Biological activity and environmental impact of anionic surfactants

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Received 1 September 2001; accepted 22 April 2002

Abstract

The newest results concerning the biological activity and environmental fate of anionic surfactants are collected and critically evaluated. The chemical and physicochemical parameters related to the biological activity and the field of application are briefly discussed. Examples on the effect of anionic surfactants on the cell membranes, on the activity of enzymes, on the binding to various proteins and to other cell components and on their human toxicity are presented and the possible mode of action is elucidated. The sources of environmental pollution caused by anionic surfactants are listed and the methods developed for their removal from liquid, semiliquid and solid matrices are collected. Both the beneficial and adversary effects of anionic surfactants on the environment are reported and critically discussed. It was concluded that the role of anionic surfactants in the environment is ambiguous: they can cause serious environmental pollution with toxic effect on living organisms; otherwise, they can promote the decomposition and/or removal of other inorganic and organic pollutants from the environment. The relationship between their chemical structure, physicochemical parameters, biological activity and environmental impact is not well understood. A considerable number of data are needed for the development of new anionic surfactants and for the successful application of the existing ones to reduce the adversary and to promote beneficial effects.

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Keywords: Anionic surfactants; Physicochemistry; Biological activity; Environmental impact

1. Chemistry and physicochemistry

Anionic surfactants are amphipatic compounds consisting of a hydrophobic (alkyl chains of various length, alkylphenyl ethers, alkylbenzenes, etc.) and a hydrophilic part (carboxyl, sulfate, sulfonates, phosphates, etc.). It has been established many times that the hydrophobic and hydrophilic parts readily interact with the polar and apolar substructures in macromolecules such as proteins (Yamaguchi et al., 1999; Xiao et al., 2000), and cellulose (Griffiths and Howe, 1998) or with the polar or apolar molecules in a mixture of compounds (Chirila et al., 2000; Von Berleps et al., 2000). Because of these interactions, anionic surfactants can decrease the energy of interaction and the energy of solvation between a high variety of heterogeneous phases in many technological processes and biological systems by adsorbing on oil-water (Staples et al., 2000), polystyrene-water (Turner et al., 1999), and air-water (Hawerd and Warr, 2000) interfaces. In order to find materials for effective surfactant removal, the adsorption of anionic surfactants on various solid surfaces have been extensively studied. Thus, it has been established that sodium lauryl sulfate is readily adsorbed onto arsenic-bearing ferrihydrite (Quan et al., 2001), other surfactants have been adsorbed by layerd double hydroxides (Pavan et al., 2000), by hydrolytically stable metal oxides (Vovk, 2000). The adsorption of anionic surfactant on solid surfaces (Somasundaran and Huang, 2000; Rodriguez and Scamehorn, 2001) can modify surface characteristic and electron transfer (Wang et al., 2000). The adsorption of anionic surfactants on solid surfaces (Somasundaran and Huang, 2000; Rodriguez and Scamehorn, 2001) can modify surface characteristic and electron transfer (Wang et al., 2000a), can result in the formation of surface aggregates similarly to micelles (Luciani et al., 2001) and can increase the film thickness of other adsorbed molecules (Churaev, 2000; Esumi et al., 2000; Miyazaki et al., 2000).

Anionic surfactants not only change the surface characteristics of solids by adsorption but can also enhance the solubility of sparingly soluble compounds in water (Harri-
son et al., 1999), and can reduce the resistance to mass transfer (Vazquez et al., 2000). Anionic surfactants are present in monomeric form in both apolar and polar solvents at low concentration. At a higher concentration (critical micelle concentration, CMC), they form regular aggregates (micelles) (Joshi et al., 1999). CMC highly depends on the polarity of the solvent, on the structural characteristics of the surfactant molecule (Okano et al., 2000; Jalali-Heravi and Konoz, 2000) and on the ionic concentration of the solution (Talens-Alesson, 1999). The hydrophobic part of anionic surfactants turns towards the bulk of the solvent in the case of apolar solvents (i.e. oil), the hydrophilic head groups turn inside the micelles forming an environment that can readily accommodate polar molecules such as water forming water-in-oil type emulsions. In polar solvents, the situation is reversed: head groups turn towards the bulk of solvent, apolar substructures pointing towards the centre of the micelle accommodating hydrophobic molecules (oil-in-water type emulsions).

Due to their favorable physicochemical characteristics, anionic surfactants are extensively used in many fields of technology and research. Anionic surfactants have been successfully employed for the enhancement of the efficacy of the active ingredient in pharmaceutical (Lawrence, 1994) and agricultural formulations (Riechers et al., 1995), in biotechnological (Chang et al., 1994) and in other industrial processes (Czapla and Bart, 1999; Tong et al., 2000), and in cosmetics (Reich and Robbins, 1993).

2. Biological activity

Anionic surfactants themselves show marked biological activity too either by binding to various bioactive macromolecules such as starch (Merta and Stenius, 1999), proteins (Nielsen et al., 2000), peptides and DNA (Marques et al., 2000) or by inserting into various cell fragments (i.e. phospholipid membranes) causing misfunction.  

