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EFFECTS OF SURFACTANTS ON THE RATE OF CHEMICAL REACTIONS

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Abstract

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. Anionic surfactants, such as sodium dodecyl sulfate (SDS), contain anionic functional groups at their head, that is, sulfate, sulfonate
and phosphate.

Keywords: Organic solvents, ionic associates, cation, tetraphenylarsonium, tetraphenylphosphonium, triphenyl lead, ionic association, benzene, toluene, xylene.

Introduction

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 amphiphilicmolecules 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.

Methods:

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 criticalmicelle 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].

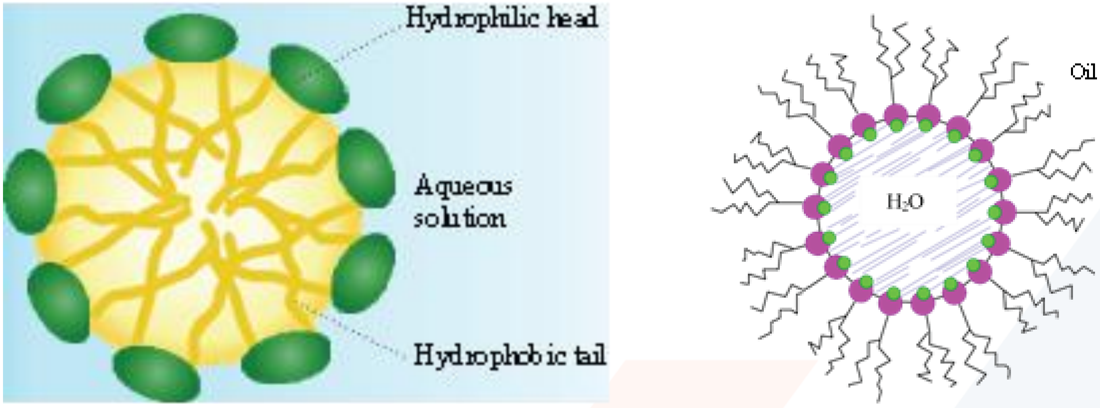


FIGURE 2: Typical structures of (a) micelle and (b) reverse micelle.

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 amicelle. Thesubstrate (S) distributes between the solvent and a micelle (Dn) as follows:where kw and km are the observed rate constants in the solvent and micelles, respectively. KS is the association constant of the substrate with the micelles. In this model, it is assumed that a single equilibriumrelation, thus oneKS value, is applied within thewhole surfactant concentration range.On the basis of the above model, the following relation for the observed rate constant ($k$obs) has been derived:

