Aquatic Toxicities of Textile Surfactants

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THE chemical structures of home product detergent compounds and their relationship to the toxicity of aquatic organisms have been widely investigated (*1-10*). With the formulation of surfactant compounds for the textile industry have come questions regarding the applicability of these earlier aquatic toxicity studies in the use of industrial grade textile surfactants. This study was based on the following questions:

- Can the amount of ethylene oxide per mole of hydrophobe (HLB) for nonionic and cationic ethylene oxide surfactants be correlated to aquatic toxicity?
- Is the toxicity of a charged surfactant related to its ability to remain in solution; i.e., not absorbed onto an oppositely charged particle of substance in the water?
- Based on charge type, can surfactant toxicity boundaries be determined for surfactant groups that would assist the textile manufacturer in choosing detergent compounds for dyehouse use?
- Are there methods other than biological waste treatment that can remove the surface activity of surfactants which would render them less toxic?

Surfactants are used in most textile wet processing operations. Known as detergents, penetrants, leveling agents, retarding agents, wetting and rewetting agents, etc., these chemical compounds are used to reduce the surface tension of water or to alter the interface between water and other liquids, solids and gases to form emulsions, dispersions and foams (*11*).

Surfactant Toxicity

The exact mechanism by which surfactants affect aquatic life is not understood. It is surmised, however, that the toxic effects are related to the wetting ability of the surfactant or its inherent property of migrating to physical interfaces. Changes in surface tension brought about by the surfactant appear to cause disruption of gill membranes and the inhibition of cellular carbon dioxide and oxygen exchange. In addition, gill epithelial cells swell and secrete mucous which further interrupts the diffusion of oxygen through the gill. The ultimate cause of death is through suffocation even when water oxygen levels reach saturation. In the case of a strongly cationic quaternary compound, such as Hyamine 3300, the surfactant's strong attraction to anionic tissues coupled with its strongly corrosive nature disrupts the cell membranes. Daphnids that have been tested in surfactant bioassays actually appear to explode or implode (*12*).

ABSTRACT

Acute and chronic static aquatic toxicities of four classes of nonbiodegraded textile processing surfactants were determined for the water fleas *Daphnia pulex* and *Ceriodaphnia dubia/affinis*. The tested compounds included a group of nonionic, anionic, cationic and amphoteric surfactants. Nonbiodegraded surfactant concentrations were toxic in the range of 1-67 ppm. Acute static LC_{50} determinations were made for all surfactants and chronic "no effect" concentrations were determined for representatives from each group. Findings indicated that nonionic surfactants were less toxic when sulfated. Test organisms, when exposed to LC_{50} concentrations of anionic, cationic and nonionic compounds and removed before death occurred, generally recovered from exposure to the nonionic surfactants.

KEY TERMS

Aquatic Organisms
Aquatic Toxicity
Biodegradable
Effluents
Surfactants
Toxicity Measurements
Waste Treatment

Test Substance

Nonionic Surfactants

Nonyl phenol ethoxylate with 10 moles ethylene oxide per mole of hydrophobe (NP-10) is one of the largest volume nonionic surfactants used in the textile industry. It has excellent emulsification properties, provides good wetting and is based on a low cost hydrophobe. Current questions dealing with the biodegradability of this surfactant and the ultimate human genotoxic effects of the bioaccumulated biodegradation products leave this surfactant, and others like it, with a questionable future (*1*).

Diethanol amide of coconut (DAC) fatty acid is a condensation reaction product between a fatty acid and diethanol amine. The textile industry uses this compound as an aftersoaping agent, a wool scouring and fulling agent, a dyeing assistant lubricant and a softener. DAC is used widely in all areas of cleaning compounds.

Linear alcohol ethoxylate (LAE) with six moles ethylene oxide per mole of hydrophobe has many of the same properties as an alkyl phenol nonionic (APE) surfactant but without the biodegradation and bioaccumulation problems. These compounds have replaced the APE group of detergents in the home products area as a result of studies done by soap producers estimating the impact on the nation's surface waters if the APE compounds are not eliminated.

Ethoxylated mercaptan with seven moles ethylene oxide per mole of hydrophobe (TTE-7) is used for wool scouring and cold water wash for polyester, and in areas where good oil scouring detergents are needed.

The aquatic toxicity of a nonionic surfactant is related to its HLB and therefore its chemical structure is similar (*6*). The LC_{50} value of the compound is related to the hardness of the water used in testing, but unlike either the anionic or cationic classes of surfactants, charged particles of any type seem to have little effect on toxicity. All surfactants will absorb on solid particles found in waste water, but nonionic surfactants have less tendency to do so than charged types.

Anionic Surfactants

Sodium dodecylbenzenesulfonate (DDBSA) is used as a leveling agent for acid dyes on nylon, a wetting agent and detergent for preparations and a dyeing assistant for cellulosic fibers. Linear DDBSA is biodegradable under aerobic treatment conditions.