2.1. Binding to proteins, peptides and membrane phospholipids

The occurrence of binding of anionic surfactants to proteins and peptides has been demonstrated many times. This binding may result in the alteration of the folding of the polypeptide chain and the change of the surface charge of the molecule. The modification of structure and charge may lead to modified biological function too.  

It has been established that sodium dodecyl sulfate (SDS) and the cationic (cetyltrimethyl ammonium bromide, CTAB) surfactants considerably influence the dissociation, α-chymotryptic degradation and enteral absorption of insulin hexamers whereas the nonionic surfactants Tween 80 and polyoxyethylene 9 laurylether have a negligible effect (Shao et al., 1993). Equilibrium dialysis measurements indicated that insulin binds up to 2.7 molecules of sodium undecyl sulfate per amino acid residues (Prieto et al., 1993). The peptide fragment 828–848 of the envelop glycoprotein of human immunodeficiency virus (HIV) type 1 underwent a transition from a random coil to an ordered conformation upon binding to negatively charged SDS micelles. It was found that the interaction between the peptide and SDS is of exclusively electrostatic character with the six positively charged arginines of the peptide acting as binding sites for SDS (Gawrisch et al., 1993). This binding may explain that similar to other polyanions, anionic surfactants show in vitro antiviral activity against HIV-1, HIV-2 and other enveloped viruses (Luscher-Mattli, 2000).

Anionic surfactants influence enzyme activities by binding to the enzyme protein. The impact of anionic surfactants on enzyme activities has been extensively demonstrated. Thus, it was proven that linear alkylbenzene sulfonate can accumulate in the hepatic liposomes of the rat and can inhibit the activity of the enzymes alkaline phosphatase and acid phosphatase (Bragadm et al., 1996). SDS inhibited the ATPase activity of P-glycoprotein at very low concentrations while Triton X-100 stimulated at low concentration and inhibited the activity at higher concentrations (Doige et al., 1993). Both anionic (SDS) and cationic detergents caused the inhibition of lecithin/cholesterol acyltransferase with a water-soluble substrate, whereas the nonionic surfactant, Triton X-100, activated the enzyme (Boneleti and Jonas, 1993). SDS and cationic surfactants (DTAB) modified the structure and enzymatic activity of jack bean urease (Hirui et al., 1993), and SDS activated latent potato leaf polyphenol oxidase (Sanchez-Ferrer et al., 1993). It has been supposed that electrostatic interaction between the surfactant head groups and ionic site in enzyme protein glucose oxidase as well as hydrophobic interactions are involved in the binding of n-alkyltrimethylammonium bromides and n-alkylsulfates to the enzyme. Surfactants can activate or inhibit the enzyme depending on the surfactant concentration and on the length of alkyl chain (Housainidkoh et al., 1993).

The binding of anionic surfactants to phospholipids has also been demonstrated. SDS increased the surface tension of phosphatidylcholine monolayers whereas CTAB inhibited the film formation below the critical micelle concentration (Ah-Fat et al., 1994).

2.2. Human toxicity

The amphoteric character of anionic surfactants facilitate their accumulation in living organisms. The negatively charged head group can bind to the positively charged molecular substructures by electrostatic forces while the hydrophobic moiety may interact with the apolar parts of the target organs or organisms by hydrophobic forces. The earlier results on the bioconcentration of surfactants were previously collected and critically evaluated (Kloeppe-Sams and Sijm, 1994). Modifying of protein structure and misfunctioning of enzymes and phospholipid membranes by anionic surfactants causes toxic symptoms in organs and
animal and human organisms. Thus, the damaging effect of surfactants on human lymphocytes was reported the effect of cationic surfactants being the highest (Antoni and Szabo, 1982). Anionic surfactants mainly show eye and skin irritation potentials. Because of the high number of surfactants in contact with humans, many in vitro methods have been developed for the prediction of the eye irritation potential of surfactants. Thus, the SIRC-NRU cytotoxicity test revealed that nonionic surfactants have a lower toxic effect than cationic, anionic and amphoteric ones (Roguet et al., 1992). According to another cytotoxicity test, the cytotoxicity order of surfactants determined on rabbit cornea epithelial cells was cationic>anionic=amphoteric>nonionic; however, Triton X-100 had a ranking similar to anionic surfactants (Grant et al., 1992). The order of toxicity of surfactants determined on an ocular lens organ culture was: benzalkonium chloride>cetylpyridinium bromide>Tri-ton-X-100=SDS>Geropen AC-78>Tween 20 (Sivak et al., 1994). A study comparing two cytotoxicity tests for predicting ocular irritancy established that red blood cell lysis test was predictive. Surfactants caused membrane disruption, anionic and cationic surfactants were more toxic than nonionic ones (Lewis et al., 1993).

