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Photodegradation of Surfactants. 11. ζ -Potential Measurements in the Photocatalytic Oxidation of Surfactants in Aqueous TiO_2 Dispersions

Jincai Zhao and Hisao Hidaka*

Department of Chemistry, Meisei University, 2-1-1 Hodokubo, Hino, Tokyo 191, Japan

Akira Takamura

Meiji College of Pharmacy, 1-22-1 Yato, Tanashi, Tokyo 188, Japan

Ezio Pelizzetti

Dipartimento di Chimica Analitica, Università di Torino, 10125 Torino, Italy

Nick Serpone

Department of Chemistry and Biochemistry, Concordia University,
Montreal, Quebec H3G 1M8, Canada

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Since the adsorption of surfactants on TiO_2 catalyst surface is one of the key factors affecting the photodegradation rate, the ζ -potentials of TiO_2 particles in aqueous surfactant dispersions have been determined before and after illumination. The pH dependence of the ζ -potential was also examined. The ζ -potential of TiO_2 particles shifted to the more positive value upon irradiation. Models of surfactant adsorption on the TiO_2 surface are proposed. The anionic DBS (sodium dodecylbenzenesulfonate) was more easily adsorbed on the irradiated TiO_2 surface and was degraded faster than the cationic BDDAC (benzyl-dodecyl-dimethylammonium chloride) surfactant.

Introduction

Environmental pollution by chemical substances has become a serious and global problem. Recently, a new and effective method is attracting much attention, in which the toxic substances can be photodegraded catalytically on semiconductor particles.¹⁻⁸ A variety of surfactants difficult to biodegrade are greatly utilized in industrial and domestic fields; they are one of the direct causes of aquatic pollution. In the past years, we have reported extensively on the photodegradation of surfactants catalyzed by the TiO_2 semiconductor under either UV irradiation or solar exposure.⁹⁻¹⁹ Under otherwise identical experimental conditions, the photodegradation rates gen-

erally followed the order anionic > nonionic > cationic surfactants.^{14,17} However, the causes that led to this result have not been clarified in detail. Additional observations in the variations of the nature of the TiO_2 surface under illumination and adsorptions of the ionic surfactant molecules on the irradiated TiO_2 surface are also required.

In this paper, ζ -potential variations of the TiO_2 particles in the surfactant dispersion were measured during irradiation. The pH effect of the dispersion on the ζ -potential was also examined. The adsorptions and degradation rates of surfactants on the TiO_2 surface are discussed from the viewpoint of electrostatic effect between the irradiated TiO_2 surface and the ionic surfactant molecules.

Experimental Details

Sodium dodecylbenzenesulfonate (DBS), obtained from Tokyo Kasei Co., Ltd., was purified according to conventional recrystallization. Benzyl-dodecyl-dimethylammonium chloride (BDDAC) was used as supplied by Wako Pure Chemical Ind., Ltd. Nonionic *p*-nonylphenyl poly(oxyethylene) ether (NPE-9, $\text{C}_6\text{H}_{19}\text{C}_6\text{H}_4\text{-O-(CH}_2\text{CH}_2\text{O)}_9\text{-H}$) was provided by Miyoshi Oil & Fat Co., Ltd. The TiO_2 (P-25) photocatalyst, supplied by Degussa AG, was mostly anatase powder with a surface of 55 m^2/g . Deionized and doubly-distilled water was used throughout.

The foaming behavior of the surfactant solutions was observed by the following procedure. Each surfactant dispersion (50 mL)

* Author to whom all correspondence should be addressed.

