Review Article

Effects of Surfactants on the Rate of Chemical Reactions

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Surfactants are self-assembled compounds that depend on their structure and electric charge can interact as monomer or micelle with other compounds (substrates). These interactions which may catalyze or inhibit the reaction rates are studied with pseudophase, cooperativity, and stoichiometric (classical) models. In this review, we discuss applying these models to study surfactant-substrate interactions and their effects on Diels-Alder, redox, photochemical, decomposition, enzymatic, isomerization, ligand exchange, radical, and nucleophilic reactions.

1. Introduction

Self-organized assemblies such as micelles can change the rates of chemical and enzymatic reactions. Effects of micelles of surfactants on these reactions can be attributed to their electrostatic and hydrophobic interactions with reactants. Surfactants are amphiphilic organic compounds, containing both hydrophobic groups (their tails) and hydrophilic groups (their heads). Thus, a surfactant molecule contains both a water insoluble component and a water soluble component. The tail of most surfactants consists of a hydrocarbon chain. Surfactants are classified into four types. (1) Anionic surfactants, such as sodium dodecyl sulfate (SDS), contain anionic functional groups at their head, that is, sulfate, sulfonate and phosphate. (2) Cationic surfactants, for example, cetyltrimethylammonium bromide (CTAB), have cationic functional groups such as quaternary ammonium cation. (3) Zwitterionic surfactants have one cationic center and one anionic center both attached to the same molecule. The cationic part is based on primary, secondary, or tertiary amines or quaternary ammonium cations and the anionic part can be, for example, sulfonate and carboxylate [1]. (4) Nonionic surfactants (such as Triton X-100) do not ionize in an aqueous solution because their hydrophilic groups are nondissociable. Gemini surfactants (such as gemini 16-2-16) are a relatively new class of amphiphilic molecules containing two head groups and two aliphatic chains, linked by a rigid or flexible spacer [2]. They show greatly enhanced surfactant properties relative to the corresponding monovalent surfactants, Figure 1.

A micelle is an aggregate of surfactant molecules dispersed in a liquid colloid. Micelles form only when the concentration of surfactant is greater than the critical micelle concentration (CMC). This type of micelle is known as a normal-phase micelle (oil-in-water micelle). In a nonpolar solvent, a reverse micelle (water-in-oil micelle) forms in which the hydrophilic groups of surfactant are sequestered in the micelle core and the hydrophobic groups extend away from the center [3], Figure 2.

2. Classification of Kinetic Models

In this study, three models used to study kinetics of reactions in the presence of surfactants are discussed.

2.1. Pseudophase Model. The pseudophase (or pseudophase ion-exchange (PPIE)) model was first introduced by Menger and Portnoy [4] in 1967 to study effects of surfactant micelles
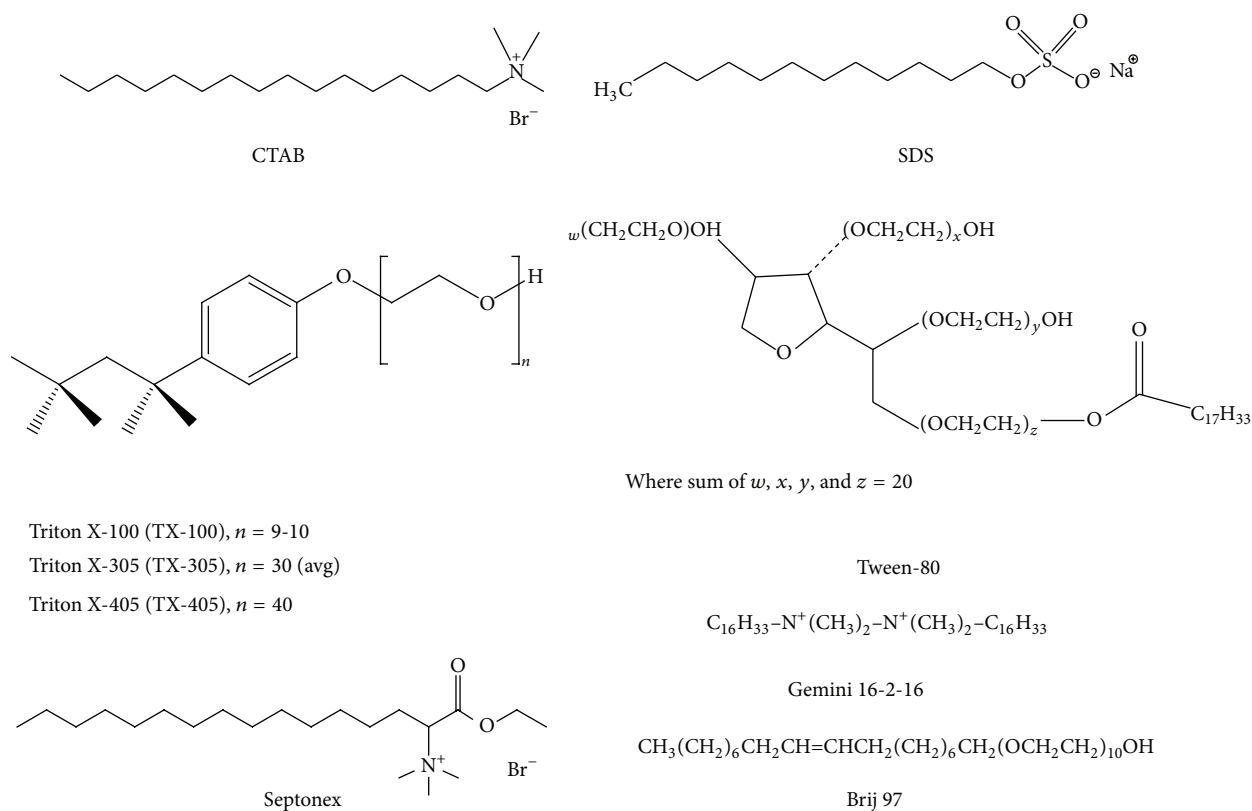
FIGURE 1: Structures of several surfactants.

