown by an increase in the contact angle at the solid-water-air interface as adsorption increases (34,35). Adsorption in this manner may account for the reduced swelling of wool fibers in aqueous solution after adsorption of anionic surfactant onto the positively charged sites (36) and the elimination of shrink resistance from oxidized wool by cationic softeners (37). In both cases, adsorption of oppositely charged surfactant ions makes the wool surface more hydrophobic. If adsorption of surfactant ions onto the substrate is continued beyond the point of zero charge, however, then the charge on the surface is reversed and the surface acquires a charge whose sign is that of the adsorbate ion. Orientation of the adsorbed surfactant ion during this process is with the hydrophilic head towards the aqueous phase, imparting increasing hydrophilic character to the substrate as adsorption continues, and the contact angle decreases again.

Adsorption in this manner may account for the increased reactivity of wool crystine disulfide bonds to attack by alkali in the presence of cationic surfactants and their decreased reactivity in the presence of anionics (38). The adsorption of cationic surfactants onto the wool surface, which is negatively charged in alkaline medium, can impart a positive charge to the surface, thus increasing its attraction for hydroxide and sulfite ions, with consequent increase in its rate of reaction with these ions. In analogous fashion, the acid hydrolysis of peptide bonds in the wool is increased by the presence of anionic surfactants, which adsorb onto the wool surface, positively charged in acid medium, and impart to it a negative charge. The presence of cationic surfactants, on the other hand, decreases the acid hydrolysis of these bonds. Nonionic surfactants have no effect.

The adsorption of surfactant ions onto solid substrates is one of the major factors governing detergency. The greater retention of carbon black in the presence of anionic surfactants by polyester than by wool, for example, has been explained by the greater attraction of the wool with charged sites for the surfactant than for the nonpolar carbon and the reverse in the case of the hydrophobic polyester (39). The action of surfactants in retarding and leveling the dyeing of fabrics also involves competitive adsorption onto charged sites, with surfactant ions of charge similar to that of the dyes adsorbing competitively onto oppositely charged sites on the fiber, thus reducing the effective rate of adsorption of the dyestuff. In all cases, the more strongly adsorbed the surfactant, the greater its retarding action.

Nonpolar substrates. Adsorption of surfactants at any concentration onto this type of substrate will occur with the adsorbate oriented with its hydrophilic group towards the aqueous phase. Thus, adsorption increases the hydrophilicity of the substrate and, in the case of ionic surfactants, increases its surface charge density, making it more wettable by the aqueous phase and more dispersible, if in finely divided form. This accounts, for example, for the greater dispersibility of carbon black in aqueous medium in the presence of ionic surfactants (13). In the case of polyoxyethylenated nonionics, adsorption may produce a steric barrier to the close approach of another similarly covered particle, because such approach would result in the restriction of the movement of the randomly coiled polyoxyethylene chains, with consequent decrease in the entropy of the system. Adsorption of a nonionic surfactant can thereby also produce an energy barrier to flocculation of a solid, if the latter is in finely divided form. These factors, in part, account for the greater desorption of carbon and other hydrophobic pigments from cotton in the presence of surfactants.

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