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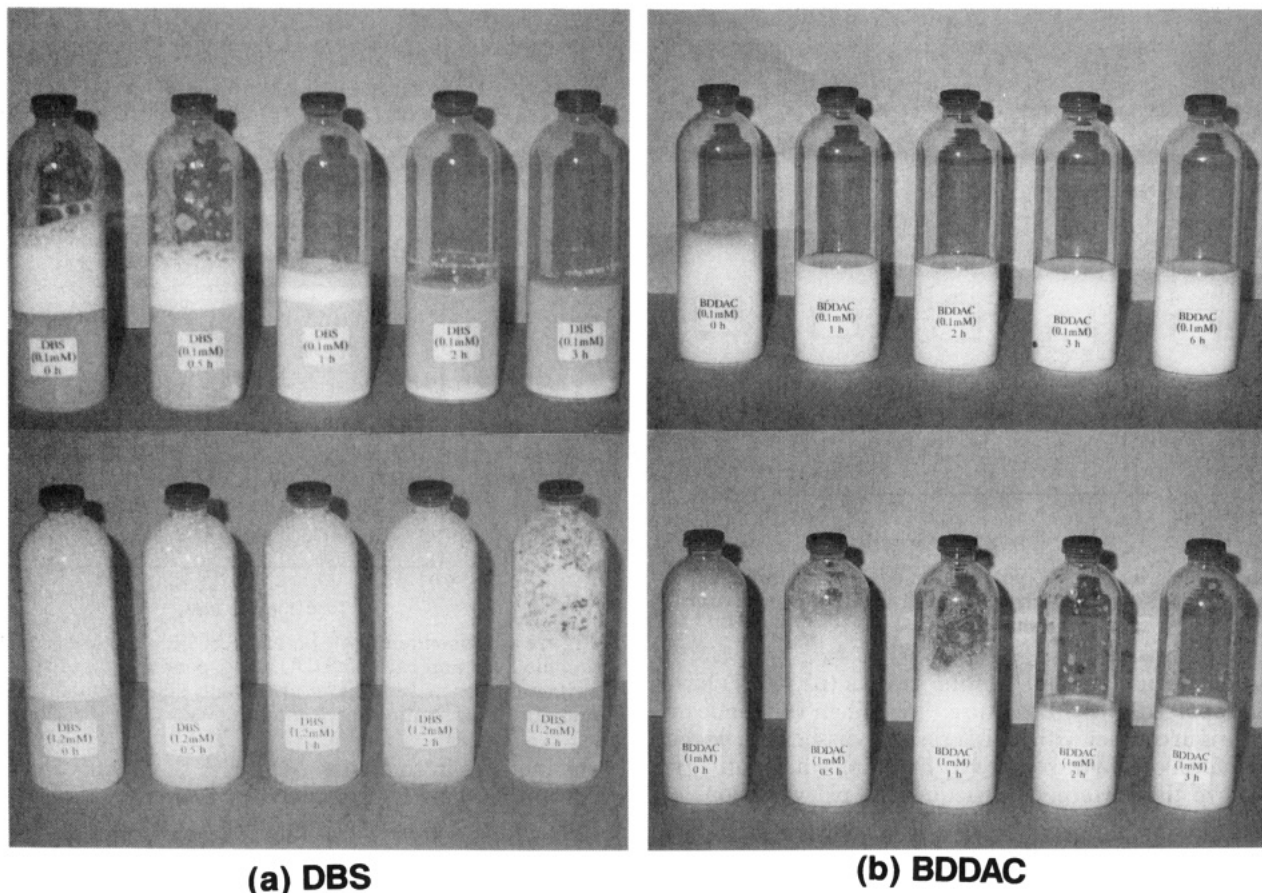
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(a) DBS

(b) BDDAC

Figure 1. Photographs of foaming power tests for (a) DBS (0.1 and 1.2 mM) and (b) BDDAC (0.1 and 1.0 mM).