$$(kobs - kw) = (km - kw) + (km - kobs)KS([D] - CMC)$$

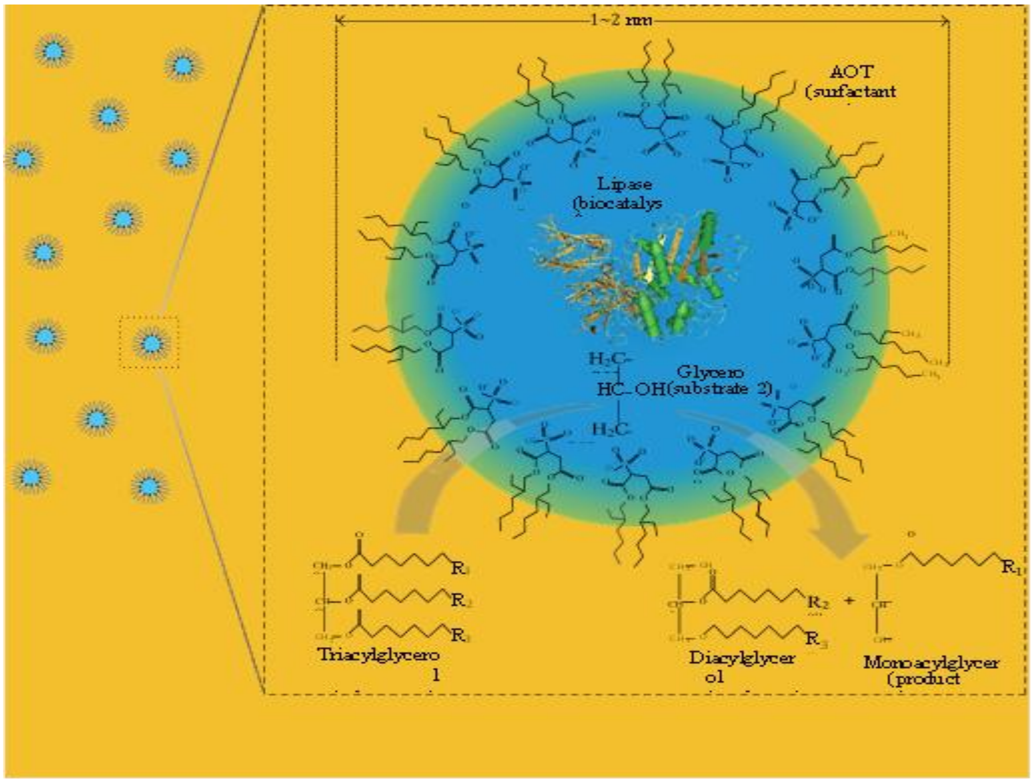
where $[D]$ is the surfactant concentration. Depending on the number of substrates and other compounds (such as salts), relations of $k$obs can be written as different forms. Piszkiewicz presented cooperativity model [5] in 1976 analogous to the enzyme-catalyzed reactions. This model is used only for reactions catalyzed by surfactants. He assumed that a micelle (Dn) forms a noncovalent complex (DnS) with the substrate (S) before the catalysis takes place: where K is the association constant of the micelle-substrate complex, km is the rate constant for micelle-catalyzed reaction, and $k0$ is the rate constant for the reaction in the absence ofmicelle. Similar to pseudophasemodel, thismodel assumed that there is only one equilibrium relation, thus one KS value within the whole surfactant concentration range.

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 cooperativitymodels, 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 inaverage there isone type of interactionbetween 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 (km) 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 substratesurfactant interaction are measured. But in the stoichiometric model, we can evaluate the stoichiometric ratios and binding constants ofmultiple type substrate-surfactant interactions in each region [6].

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

Isomerization, Ligand Exchange, and Radical Reactions. Gille et al. [54] studied the thermal *cis-trans*-isomerization of 4,4′-nitroanilinoazobenzene dye in the presence SDS, TX-100, and Igepal CA-520. In microheterogeneous water/surfactant solutions isomerization rate constant values of selected azo dyes were strongly dependent on the concentrations of SDS and TX-100 in water and varied with the composition of bicontinuous microemulsions of Igepal CA-520/heptane/water. The large spread of isomerization rate constants is in part due to varying microviscosity. They showed that the *trans*-azo dyes have a constant balancing average microenvironment in the water/surfactant interface layer in a wide range of micelle concentrations. The isomerization rates of *cis*-isomer decrease by an order of magnitude with increasing the surfactant concentration, in part due to increasing microviscosity. The rate of ligand substitution reaction between Fe(CN)5H2O3− and pyrazine is decreased in the presence of CTAB. The kinetic data showed that both nonmicellized and micellized CTAB are operative kinetically and interact with Fe(CN)5H2O3−.The pseudophase model can be used to study this interaction only for CTAB concentrations above its CMCand the calculatedKS and km were 260M−1 and 12.7 s−1, respectively.This strong interaction competes with the ligand substitution reaction. Similarly, the study of substitution rate of 4-cyanopyridine (4-CNpy) in Fe(CN)(4-CNpy)3−by S2O8 2− in the presence of CTAB and TTAB shows that the longer the chain length of surfactant is, the more the reaction rates decreased.