Anionic surfactants also damage human skin as determined by differential scanning calorimetry and permeation studies. Interestingly, nonionic surfactants were able to reduce the damaging effect of anionic surfactants; however, the molecular basis of the phenomenon has not been elucidated (Eagle et al., 1992). The dependence of the skin irritancy potential of anionic surfactants on the molecular structure was well established. The results indicated that the length of the alkyl chain of sodium alkyl sulfates has a considerable impact on their skin irritating potential. C18 compounds caused cell injury whereas C10 and C16 compounds caused more severe membrane destruction and protein denaturation (Kotani et al., 1994). Sodium lauryl sulfate causes more severe skin dehydration than dodecyl trimethyl ammonium bromide; complete repair of the irritant reaction was achieved 17 days after surfactant exposure (Wilhelm et al., 1994). The test of the cutaneous toxicity of surfactants in normal human keratinocytes assessed by cytotoxicity, arachidonic acid release and regulation of interleukin-1α mRNA revealed that the effect of SDS was higher than that of the nonionic surfactants Triton-X-100 and Tween 20 (Shirvi et al., 1994). A quantitative structure–activity relationship (QSAR) study revealed that the hydration capacity of n-alkyl sulfates was closely correlated with the irritational potential, the maximum was found at C12 analogue (Wilhelm et al., 1993).

3. Adjuvant effects in pharmaceutical formulations

Anionic surfactants can considerably influence the biological efficiency of the active ingredients in pharmaceutical formulations (Gould et al., 2000) either by direct binding to the drug (Secccher, 2000) or by influencing the adsorption and absorption processes and the partition of drugs between hydrophobic and hydrophilic compartments in the organs and organisms (Yushkanov et al., 1994). The beneficial effect of surfactants on the dissolution rate and release of various active ingredients has been frequently demonstrated (Saers et al., 1993). SDS and the nonionic surfactants Brij 35 and polysorbate 80 increased the dissolution rate of griseofulvin in PEG 3000 as carrier (Sjokvist et al., 1992), and SDS and DTAB (dodecyltrimethylammonium bromide) had a higher influence than Brij 35 (Alden et al., 1993). SDS further enhanced the release of a highly water-soluble cationic medicinal compound (procain) from an inert, heterogeneous matrix probably by forming a complex by electrostatic interactions (Wells and Parrott, 1992). However, in the case of clofazimine analogues, the effect of Triton-X-100 on the micellar solubilization was higher than that of SDS (Fahey et al., 1993). Ionic surfactants influenced the distribution of the hormone secretin between the hydrophobic and hydrophilic phases of a water-in-oil-in-water multiple emulsion (Ohiwaki et al., 1993).

Anionic surfactants exert a considerable influence on the pharmacokinetic parameters of drugs. It has been established that the effect of cationic and anionic surfactants on the transdermal flux of methyl nicotinate was higher than that of the nonionic surfactant (Ashton et al., 1992), and SDS improved the intestinal absorption of the anthelmintic drug albendazole (Del Estal et al., 1993). The iontophoresis of hydrocortisone across hairless mouse skin has also been influenced by SDS (Wang et al., 2000b).

4. Anionic surfactants in the environment

4.1. Ground and waste waters: pollution and purification

Because of extensive application, a considerable amount of anionic surfactants are released in the environment causing serious pollution of rivers (Odekuma and Okpokwasili, 1997) and sea (Baglimieri et al., 1980; Romano and Garabedian, 1996) and can accumulate in sludge sewage treatment plant (Holt et al., 1995). The concentration of anionic surfactants in rivers and lakes showed marked variation according to the season (Marcomini et al., 2000) and the distance of residential districts (Inaba and Amano, 1988; Muramoto et al., 1996; Souza and Wasserman, 1996), and it depended heavily on the environmental conditions such as the density of sea traffic (Decembrini et al., 1995), the intensity of offshore oil and gas exploration (Tkalin, 1993) and the diurnal discharge of sewage (Kantin et al., 1981). The efficiency of the wastewater purification processes concerning the concentration of alkyl sulfate detergents in the effluent has to be controlled (Fendinger et al., 1992) because the incomplete purification of waste waters may result in the contamination of the groundwater by anionic...
detergents (Zoller, 1993). Many methods have been developed for the extraction and removal of anionic surfactants from water by both physicochemical and microbiological techniques. Physicochemical processes included the application of supported liquid membrane that removed efficiently linear alkylbenzene sulfonates from water at trace level (Milotis et al., 1996), and various adsorption processes. Thus, adsorption on activated carbon and coagulation/precipitation procedures have been tested for the removal of anionic and nonionic surfactants from wastewater. It was found that the methods were more effective for anionic than for nonionic surfactants, the average removal being 67.4% and 31.7%, respectively (Adachi et al., 1990).