CTAB

SDS

Triton X-100 (TX-100), n = 9-10
Triton X-305 (TX-305), n = 30 (avg)
Triton X-405 (TX-405), n = 40

Tween-80

Where sum of w, x, y, and z = 20

$C_{16}H_{33}-N^+(CH_3)_2-N^+(CH_3)_2-C_{16}H_{33}$

Gemini 16-2-16

$CH_3(CH_2)_6CH_2CH=CHCH_2(CH_2)_6CH_2(OCH_2CH_2)_{10}OH$
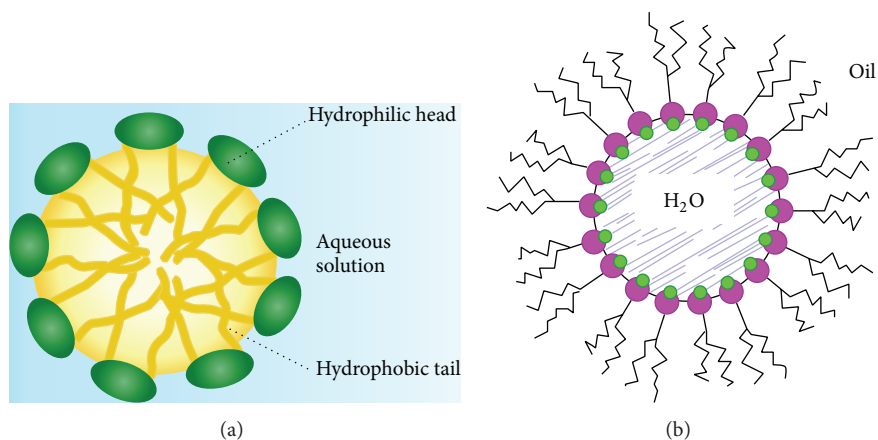
Septonex

Brij 97

FIGURE 2: Typical structures of (a) micelle and (b) reverse micelle.

on the chemical reaction rates. They considered surfactant micelles as a pseudophase that can interact with some or all of reactants (or substrates), can further dissolve substrates, and can alter the reaction rate of substrates. Therefore, this model cannot study the interaction between the substrate and surfactant molecules below the CMC. With respect to the definition of micelle as a pseudophase, there is no stoichiometric ratio between the substrate and surfactant molecules for the presence of this interaction. The distribution constant of each substrate between solvent and micelle is defined as the binding constant of the substrate with a micelle. The substrate