with TiO_2 particles (0.1 g) was irradiated in a 115-mL glass vessel. After a given irradiation time, the vessel was vigorously shaken for 5 min and photographs were taken. The ζ -potentials of TiO_2 particles in a surfactant suspension (50 mL) with TiO_2 powder (2 mg) were measured with a Laser Zee Model 501 before and after illumination. A temperature correction to 20 °C was made for all measurements. The photodegradation of surfactants was carried out according to the following method. A dispersion consisting of a surfactant solution (0.1 mM, 50 mL) and TiO_2 (0.1 g) was contained in a 70-mL Pyrex glass vessel and was illuminated with a Hg lamp ($\lambda > 330$ nm, Toshiba SHLS-1002A, 100 W) under continuous magnetic stirring. Oxygen was replenished by opening the reaction vessel to the atmosphere when the dispersion was sampled after an appropriate irradiation time. A 2-mL dispersion aliquot was subsequently taken, centrifuged, and filtered through a Millipore membrane (pore size 0.22 μm). The surfactant concentration in each degraded solution (DBS, BDDAC, or NPE-9) was monitored by both a dye extraction procedure²⁰ and UV spectroscopy (224 nm, absorption of aromatic moiety). The quantities of peroxide and aldehyde intermediates in the degraded solution were determined according to a modified iodometric spectroscopic method and by Nash's procedure as mentioned before.¹⁷ The temporal CO_2 evolution during the photodegradation was assayed by gas chromatography using a thermal conductivity detector,¹⁴ where the vessel containing the dispersion was closed and purged with pure oxygen gas before irradiation.

Results and Discussion

The photographs which illustrate the foaming behaviors for the photodegraded surfactant solutions (DBS and BDDAC) are shown in Figure 1. The initial surfactant solution foamed extensively and the TiO_2 particles were well suspended. The foam height decreased with increasing the irradiation time. No foaming action was observed after 2 h of illumination. The TiO_2 catalyst was sedi-

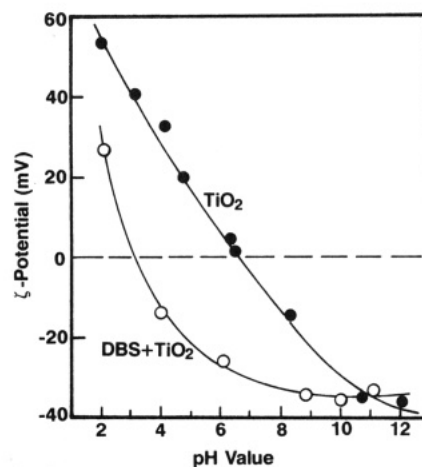


Figure 2. pH dependence of ζ -potentials of TiO_2 particles (2 mg) in an aqueous dispersion (50 mL) and in an aqueous DBS dispersion (0.024 mM, 50 mL).

mented at the bottom of the vessel owing to the decomposition of the surfactant and the removal of protection power of the colloids of TiO_2 particles by the surfactant molecules.

The pH dependence of the ζ -potential of TiO_2 particles in both an aqueous DBS dispersion and a surfactant-free dispersion is illustrated in Figure 2. In a TiO_2 dispersion system free of surfactants, the ζ -potential of TiO_2 particles decreased with increasing the pH value of the dispersion. The TiO_2 particles were positively charged and the ζ -potential of TiO_2 particles exhibited a positive value in acidic media (pH < 6.8). On the other hand, a negative potential value was observed under alkaline conditions (pH > 6.8). The isoelectric point is $\text{pI} = 6.8$ for the aqueous

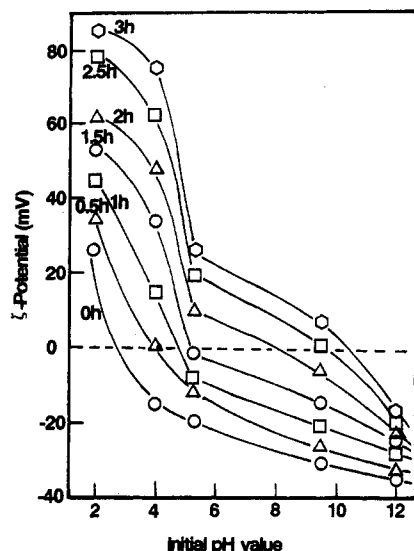
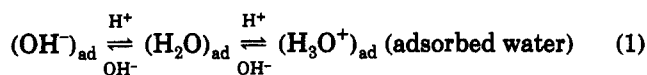
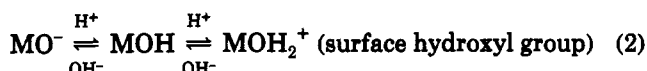


Figure 3. Variations in ζ -potential of TiO_2 particles (2 mg) in an aqueous DBS suspension (0.024 mM, 50 mL) at various initial pH values for several irradiation times.