Various destructive techniques have also been applied for the removal of anionic surfactants from waters. The effect of aqueous ozonation on the decomposition of anionic, cationic and nonionic surfactants has been established many times. The results were earlier reviewed (Delanghe et al., 1991). The oxidative treatment of p-toluenesulfonic acid using hydrogen peroxide has been reported too (Stoffers and Luft, 1999). Gamma irradiation has also been proposed for the destruction of nonionic and anionic surfactants in industrial wastes (Perkowski et al., 1984).

Because of simplicity and relatively low cost, a considerable number of microbiological systems using various pure and mixed cultures and different fermentation conditions have been employed for the enhancement of the decomposition rate of surfactants. Because of the considerable quantity of anionic surfactants released in ground and waste waters, the fate of this class of pollutants has been extensively studied (Write and Russell, 1992). Thus, the successful stream periphytic biodegradation of C12-alkyl sulfate at concentrations two orders of magnitude higher than usual was reported (Lee et al., 1997). The rapid degradation of C12-alkyl sulfate was also observed in a continuous-flow stream mesocosm (Guckert et al., 1996) and the use of the surfactant-degrading bacterium Pseudomonas 12B immobilized in polyacrylamide gel (White and Thomas, 1990; Thomas and White, 1990, 1991), glass support (Jeníkova et al., 1999), and polyurethane foam (Roig et al., 1999) has been reported. However, another study revealed that the ability of epilithic bacteria to degrade sulfonated surfactants was lower than their overall capacity to degrade other surfactants (Lee et al., 1995). The biodegradation of alkyl sulfate surfactants in heterogeneous (water–sediment) environments has been studied in detail (Russell et al., 1991). The results suggested that the surfactants adsorb to the river sediment, stimulating the simultaneous attachment of bacteria. The adsorption process accelerates the biodegradation of alkyl sulfate surfactants (Marchesi et al., 1991a,b; White, 1995). It has been further established that the biodegradation of anionic surfactants was more rapid in mixed cultures than in isolated ones. Bacteria preferably degraded the alkyl substructures of the surfactant molecules (Sigoillot and Nguyen, 1990; Goudar et al., 1999). It was found that an automated pressure transducer system is suitable for the evaluation of the aerobic biodegradability of anionic sulfate and nonionic ethoxylated surfactants. Surfactants were decomposed in 12 days at 25 °C except ethoxylates prepared from alcohols with a high degree of branching (Diaz and Kravetz, 1995). The biodegradability of anionic and nonionic surfactants under anaerobic conditions was also established in the automated pressure transducer system (Salanitro and Diaz, 1995). The relationship between molecular structure of linear alkylbenzenesulfonates and their decomposition rate in river water and sediments was determined. The data indicated that decomposition followed a first-order kinetics, the half-life of mineralization being 15–33 h. The length of alkyl chain, the position of the phenyl group did not influence the decomposition rate (Larson, 1990). The influence of salinity, temperature and the presence of sediment on the decomposition rate of sodium dodecylbenzenesulfonate in seawater was investigated. It was concluded that the effect of salinity is negligible but the degradation rate increased considerably with increasing temperature. The presence of sediment also enhanced the rate of biodegradation probably due to the accumulation of surfactants and bacteria on the surface of the sediment (Quiroga et al., 1989). An extensive screening project resulted in the selection of alkyl sulfo succinate-degrading bacteria more efficient than those found in culture collections (Proksová et al., 1998a). The capacity of Comamonas terrigena N3H and C. terrigena NIC was the highest for the biodegradation of alkyl sulfo succinate surfactants (Proksová et al., 1997). It was found that the decomposition of dialkyl sulfo succinates followed first-order kinetics (Vrbanová et al., 1997). Bacteria (C. terrigena N3H) immobilized in polyurethane foam have also been successfully used for the biodegradation of the anionic surfactants dihexyl sulfosuccinate and dioctyl sulfosuccinate (Roig et al., 1998). The highest decomposition rate was found at pH 7.5 and at 50 °C temperature (Huska et al., 1998a). Not only polyurethane foam but also alginate gel was successfully employed for the immobilization of the strain C. terrigena N3H (Huska et al., 1996a, 1997a). It was further established that starvation enhanced the biodegradation capacity of C. terrigena (Tóth et al., 1996b; Huska et al., 1997b). The decomposition process of anionic surfactants is not entirely understood. Not only the biodegradation of the alkyl chain but also the desulfonation of linear alkylbenzenesulfonate surfactants and related compounds by bacteria was reported (Kertesz et al., 1994). It was established that the hydrophobicity of the bacterial cell is modified during the biodegradation of anionic surfactants (Marchesi et al., 1994a) and the first biodegradation product of SDS is dodecan-1-ol (Marchesi et al., 1994b). The biodegradability of anionic surfactants is highly different; therefore, the identification of persistent anionic surfactants in sewage effluent is of considerable practical and theoretical importance (Carre and Dufils, 1991). Various combined chromatographic techniques identified the persistent anionic surfactants as linear alkylbenzene sulfonates, sulfophenyl-
carboxylated linear alkylbenzene sulfonates, teratilin and indane sulfonates, and alkylphenol polyethoxylate carboxylates (Field et al., 1992).