(S) distributes between the solvent and a micelle (D_n) as follows:

$$S + D_n \xrightleftharpoons{K_S} SD_n$$

$$\downarrow{k_w} \qquad\qquad \downarrow{k_m}$$

$$\text{Products} \qquad \text{Products} \tag{1}$$
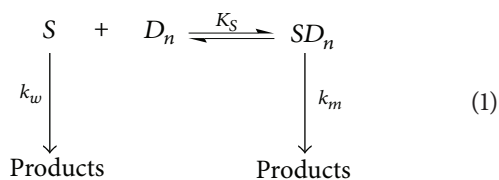
where k_w and k_m are the observed rate constants in the solvent and micelles, respectively. K_S is the association constant of

the substrate with the micelles. In this model, it is assumed that a single equilibrium relation, thus one K_S value, is applied within the whole surfactant concentration range. On the basis of the above model, the following relation for the observed rate constant (k_{obs}) has been derived:

$$\frac{1}{(k_{obs} - k_w)} = \frac{1}{(k_m - k_w)} + \frac{1}{(k_m - k_{obs}) \, K_S \, ([D] - CMC)}, \tag{2}$$

where $[D]$ is the surfactant concentration. Depending on the number of substrates and other compounds (such as salts), relations of k_{obs} can be written as different forms.

2.2. Cooperativity Model. Piszkiewicz presented cooperativity model [5] in 1976 analogous to the enzyme-catalyzed reactions. This model is used only for reactions catalyzed by surfactants. He assumed that a micelle (D_n) forms a noncovalent complex (D_nS) with the substrate (S) before the catalysis takes place:

$$D_n + S \xrightarrow{K} D_nS,$$

$$D_nS \xrightarrow{k_m} \text{products}, \tag{3}$$

$$S \xrightarrow{k_0} \text{products},$$
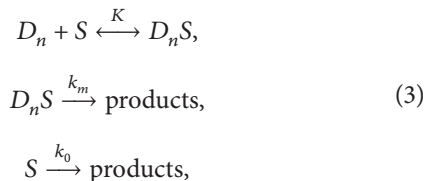
where K is the association constant of the micelle-substrate complex, k_m is the rate constant for micelle-catalyzed reaction, and k_0 is the rate constant for the reaction in the absence of micelle. Similar to pseudophase model, this model assumed that there is only one equilibrium relation, thus one K_S value within the whole surfactant concentration range. The k_{obs} at any concentration of surfactant is given by

$$k_{obs} = \frac{k_0 + k_m K \left(([D] - CMC) / n\right)}{1 + K \left(([D] - CMC) / n\right)}, \tag{4}$$

where n is the number of surfactant molecules per micelle. Thus, this model can study interactions between the substrate and surfactant molecules above the CMC. An alternative cooperativity model, analogous to the Hill model applied to enzyme-catalyzed reactions, was proposed that the substrate and surfactant molecules aggregate to form micelles, D_nS, which may then react to yield product

$$nD + S \xrightarrow{K_D} D_nS,$$

$$D_nS \xrightarrow{k_m} \text{products}, \tag{5}$$

$$S \xrightarrow{k_0} \text{products}.$$
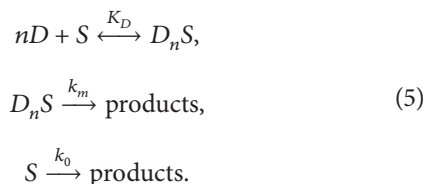
The model gives the following rate equation:

$$\log \left[\frac{(k_{obs} - k_0)}{(k_m - k_{obs})} \right] = n \log [D]_t - \log K_D, \tag{6}$$

where K_D is the dissociation constant of micellized surfactant-substrate complex and $[D]_t$ is the total surfactant
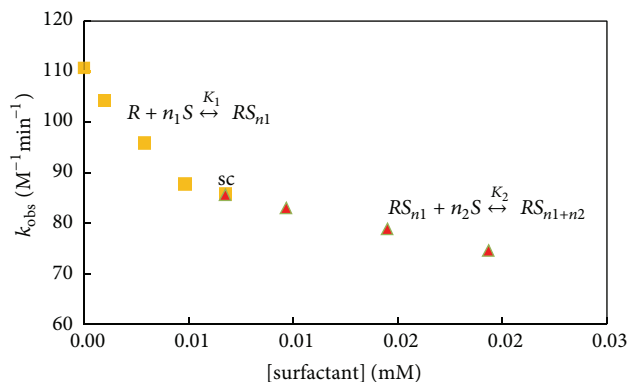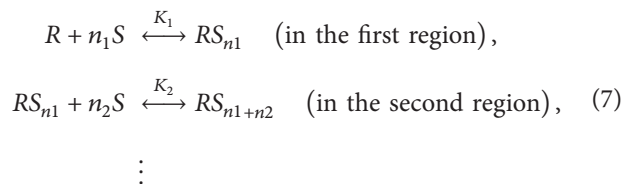

FIGURE 3: Typical equilibrium relations between reactant and surfactant molecules in a two-region system.

concentration. n is known as the cooperativity index and is a measure of the association of additional surfactant molecules to an aggregate in the whole surfactant concentration range. If n value is greater than one, the cooperativity of interaction is positive and if its value is less than one, the cooperativity of interaction is negative and if its value is equal to 1, the interaction is noncooperative.