TiO_2 dispersion system. Similar results ($\text{pI} = 5\text{--}7$) have been reported in the literature.^{21–23} When the semiconductor is in contact with moisture, both dissociated water, in the form of a hydroxyl group, and molecular water are bound to the surface.² Consequently, pH variations of the dispersion would cause a change in the surface charges of the TiO_2 particles (eqs 1 and 2)



or



Although both DBS adsorption and ionic strength will affect the measured ζ -potential, the specific adsorption of DBS on the TiO_2 surface was confirmed by Figure 2, which showed a change in the pH of the isoelectric point. Addition of the anionic surfactant DBS to the aqueous TiO_2 suspension led to a decrease in the ζ -potential of TiO_2 particles at the same pH values. This implies that the anionic DBS molecules must adsorb easily and strongly on the TiO_2 surface, which would result in an increase of the negative charges on the TiO_2 particles. Motschi et al.²⁴ reported that such hydrous oxides as TiO_2 have a stronger tendency to adsorb the alkylbenzenesulfonate at an appropriate pH region (below $\text{pH} = 10$).

Figure 3 depicts the changes in ζ -potential of TiO_2 particles in the TiO_2 /DBS aqueous dispersion at various initial pH values for several irradiation times. The ζ -potential of TiO_2 particles increased with the irradiation time for each dispersion at different initial pH values. The increase in the ζ -potential with the irradiation time for the acidic dispersion ($\text{pH} = 2$ or 4) was faster than that for the alkaline dispersion ($\text{pH} = 12$). The experimental results also showed that the ζ -potential values shifted to more positive side upon irradiation for the surfactant-free aqueous TiO_2 dispersion and for the cationic BDDAC/ TiO_2 dispersion at various initial pH values. However,

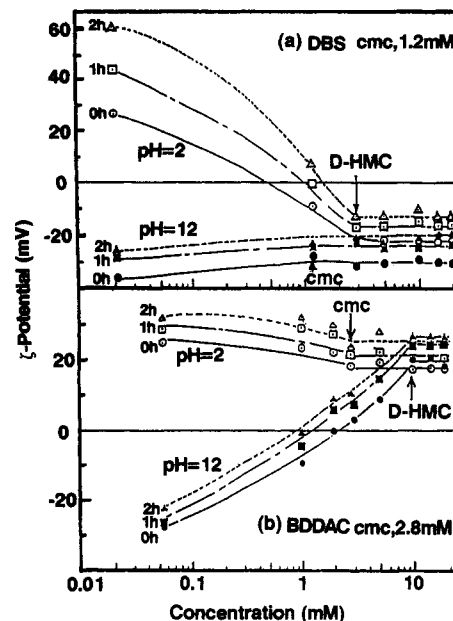


Figure 4. Dependence of ζ -potential of TiO_2 particles (2 mg) in anionic DBS and cationic BDDAC dispersions (50 mL) on the surfactant concentrations in acidic and alkaline media before and after illumination for 1 and 2 h.

the increase in the ζ -potential with the irradiation time for the TiO_2 /DBS dispersion was more remarkable than that for the TiO_2 dispersion or TiO_2 /BDDAC dispersion, particularly at acidic initial pH values. As reported earlier,^{14,17–19} the surfactant/ TiO_2 system becomes immediately acidic from initially alkaline or neutral media due to the concomitant generation of H^+ ions under illumination, followed by a shift of the ζ -potential of TiO_2 particles to more positive values. The adsorption of DBS molecules on the TiO_2 surface appears to promote the generation of H^+ ions. The ζ -potential for TiO_2 /DBS dispersion under adequate acidic conditions increased more rapidly upon irradiation, since the DBS molecules are easily adsorbed on the TiO_2 surface at acidic pH values.