4.2. Adsorption, desorption and leakage from solid matrices

Pollution of solid matrices such as soil, sediment, etc. by anionic surfactants has also been frequently demonstrated. Because of their marked biological activity, the mechanism of adsorption, desorption and leakage of anionic surfactants in soils and sediments has been studied in detail (Marchesi et al., 1991a) and the parameters influencing these physicochemical parameters have been vigorously discussed. It is generally accepted that advection and dispersion are the most important processes governing soil transport. However, it was indicated that capillary forces in dried soils may have a considerable impact on the mobility of anionic surfactants (Zhu et al., 1993). The leakage of an alkyl ether sulfate and a linear alkylbenzene sulfonate (LAS) surfactant was studied using various soils. It was established that the soil parameters exert a considerable influence on the mobility of the anionic surfactants (Alfred and Brown, 1996). Another study indicated that addition of SDS to the soil reduces the soil's hydraulic conductivity; the effect depends on the concentration of SDS and on the clay content of the soil (Liu and Roy, 1995). It was further found that anionic surfactants with twin head group are less liable to precipitate and to adsorb to soil particle while their ability to soluble organic contaminants is similar to the surfactants with a single head group (Rouse et al., 1993). The behavior of the anionic surfactant, dodecylsulfate, in sediment and soil was studied in detail. The results indicated the involvement of precipitation, micellization and micellar counterion binding in the adsorption. The relative importance of these physicochemical processes markedly depended on the concentration of the surfactant (Jafvert and Heath, 1991). The marked dependence of pH on the adsorption of sulfated surfactants to a sandy soil has also been demonstrated (Huang and van Bentschoten, 2000). A model was proposed for the description of the sorption of anionic surfactants on soils, sediments and sludges. Unfortunately, the model was not suitable for the prediction of desorption processes (Di Toro et al., 1990).

Because of the complexity of soil–surfactant systems, the number of studies dealing with the decomposition of anionic surfactants adsorbed on solid matrices is fairly low. High differences were observed between the adsorption capacity and biodegradability of surfactants in soil. Ethoxylated anionic surfactants (sodium lauryl ether sulfates) showed lower adsorption capacity than nonethoxylated anionic and nonionic surfactants; however, these surfactants were easily biodegradable (Sabatini et al., 1996). The temperature also exerts a marked influence on the behavior of anionic surfactants in soil. Thus, the half life of LAS in the soil strongly depended on the season being 5–25 days in summer and 68–117 days in winter (Litz et al., 1987).

4.3. Beneficial effects

Because of their amphoterically character, anionic surfactants can adsorb on both hydrophobic and hydrophilic surfaces, can interact with hydrophobic and hydrophilic molecules either by binding or by forming mixed micelles. The interactions can facilitate desorption of a wide range of polar and apolar environmental pollutants (Burris and Awtorth, 1992).

4.3.1. Enhancement of the desorption and leakage of pesticides

The enhancement of desorption of pesticides by various surfactants has been vigorously studied. Thus, a thin-layer chromatographic method was employed for the elucidation of the effect of anionic, cationic and nonionic surfactants on the mobility of the pesticides diazinon, atrazine, metolachlor and acephate in soil. The results indicated that both the character of the surfactant and the hydrophobicity of the pesticide play a decisive role in the strength and selectivity of the effect (Arienz et al., 1995). Anionic surfactants may promote the removal of pesticides from soil while carbon-rich wastes reduced the leakage of the same pesticides (Iglesias-Jimenez et al., 1997). It was established that not only the leakage but also the adsorption of pesticides on a sandy loam soil considerably depended on the character (anionic, cationic, nonionic) and concentration of the surfactants and on the hydrophobicity of the pesticides (Iglesias-Jimenez et al., 1996). Anionic and cationic surfactants influence the adsorption strength of the pesticide carbofuran in soil, indicating that the addition of surfactants may influence the efficacy of carbofuran to control nematodes (Singh, 1994; Singh et al., 2000). Anionic surfactant not only modifies the desorption rate of pesticides but also accelerate their photocatalytic decomposition as demonstrated on the case of the hydrophobic pesticide permethrin (Hidaka et al., 1992).

4.3.2. Enhancement of the desorption and leakage of other environmental pollutants

Surfactants can also be employed for the enhancement of the desorption of other environmental pollutants. Thus, the influence of anionic, cationic and nonionic surfactants on desorption of the explosive trinitrotoluol (TNT) from soil was compared. It was established that desorption-enhancing effect of SDS was higher than that of the cationic and nonionic surfactants (Taha et al., 1997). The influence of SDS and hydroxpropyl- and methyl-β-cyclodextrin on the recovery of another explosive, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), from soil was also studied. The results proved that both cyclodextrins (CDs) and SDS increase the water solubility of RDX. The effect of CDs was attributed to their capacity to form inclusion complexes with the explosive (Hawari et al., 1996).