2.3. Stoichiometric Model. Samiey introduced the stoichiometric (classical) model [6] in 2004. In the stoichiometric model [6], it is assumed that, in each range of surfactant concentration, the surfactant and substrate can bind together and an equilibrium relation exists. The surfactant concentration in which the equilibrium relation between the added surfactant (S) and the species already present in the solution (R) ends and a new equilibrium relation between the added surfactant and the compound resulted from previous equilibrium relation (RS_{n1}) starts which is called "*substrate-surfactant complex formation point*" (or abbreviated as sc point) and is as follows:

$$R + n_1 S \xrightarrow{K_1} RS_{n1} \quad \text{(in the first region)},$$

$$RS_{n1} + n_2 S \xrightarrow{K_2} RS_{n1+n2} \quad \text{(in the second region)}, \tag{7}$$

$$\vdots$$

The CMC value of a surfactant is also a sc point and there may be some sc points higher and lower than CMC as well. The range of surfactant concentration which covers an equilibrium relation is named "*region,*" Figure 3.

Surfactant molecules either monomeric or micellar can bind to the substrate molecules. Micelles can bind to the substrate by one or more number of their surfactant molecules. Thus, we can obtain the stoichiometric ratios and binding constants of interactions between surfactant molecules and with the substrate in various surfactant concentration ranges. The following equation holds for each equilibrium relation [6]:

$$\ln k' = c - \frac{E_S}{RT} [S]_t, \tag{8}$$

where k', c, $[S]_t$, R, and T are the rate constant in the presence of surfactant, $\ln k$ (at first region) or $\ln k_{sc}$ (for other regions), total surfactant concentration, universal gas constant, and absolute temperature, respectively. E_S is the catalytic or inhibition energy of reaction at constant temperature and various surfactant concentrations. k_{sc} is the k_{obs} in the starting of each region except region one and k is the k_{obs} in the absence of surfactants. Equation (8) is introduced as "Samiey equation" [6] and determines the concentration range of each region. If the reaction rate decreases with the increase of surfactant concentration, the sign of E_S is positive and is called "*inhibition energy*" and if the reaction rate increases with increasing the surfactant concentration, the sign of E_S is negative and is named "*catalytic energy*" at constant temperature and various surfactant concentrations [6]. The unit of E_S is kJ (mol molar (surfactant))$^{-1}$. In this model, it is assumed that in each region one substrate molecule, R, binds to n molecules of surfactant and we have

$$R + nS \overset{K}{\longleftrightarrow} RS_n, \tag{9}$$

where K is the binding constant of the substrate-surfactant interaction in each region. According to stoichiometric model, these interactions contain two types: Type I is the interaction of which surfactant molecules have an inhibitory effect on the reaction rate, yielding a decreased reaction rate; Type II is the interaction of which surfactant molecules exert a catalytic effect on the reaction rate, resulting in an increased reaction rate [6]. Some surfactants, show an increased reaction rate in a certain concentration range (type I) and a decreased reaction rate in the other range (type II). The k_{obs}, which indicates the interaction between one species of substrate with one kind of the surfactant, is species dependent and is related to the surfactant concentration as follows [6]:

$$k_{obs} = \begin{cases} \dfrac{k + k_S K\,[S]_t^n}{1 + K\,[S]_t^n} & \text{(region one)}, \\[3mm] \dfrac{k_{sc} + k_S K\left([S]_t - [sc]\right)^n}{1 + K\left([S]_t - [sc]\right)^n} & \text{(all other regions)}, \end{cases} \tag{10}$$

where k and k_{sc} are the k_{obs} in the absence of surfactant (beginning of the first region) and at each sc point, respectively. k_S is the reaction rate constant in the substrate-surfactant complex and is greater than reaction rate in pure solvent (k) but when the surfactant has an inhibitory effect, $k_S = 0$. Going from one region to the next one, if $K^{1/n}$ value (the average binding constant of interaction between one substrate molecule and one surfactant molecule in each region) increases, the cooperativity of interaction is positive and if $K^{1/n}$ value decreases, the cooperativity of interaction is negative. The total binding constant (K_{tot}^i) and total stoichiometric ratio (n_{tot}^i) values for each substrate, in the ith region, can be obtained from following equations:

$$K_{tot}^i = K_1 \cdots K_{i-1} K_i = \prod_{j=1}^{i} K_j,$$
$$n_{tot}^i = n_1 + \cdots + n_{i-1} + n_i = \sum_{j=1}^{i} n_j. \tag{11}$$