Owing to technical reasons, a surfactant dispersion (50 mL) containing 2 mg of TiO_2 was used for the ζ -potential measurements, while a dispersion consisting of TiO_2 (100 mg) and an aqueous surfactant solution (50 mL) was commonly employed for the photodegradation of surfactants and the pH measurements. The ζ -potential shift (to positive side) under irradiation is expected to be more rapid in the surfactant photodegradation system than under the conditions of Figure 3. In addition, the TiO_2 surface is charged more positively because the structure of the TiO_2 surface has undergone reconstruction after irradiation is terminated to measure the ζ -potential values. Therefore, the irradiated TiO_2 surface under initial acidic, neutral, or slightly alkaline conditions would adsorb more easily anionic surfactant molecules than cationic ones. The photooxidation of anionic surfactants proceeds more easily than that of cationic surfactants (see Figures 6 and 7 below).

The surfactant (DBS or BDDAC) concentration dependence of the ζ -potential of TiO_2 particles before and after irradiation is illustrated in Figure 4. As DBS was added to an acidic TiO_2 dispersion ($\text{pH} = 2$), the ζ -potential of TiO_2 particles decreased significantly and varied from a positive value to a negative one with increasing the DBS concentration, finally reaching a constant value above a concentration of about 3 mM. Anionic DBS molecules are easily adsorbed on the positively charged TiO_2 surface under acidic conditions ($\text{pH} = 2$) owing to electrostatic effects. At higher concentrations, the ζ -potential exhibited

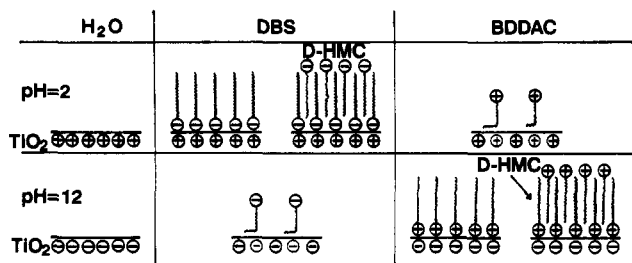
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Chart I. Adsorption Models for Anionic DBS and Cationic BDDAC on the TiO_2 Surface at Different pH Values



a negative value in spite of the acidic media. This result means that adsorbed anionic DBS molecules are more than the hydrogen ions on the TiO_2 surface yielding a double layer hemimicelle (D-HM) by a lateral hydrophobic interaction between the long hydrocarbon chains of two surfactant molecules with opposite orientations. The breakpoint at 3 mM (above the cmc of 1.2 mM) refers to the double layer hemimicelle concentration (D-HMC). Adsorption models are illustrated in Chart I. Adding additional layers to the double layer is difficult due to electrostatic repulsion. By contrast, the addition of anionic DBS did not cause significant variations in the ζ -potential of TiO_2 particles under alkaline conditions. Anionic surfactant molecules cannot be adsorbed strongly on the negative TiO_2 surface in alkaline media (pH = 12) owing to electrostatic repulsion.^{24,25} They are weakly adsorbed through the hydrophobic moiety on the negative TiO_2 surface rather than through the negative sulfonate moiety of DBS. The adsorption of DBS molecules led to a slight increase in the ζ -potential of TiO_2 particles possibly because the adsorption of surfactant molecules reflects some intermediate properties between the surface of TiO_2 particles and the bulk dispersion. Above the cmc, the adsorption of DBS⁻ ions would reach an equilibrium since the concentration of the monomer-like DBS in the bulk phase remains unchanged. The ζ -potential of TiO_2 particles attained a constant value above the cmc.

The cationic BDDAC system exhibited opposite tendencies to the anionic DBS system. Addition of cationic BDDAC to an alkaline TiO_2 dispersion (pH = 12) greatly altered the ζ -potential of TiO_2 particles from a negative value to a positive one and finally reached a constant value above 10 mM. Cationic BDDAC molecules are easily adsorbed on the negative TiO_2 surface in alkaline media. Similar to DBS in an acidic dispersion, a D-HM adsorption of BDDAC on the TiO_2 particles can be formed at higher concentrations. Under acidic conditions, the ζ -potential of TiO_2 particles decreased slightly with increasing the BDDAC concentration and remained unchanged above the cmc (2.8 mM).