The enhancement of the dissolution of various halogenated pollutants and PAHs has been many times established. Sodium dodecylbenzene sulfonate was more effective than
the nonionic surfactant Triton X-485 for the desorption of pentachlorophenol adsorbed on soil particles (Banerji et al., 1993). Anionic surfactants can form micromulsions with various chlorocarbons, enhancing in this manner their solubility in water and promoting soil remediation (Buran et al., 1994). SDS enhanced also the apparent solubility of 1,2,4-trichlorobenzene (DiVincenzo and Dentel, 1996), hexachlorobenzene and anthracene (Li et al., 1995) in the aqueous phase of the soil (Payá-Pérez et al., 1996). The efficacy of anionic, cationic and nonionic surfactants to remove hazardous organic compounds (1,2,4-trichlorobenzene, aniline, phenol and 2,4-dichlorophenol) from soil was compared. The data indicated that the performance of cationic surfactants was inferior to the other class of surfactants (Rajput et al., 1994). The micellar solubilization of decahydronaphthalene, naphthalene and 1-naphthol by hexadecylphenyl oxide and disulfonate were assessed. Semiequilibrium dialysis proved that the effect of surfactants highly depended on the type of contaminants (Rouse et al., 1995). The suitability of anionic, cationic and nonionic surfactants and colloidal gas aphron suspensions was checked for the removal of naphthalene from soil. Each adjuvant caused the increase of the removal of naphthalene (Roy et al., 1995). The partition of pyrene, phenanthrene and naphthalene between dodecylsulfate micelles and natural media (sediment and soil) was determined. The results indicated that the sorption potentials of the hydrophobic compounds are similar to surfactant micelles and natural media (Jafvert, 1991). The improvement of the removal of polyaromatic hydrocarbons from soil with surfactant solution has also been proven (Dür et al., 2000a) and the heterogeneous dissolution of bezao(apyrene from solid deposit has been demonstrated (Dür et al., 2000b). The efficacy of micellar-enhanced ultrafiltration and air-stripping processes was tested for the recovery of hexadecyl diphenyl oxide disulfonate and dodecyl diphenyl disulfonate together with naphthalene and trichloroethylene. Both methods successfully concentrated the surfactant-contaminant systems but were not able to separate them (Lipce et al., 1996).

Surfactants can also be used for the removal of petrochemical products from polluted soil. It was found that from the 22 surfactants investigated, anionic ones showed the best performance, promoting the removal of diesel oil adsorbed in various soils. (Peters et al., 1992). Anionic and nonionic surfactants have been successfully employed for the removal of residues of petroleum products from shallow sandy aquifers (Abdel et al., 1990). It was further proved that oily wastes pretreated with anionic surfactants can enhance the dispersibility of oils in soil, resulting in increased biodegradability (Rastia and Voroney, 1993). A combined technique was proposed for boosting the decomposition rate of nonvolatile petroleum hydrocarbons in soil. The method employed the anionic surfactant guaniinium cocrate, hydrocarbon-degrading bacteria and the bulking agent vermiculite (Walter et al., 1997). The presence of petroleum contaminants has also influenced the biodegradation of anionic surfactants (Sarwar et al., 1994). Natural anionic surfactants can effectively enhance oil recovery in hot water flotation from bitumen and tar sands (Schramm and Smith, 1987). Rhamnolipid surfactant consisting of two rhamnose sugar molecules bonded to one or two hydroxydecanoic acids modified the partition of a polar hexadecane in the subsurface (Thangaraj and Shreve, 1994). The application of various surfactants in the oil industry has been discussed in detail and the influence of the physicochemical characteristics of surfactants on their performance is emphasized (Hall, 1986).

4.3.3. Enhancement of the removal of inorganic pollutants

Anionic surfactants may influence not only the mobility of organic molecules in various systems but also that of the inorganic ones. Thus, it has reported that the desorption of lead from soil particles can be increased by the addition of anionic surfactants (Huang et al., 1997). SDS enhanced markedly the efficiency of the extraction of chromium from soil but the efficacy was lower than that of sodium phosphate (Puls et al., 1994). The concentration of free cadmium has been successfully reduced by complexing it with an anionic monohammoglobin biosurfactant produced by Pseudomonas aeruginosa ATCC9207 (Tan et al., 1994). Anionic and cationic surfactants can also be employed to enhance the efficiency of the removal of arsenic from high ionic strength geothermal fluids by adsorptive bubble flotation (De and Thomas, 1985). Anionic surfactants decreased the uptake of various elements (Cd, Ni, Al, Ca, Mn) in the root and top of water hyacinth (Eichhornia crassipes) but the underlying mechanism was not explained in detail (Muramoto and Oki, 1984; Muramoto et al., 1989).