Also, using this model we can study interactions of mixed micelles with substrate molecules and calculate the stoichiometric ratios and binding constants of their surfactant molecules with substrate molecules [6].

2.4. Comparison of Stoichiometric, Cooperativity, and PPIE Models. (1) In the PPIE model, the colloidal particles of surfactant (after cmc) are considered as an ion exchanger and the binding of substrate to them is considered like the partition of a substrate between the two phases (micelle and solvent). In the PPIE and cooperativity models, the stoichiometric ratio of surfactant (as micelle) to the substrate is 1 : 1 and there is one average binding constant for substrate-surfactant compound in the whole surfactant concentration range, while in the stoichiometric model the stoichiometric ratio of surfactant (either micellar or monomeric) to the substrate is n : 1 and in each region there is a new equilibrium relation and therefore a new binding constant, a new stoichiometric ratio, and negative or positive cooperativity [6].

(2) The PPIE and cooperativity models is not applicable in the region before the cmc point of surfactant, but in the stoichiometric model the binding of substrate to the monomeric surfactant is considered.

(3) In the PPIE and cooperativity models, for the cases in which the reaction rate increases in one range of surfactant concentration and decreases in another range, it is assumed that in average there is one type of interaction between surfactant and substrate molecules. Therefore, there is one binding constant for whole range of the surfactant concentrations. But, in these cases, in the stoichiometric model it is assumed that the substrate molecules have different interactions with surfactant molecules and the reaction is catalyzed in one or more regions and inhibited in another region(s). Therefore, the binding constants are not identical in different regions.

(4) In the PPIE and cooperativity models, it is assumed that the rate constant in micelle (k_m) is not usually equal to zero. But in the stoichiometric model, it is assumed that the rate constant in micelle for catalysis of reaction is more than the rate constant of free substrate and in the state of inhibition of reaction, it is equal to zero.

(5) In the PPIE and cooperativity models, only one sc point is assumed which corresponds to the cmc of surfactant. But in the stoichiometric model, there are various sc points including cmc.

(6) In the PPIE and cooperativity models, the binding constant and stoichiometric ratio of single type substrate-surfactant interaction are measured. But in the stoichiometric model, we can evaluate the stoichiometric ratios and binding constants of multiple type substrate-surfactant interactions in each region [6].

(7) In the stoichiometric model, K values calculated for each region obey the Van't Hoff equation whereas the binding constants obtained from the PPIE and cooperativity models are not so in most of the cases.

3. Change in the Chemical Reaction Rate in the Presence of Surfactants

Interaction of surfactant molecules with substrates can result in decreasing or increasing the reaction rate or changing the yield of reaction and sometimes these surfactant molecules act as reactants. In this section, we discuss the role of temperature and cosolvents on the interactions between surfactants and substrates as well as the effects of head group, chain length, charge, and concentration of surfactants in a series of reactions, for example, Diels-Alder, redox, photochemical, decomposition, enzymatic, isomerization, ligand exchange, radical, and nucleophilic reactions. Furthermore, this section also discusses the potential role of surfactants as a reactant.

3.1. Diels-Alder Reactions. The Diels-Alder reaction is an organic chemical reaction (specifically, a [4 + 2] cycloaddition) between a conjugated diene and a substituted alkene, commonly termed the dienophile, to form a substituted cyclohexene system. Because the majority of the diene and dienophile intermolecular Diels-Alder reactions have a rather pronounced nonpolar character, an efficient binding of both substrates to micelles is anticipated. This would imply that the effective reaction volume for the Diels-Alder reaction is significantly reduced, leading to micellar catalysis [7].

A study on the reaction of cyclopentadiene with a series of dienophiles shows the roles of charge and substituent groups in their interaction with surfactants [8–12].