As shown in Figure 4, the ζ -potential of TiO_2 particles for both DBS and BDDAC systems always shifted to more positive values after irradiation, irrespective of the initial concentrations and initial pH values. Upon illumination, the TiO_2 surface becomes more positively charged, which should lead to variations in the photodegradation rates between anionic and cationic surfactants.

The ζ -potential of TiO_2 particles in a nonionic NPE-9 suspension system is depicted in Figure 5. In acidic media, the ζ -potential of TiO_2 particles decreased slightly with increasing the surfactant concentration and then reached a constant value above the cmc of NPE-9. Under alkaline conditions, however, the ζ -potential of TiO_2 particles

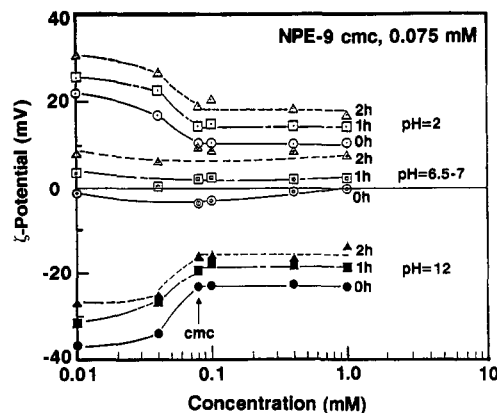


Figure 5. Dependence of ζ -potential of TiO_2 particles (2 mg) in nonionic NPE-9 dispersions (50 mL) on the NPE-9 concentration under acidic and alkaline conditions before and after illumination for 1 and 2 h.

increased with an increase in the NPE-9 concentration. Similarly, the ζ -potential remained constant above the cmc of NPE-9. In neutral media, the effect of the NPE-9 concentration on the ζ -potential of TiO_2 particles is small. Paralleling the anionic and cationic systems, the ζ -potential of TiO_2 particles shifted to more positive values upon illumination at all the pH ranges used.

The adsorption of nonionic NPE-9 molecules on the positively charged TiO_2 surface (pH = 2) leads to a decrease in the positive charges on the TiO_2 particle surface. After the NPE-9 molecules adsorb on the TiO_2 surface, the position of the shear plane would become further away from the protonation layer reflecting a lower potential. Above the cmc, an equilibrium of the adsorption is achieved since the concentration of the monomer-like NPE-9 in the bulk phase becomes unchanged and hence the ζ -potential of TiO_2 particles remains constant. In the same way, the negative charge on the TiO_2 particles, under alkaline conditions, is expected to decrease with increasing the NPE-9 concentration and to remain unchanged above the cmc. The effect of nonionic NPE-9 addition on the ζ -potential of TiO_2 particles is negligible under neutral conditions (pH = 6.5–7).

The photooxidation results of DBS and BDDAC surfactants (initial pH = 6.5–7) are given in Figure 6. Two analytical procedures were employed to monitor the photodegradation process. One was a dye extraction method that addresses mainly the variation in surface activities of these surfactants but cannot determine which bond of the surfactant structure is cleaved. The other was an UV spectroscopic approach in which the UV absorption (224 nm) of the aromatic moiety in the surfactant structure was measured. Both of the experimental results show that anionic DBS was degraded more rapidly than the cationic BDDAC. Similarly, the rate of DBS mineralization to CO_2 was also greater than that of BDDAC.