4.3.4. Adsorption-increasing effects

Anionic surfactants not only facilitate the dissolution and removal of various environmental pollutants but they can increase adsorption under given conditions. Thus, anionic surfactants can increase the adsorption of tetrachloride, naphthalene and phenanthrene on the surface of aluminium oxide resulting in improved water pollution control (Park and Jaffe, 1993). Anionic surfactants coated on the surface of alumina support considerably enhanced the sorption of phenanthrene from water. The effect was higher with the diphenyl oxide disulfonates having a longer apolar alkyl chain in the molecule (Sun and Jaffe, 1996). Phenanthrene can also be removed from a soil-slurry by using anionic surfactant coated oxide support and separating the coated oxides by magnetic separation technology (Park and Jaffe, 1995). SDS adsorbed on the surface of titanium dioxide promoted the adsorption of 2-naphthol and Cu²⁺ facilitating their simultaneous removal (Esumi et al., 1998). SDS has also been adsorbed onto ferrhydrite and employed for the extraction of sparingly soluble organic compounds from water. The model compounds (toluene, trichloroethylene and p-xylene) were successfully removed form water at low pH. Desorption of both SDS and organic pollutants occurred at higher pH (Holm et al., 1991). It was further
confirmed that adsorptive micellar flocculation using SDS is a suitable technique for the removal of 2,4-dichlorophenoxy acetic acid from solution (Talens-Alessson, 2001).

4.3.5. Miscellaneous beneficial effects

It was established that sodium dodecylbenzenesulfonate increases the efficiency of the precipitation flotation technique to remove fine particles from an aqueous medium (Kubota et al., 1990). Anionic surfactant sodium lauryl sulfate enhanced markedly the photopotential and photocurrent in a solar energy cell (Khamest et al., 1990). The influence of various types of surfactants on the mechanical dewatering of highly decomposed fuel-farde peat was compared. Cationic surfactants show marked positive effect, nonionic surfactants were ineffective and anionic ones exerted a negative impact on the dewatering process (Cooper et al., 1988).

4.4. Adversary effects

Much efforts were devoted for the evaluation of the adversary effects of anionic surfactants on the environment. The earlier results concerning the consumption of anionic surfactants, their impact on marine environment, on the coastal flora and their fate in wastewater treatment facilities have been previously reviewed (Lesouef et al., 1993). Much efforts has been devoted to the elucidation of the relationship between toxicity and molecular parameters of anionic surfactants, the results considerably depending on the surfactant–organism pair under investigation. Thus, QSAR studies indicated that molecular lipophilicity exerts a considerable influence on the toxicity (Roberts, 1971), and the effect depends on both the character of the polar head group and the length of apolar alkyl chain (Dyer et al., 2000).

4.4.1. Toxicity towards microorganisms

The effect of SDS and Tween 80, a nonionic surfactant, on the growth and nitrogen fixing capacity of the cyanobacterium Gloeocapsa was compared. Both growth and nitrogen fixation was inhibited at 50 ppm SDS and 500 ppm Tween 80. The results clearly prove that the toxicity of SDS considerably higher than that of the nonionic surfactant (Tuzum-Culgan and Atay-Gureyman, 1994). It was proved that dialkyl sulfosuccinates also influence the activity of microorganisms. Thus, they stimulate respiration rate at low concentration and inhibit it at higher concentrations. The EC50 value depended markedly on the chemical structure of the surfactant (Gregorova et al., 1996). Dialkyl sulfosuccinate anionic surfactants influence not only the respiration but also the activity of enzymes and the growth of the degradative bacteria (Proksova et al., 1998a).

4.4.2. Toxicity towards aquatic plants

The toxicity of anionic surfactants towards algae has been demonstrated. It has been found that the toxic effect show high differences according to type of the surfactants and the species under investigation (Lewis, 1990). The effect of SDS on the duckweed Lemma minor L. depended significantly on the concentration. SDS increased the relative growth rate at lower concentrations but showed marked inhibition and accumulation at higher concentrations (Dirilgen and Ince, 1995). Another study showed that increasing concentration of anionic detergents and other organic compounds resulted in the considerable enhancement of phytoplankton biomass, density and primary productivity in polluted seas (Yalin et al., 1993). Anionic–nonionic surfactants mixtures used as oil dispersants showed marked toxicity to the early life stages of topsmelt (Atherinops affinis) and kelp (Macrocystis pyrifera) (Singer et al., 1994).