In the reaction of acridizinium bromide (a cationic dienophile) with cyclopentadiene, a 10-fold reaction rate is induced by anionic SDS micelles, whereas nonionic TX-100 and cationic 1-N-dodecyl-4-methylpyridinium bromide have only modest effects on the reaction rate [8]. The efficient catalysis by SDS most likely results from electrostatically enhanced binding of the dienophile to the micelles [8, 9]. But the reaction rate of 1,2-dicyanoethylene with cyclopentadienedecreases with the increase of SDS concentrations which is due to weak interactions between 1,2-dicyanoethylene and SDS micelles [10]. It seems to point toward the Stern region of the micelles as the prominent site for this Diels-Alder reaction.

Rispens and Engberts [11] studied the reaction rate of cyclopentadiene with a series of N-substituted maleimides in SDS micellar media. They observed that, up to 30 mM of SDS, the reaction rate of cyclopentadiene with N-methyl maleimide is constant while its rate with N-butyl and N-benzyl substituted maleimideincreases with the size of substituent group. This is because the butyl and benzyl substituent groups lead to deeper solubilization of N-substituted maleimide in the SDS micelle compared to the methyl-substituted compound. Evidence suggests that the reaction in the micellar phase mainly takes place in the region between the core and the Stern layer, thereby still experiencing a polar environment. In all the above-mentioned cases, the

apolar cyclopentadiene might be expected to mainly reside in the apolar micellar core. It was observed that if the SDS concentration is more than 30 mM, the reaction rate decreases. Pseudophase model considers just one kind of interaction occurring between SDS and substrate molecules within the whole SDS concentration range and calculated that k_m value is less than k_w. However, it seems that pseudophase model fails to show that k_m is greater than k_w when the SDS concentration is less than 30 mM.

Simonyan and Gitsov [12] studied the first Diels-Alder reaction performed in an aqueous medium with highly hydrophobic compounds, such as fullerene (C_{60}) as the dienophile and anthracene or tetracene as the dienes, respectively. The reactions were performed in nanocontainers, constructed by self-assembly of linear-dendritic amphiphilic copolymers, Figure 4. Surfactants can also affect the endo/exoselectivity [13], regioselectivity [14], and enantioselectivity [15] of the Diels-Alder reactions.

3.2. Redox Reactions. The catalytic effects of SDS, NaBDS (anionic gemini surfactant), and mixed surfactants (SDS + NaBDS) on the oxidation rate of D-fructose by alkaline chloramine-T have been investigated [16]. The observed catalytic effect of mixed micelle on the oxidation rate was always less than the combination of the catalytic effects of two individual surfactants, suggesting an antagonism (negative synergism) in the mixed micelle. The antagonism has also been confirmed by determining the CMC and the interaction parameter (β^m) of mixed micelle. According to the pseudophase model, K_S and k_m values of interaction of D-fructose with SDS were 8.2 M^{-1} and 16.5 × 10^{-4} s^{-1} and those of D-fructose with NaBDS were 400 M^{-1} and 17.9 × 10^{-4} s^{-1} at 35°C, respectively.

The catalytic effects of zwitterionic micellar solutions of SB3-14 and SB3-16 on the redox reaction of Br^- + BrO_3^- have been studied using the pseudophase model [17]. The K_S and k_m values of BrO_3^- with SB3-14 were 310 M^{-1} and 1.24 × 10^{-3} s^{-1} and those of BrO_3^- with SB3-16 were 3100 M^{-1} and 0.99 × 10^{-3} s^{-1}, respectively. In the presence of the same concentrations of surfactants, the reaction rate of using SB3-16 is less than that of using SB3-14. It seems that deeper solubilization of BrO_3^- in SB3-16 micelles decreases its reaction rate with Br^-.

Vanadium (V) oxidation of D-glucose was studied in the presence of CPC, SDS, and TX-100 [18]. CPC inhibits the reaction, while SDS and TX-100 accelerate the reaction to different extents. The observed effects were studied by the cooperativity model and were explained by considering the hydrophobic and electrostatic interactions between the surfactants and substrates. Similarly, oxidation reactions of Ce(IV) [19] or oxyanions such as CrO_4^{2-} [20, 21] and MnO_4^- [22] with organic compounds have been studied in the presence of surfactants.

Surfactants can affect the nucleation and growth kinetics [23, 24] and the reduction [25] of nanocompounds. For instance, colloidal silver particles in the nanometer size range were synthesized in ethanol, by the reduction of $AgNO_3$ with nonionic surfactants Brij 97 and Tween 80 [25]. The main conclusion is that surfactants reduce silver ions to the

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