On the other hand, it was observed that the reaction rate is not influenced by changes in the concentration of TX-100 and SDS. This observation shows the importance of preliminary electrostatic and then hydrophobic interactions of surfactants and substrates on the ligand substitution reaction rate. Graciani et al. showed that the rate of substitution of bipyridine (bpy) in Fe(CN)4(bpy)2− by S2O8 2− increases in the presence of zwitterionic surfactant SB3-14. The moderate interaction of positive headgroup of SB3-14 with substrates increases their concentrations on the surface of SB3-14 micelles and increases the reaction rate. Here, the authors calculated binding constants of SB3-14 to Emulsion polymerization is an example for radical reactions in the presence of surfactants Tang et al. studied copolymerization of methyl methacrylate, butyl acrylate, and styrene in combination with a water-soluble anionic monomer (methacrylic acid or acrylic acid) and a nonionic monomer (*N*-methylol acrylamide).



Schematic representation of AOT/isooctane reversed micellar system

The emulsifier surfactant, DSB, at a level greater than its CMC generated particle nuclei by micelle nucleation and controlled the particle size, particle size distribution, and the rate of polymerization. On the other hand, the reaction rates of a number of nucleophiles (other than hydroxide ion) with neutral and anionic substrates are increased in the presence of cationic surfactants. It was observed that the increase in the chain length of cationic surfactants and adding TX-100 to the reaction media decreases the reaction rate. Also, results show that adding organic cosolvents to the surfactant-contained media further decreases the reaction rate compared to that in the presence of surfactant only. These observations are due to the added organic cosolvents increase the CMC of surfactants and the interaction of TX-100 with cationic surfactants (in theirmixed micelles) competes for its interaction with substrate molecules. In addition to interaction with substrate molecules, surfactants sometimes can form ion pairs with them. As an example, it has been reported that SDS attacks cationic crystal violet dye and causes the formation of dye-surfactant ion pair.

Methodology of work and processing of experimental results:

As reported, reactions of some triphenylmethane dyes with hydroxide ion (fading) in the presence of surfactants have been studied by cooperativity, pseudophase, and stoichiometric models [81–84]. For comparing the results obtained from these models, the fading rate of cationic methyl green (ME2+) dye in the presence of SDS [83] is studied. According to the stoichiometric model, in the used concentration range of SDS, there are three regions (or three kinds of interactions) at each temperature and the data of collectedbelowtheCMCare used in the calculations, Preliminary electrostatic and then hydrophobic interactions of SDS with ME2+ decrease the positive charge of ME2+ and decrease the reaction rate ofME2+ with hydroxide ion.

With the increase of SDS concentration, the reaction rate decreases and thus $kS = 0$ in each region. Also, from the first to the third region, the impact of SDS on the reaction rate decreases and thus ES values decrease. At each temperature, from the first to the third region, the $(K)1/n$ values in each region decrease and thus the cooperativity of reaction is negative. Reactions in the first and second regions are exothermic and those in the third region are endothermic, resulting in a negative value of ΔHtot. Using the data of different regions of SDS and TX-100, the data of fading reaction of ME2+ in their mixtures was analyzed
and stoichiometric ratios and binding constants of them with ME2+ were calculated.

Results

According to the cooperativity model, the interaction of SDS with ME2+ is endothermic and $kS = 0$ and, at all temperatures, the cooperativity of process is positive. The data of fading reaction in the presence of SDS did not fit to the pseudophase model. This example shows that the obtained results are not similar to each other due to the different presumptions used in pseudophase, cooperativity, and stoichiometric models.

This review discusses effects of different kinds of surfactants in a series of chemical reactions including Diels-Alder, redox, photochemical, decomposition, enzymatic, isomerization, ligand exchange, radical, and nucleophilic reactions. These interactions were catalyzed or inhibited via the change in the dielectric constant ofmicroenvironment or/and the charge of substrate molecules. As observed in all discussed examples, preliminary electrostatic and then hydrophobic interactions occur between surfactants and substrate molecules. Substrate/ surfactant interactions are studied using pseudophase, cooperativity, and stoichiometric models.

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