4.4.3. Toxicity towards invertebrates and crustaceans

Because of the considerable amount of anionic surfactants released in water, the life cycle of aquatic animals has also been influenced by the anionic surfactants. A QSAR study has been employed for the elucidation of the relationship between the chronic toxicity of various surfactants and other compounds towards the rotifer Brachionus calyciflorus. Calculations indicated that toxicity increases with increasing length of the alkyl chain within the different classes of surfactants. The result suggests the involvement of hydrophobic interactive forces in the mode of action of surfactants. In this instance, anionic surfactants exposed relatively low toxicity (Versueeg et al., 1997). Another study indicated that linear alkylbenzene sulfonate can inhibit the development of the soil-living collembolan Folsomia candida. The EC50 values causing 10% inhibition were 185 mg/kg for frequency of molting, 163 for juvenile growth and 147 for reproductive effects (Holmstrup and Krogh, 1996). The LC50 values of SDS were determined for several estuarine crustaceans. The data indicated that the sensitivity of crustaceans towards SDS shows high variations: blue crab (Callinectes sapidus) 9.8 mg/l; grass shrimp 34 mg/l and mysids 48 mg/l (Whiting et al., 1996). The influence of alkyl ethoxylate sulfates and alkyl sulfate on various invertebrates and fish was determined. The results indicated that snails were not affected by surfactants, the sensitivity of clams was the highest to the anionic surfactants (Belanger et al., 1995a). It was found that high concentrations of alkyl sulfate and alkyl ethoxysulfate impaired the populations of clams and mayflies in a stream mesocosm the no effect concentrations being 224 and 251 mg/ml, respectively (Belanger et al., 1995b). Another study indicated that the chronic and sublethal toxicity of surfactants to aquatic animals occur at very low concentrations such as 0.1 and 0.002–40 mg/l, respectively (Lewis, 1991). The effect of linear alkylbenzenesulfonates on the freshwater tubific species Branchiura sowerbyi and Limnodrilus hoffmeisteri was determined. It was established that the surfactant exerted a considerable effect only on the number of coocoon (Castellato and Negrisolo, 1989). The sensitivity of aquatic inver-
tebrates show high variations both according to the species and the type of surfactants. *Daphnia magna* was found to be the most sensitive. The acute toxicity values varied between 1.7 and 270 mg/l for linear alkylbenzene sulfonate, 1.0 and 6.8 mg/l for nonionic alkylethoxylate, and 0.1 and 58 mg/l for the cationic cetyl trimethyl ammonium chloride (Lewis and Suprenant, 1983; Verge and Moreno, 2000).

### 4.4.4. Toxicity towards vertebrates

Not only bacteria, aquatic plants and invertebrates are sensitive to anionic surfactants but also vertebrates can show typical toxic symptoms. LAS and SDS displayed toxic effects to juvenile rainbow trout (*Oncorhyncus mykiss*), with SDS being the less toxic one (Buhl and Hamilton, 2000). The anionic surfactant dodecylbenzene sodium sulfonate caused marked alterations in the lipid composition of the fish *Rita rita*. A decrease in the lipid moieties in the peripheral region of the goblet mucous cells, of the epithelial and club cells was observed (Roy, 1988a). The protein content of the epithelial and goblet mucous cells also decreased in the presence of the same anionic surfactant (Roy, 1988b). High concentrations of the surfactant modified the behavior of the fish (eratic movements, muscle spasms, body torsion) too (Roy, 1988c). Polysorbates and laurylsulphates modify the absorption of phenylalkylcarboxylic acids in the colon of male Wistar rats (Garrigues et al., 1994). Both the nonionic surfactant (Emulger 913) and SDS inhibited slightly the weight gain of rats and caused the decrease of liver weights. Both surfactants modified the hemoproteins and heme-metabolizing enzymes. It was assumed that the potential inducibility of hepatic heme oxygenase may be a common active site in mammals for anionic surfactants (Baglimieri et al., 1994). More recently, a decrease of liver weights. Both surfactants modified the decrease of liver weights. Both surfactants modified the production of specific IgE antibodies in mice (Claussen et al., 2000).

### 5. Conclusions

The advantageous physicochemical characteristics of anionic surfactants resulted in their industrial scale production and application all over the world. Besides the beneficial effects, they show marked toxicity and can cause marked environmental pollution. The molecular basis of their biological and toxicological activity is not entirely understood. They can bind to proteins modifying the activity of various enzymes or to other cell constituents resulting in dysfunction. The quantitative relationship between their molecular parameters and manifold biological and environmental activities has not been elucidated in detail. We need a considerable amount of additional data for the more profound understanding of the underlying biochemical and biophysical processes. It is highly probable that the exact knowledge of the processes mentioned above may lead to the rational selection of anionic surfactants for each purpose with minimal adversity and maximal beneficial effects.

### Acknowledgements

This work was supported by the grant HP-206 from the Ministry of Environmental Protection.

### References


Hall BE. Workover fluids, Part 1: surfactants have differing chemical properties that should be understood to ensure proper application. World Oil 1986;202:111-4.


Litz N, Doering HW, Thiele M, Blunie HP. The behavior of linear alkylbenzenesulfonate in different soils: a comparison between field and laboratory studies. Ecotoxicol Environ Saf 1987;14:103-17.


Muramoto S, Anyama H, Hashimoto K, Kungolos A. Distribution and fate of


Staples E, Singh Sun, Sivak JG, Herbert KL, Segal L.  

Optimizing desorption of TNT and Ca\textsuperscript{2+} on the adsorption of carbofuran on three different types of soils. Ecotoxicol Environ Safety 1994;29:70-80.  