Since the TiO_2 /surfactant dispersion system becomes acidic (below pH = 6.8) immediately under illumination and the TiO_2 surface becomes positively charged,^{14,18,19} the anionic DBS molecules are adsorbed more easily on the positive TiO_2 surface caused by irradiation than the cationic BDDAC ones. The catalyzed photooxidation process involves attack of $\cdot\text{OH}$ (and/or $\cdot\text{OOH}$) radicals, produced on the illuminated TiO_2 surface, on the surfactant molecules as evidenced by spin-trapping ESR data and by peroxide measurements.^{16,17} The lifetime of $\cdot\text{OH}$ (or $\cdot\text{OOH}$) radicals is relatively short and they are unlikely to migrate far from the TiO_2 surface and hence the

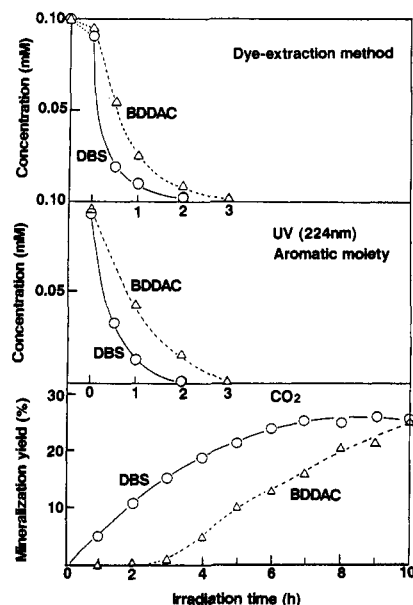


Figure 6. Comparison of the photodegradations between anionic DBS and cationic BDDAC (0.1 mM, 50 mL) in the presence of TiO_2 particles (100 mg).

degradation process occurs at the surface or within a few monolayers around the photocatalytic surface.^{17,26,27} The photooxidation of anionic DBS is expected and found to be faster than that of cationic BDDAC.

Figure 7 represents the formation of peroxide and aldehyde as intermediate products in the photocatalytic oxidation of DBS and BDDAC. The amount of peroxide formed in both DBS and BDDAC degradation processes increased with irradiation time to reach a maximum and subsequently decreased with further irradiation. Both the formation and decomposition of the peroxide from the DBS photooxidation were more rapid than those from the degradation of BDDAC. The aldehyde also reached a maximum and subsequently decomposed. Similarly, the DBS system reached a maximum value of aldehyde formation faster than the BDDAC system. It should be noted that the analytical method used for aldehyde mainly addresses formaldehyde, but small quantities of other

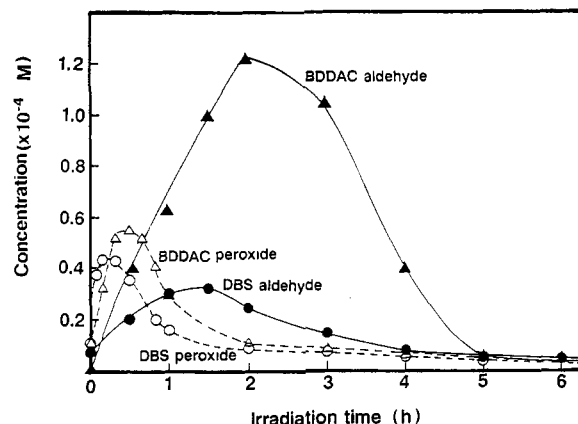


Figure 7. Formation of peroxide and aldehyde in the photo-oxidation of DBS and BDDAC (0.1 mM, 50 mL) in the presence of TiO_2 particles (100 mg).

aldehydes can be also detected. The detailed studies concerning the structure and the amount of aldehydes formed and other intermediates are now in progress. These results are consistent with those in Figure 6. Since anionic DBS is more readily adsorbed on (or near to) the irradiated TiO_2 surface, the degradation of the substrate, the formation and decomposition of intermediates, and the mineralization to CO_2 for anionic DBS would be faster than for cationic BDDAC.

Conclusion

Upon illumination of an aqueous TiO_2 dispersion, the ζ -potentials of TiO_2 particles shift to positive values and the TiO_2 surface becomes positively charged. The adsorption of anionic DBS molecules on the irradiated TiO_2 surface is easier than that of the cationic BDDAC ones. This explains the faster photooxidation of anionic DBS over the other surfactants examined.

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