Sodium lauryl sulfate (SLS) is used as a general scouring agent and for aftersoaping cellulosic fibers and wools. It is found in many commercial shampoos and some laundry detergents. The SLS molecule is produced from coconut alcohols, or synthetics to match the same, and is sulfated by thin film SO_3 sulfation techniques or with chlorosulfonic acid. SLS is readily hydrolized in hot acidic medium and is readily biodegradable.

Sodium alcohol ether sulfate (AES) is an ethoxylated alcohol surfactant that has been sulfated. Addition of the sulfate group increases the lime dispersing ability of the detergent and provides the textile industry with a high foaming, very mild detergent with good characteristics for aftersoaping various fibers following dyeing. The biodegradation of the compounds occurs readily as long as the hydrophobic chain is not highly branched.

Most surfactant aquatic toxicity studies have involved the anionic surfactants SLS and lauryl alkyl sulfate (LAS). These compounds are easily monitored in test solutions by the methylene blue active substance method. Their concentrations in surface waters would be expected to be higher than any other class of surfactants because of the high percentage of anionic detergents used annually.

Cationic Surfactants

There are two main categories of chemical types of cationic surfactants used in significant volumes in the textile trade: quaternary and ethoxylate tertiary amine compounds. The quaternary benzyl trimethyl ammonium chloride 60% (BTMAC) is claimed to have no surface active properties but is used extensively by the textile industry as an acrylic dyeing assistant. Tallow amine ethoxylate with 15 moles of ethylene oxide per mole of hydrophobe (TAM-15) is used as an antistatic and dyeing assistant in the dyeing of cotton, nylon and acrylic. Tallow amine ethoxylate with 150 moles of ethylene oxide per mole of hydrophobe (TAM-150) is used as an antistatic and disinfectant for hard surfaces and fabrics.

Table I. Acute Static Bioassay LC_{50} (48-hour, *Daphnia pulex*) for Industrial Surfactants

Surfactant	LC_{50} (ppm)	Mean	±1SD	Var.
Nonionic				
NP-10	15.43 10.95 11.18	12.52	2.52	6.36
LAE	5.14 5.79 5.14	5.36	0.38	0.14
DAC	2.15 2.64	2.39	0.35	0.12
TTE-7	15.81 18.75	17.28	2.08	4.32
Anionic				
DDBSA	19.87	—	—	—
SLS	27.04 7.07 49.38	27.83	21.16	448.00
AES	24.61 15.81	20.21	6.22	38.72
Cationic				
BTMAC	6.94 16.94	11.94	7.07	50.00
TAM-15	5.85 2.35	4.10	2.47	6.12
TAM-150	66.09	—	—	—
NADBAC	0.5	—	—	—
Amphoteric				
CCP	159.11	—	—	—

Amphoteric Surfactant

Cocoamphocarboxypropionate (CPP) is used in the textile wet processing industry as a mild scouring agent for wool and silk. In a more purified form, this compound is used as a mild hair shampoo.

Aquatic Toxicity Testing

An aquatic bioassay is a procedure in which the response of an aquatic organism, such as a fish or crustacean, is used to measure the effect of a chemical substance. Various flow systems are used for the test substance including flow through, static nonrenewal and static renewal. For static testing, solutions and test organisms are placed in test chambers and kept there for the duration of the test or over a specified period of time. Bioassay test duration times are classified as acute (short term) and chronic (long term). Toxicity measurements evaluate the relatively short term effect of a chemical, such as death, or the long term effect, such as changes in reproduction (*13*).

For acute tests bioassay results are generally expressed as an LC_{50} concentration, representing the concentration of chemicals in the water which kills 50% of the test animals. The lower the LC_{50} concentration the more toxic the substance. A chronic bioassay result is expressed as 'no effect' concentration (NOEC). These values can indicate what effect a substance will have in a natural environment and be used as a gauge for industr[illegible]n stream discharge (*13*).

Methods

Acute static bioassays were conducted according to standard EPA protocol for a 48 hour test (*14*) and chronic statics adhered to the seven day procedure outlined by Mount and Norberg (*15*). Generally, an initial acute static bioassay was set up with a surfactant concentration range of 1-120 ppm. Based on this LC_{50} determination, a more defined range was applied to consequent acute and chronic tests. Data were analyzed using the trimmed Spearman-Karber method for acute bioassay data (*16*) and Bootstrap variance analysis for chronic test data (*17*).

Results

Dilution water hardness ranged from 25-40 mg/L as $CaCO_3$. Final dissolved oxygen and pH measurements ranged from 3.7-7.5 ppm and from 7-8, respectively, for the highest test concentrations. Temperature was maintained at 20-21C. Acute static bioassays ranged from $LC_{50} < 0.5$ ppm for the cationic surfactant NADBAC to $LC_{50} = 159.11$ ppm for amphoteric CPP. These data are shown in Table I.

The lowest statistical variance was seen for the nonionic compounds. Chronic test results, as shown in Table II, ranged from 1.0 ppm for LAE to 20.0 for TAM-150.

Discussion

The low statistical variance for the nonionic surfactants is a reflection of charge absence and the consequent decreased absorption onto the test chamber walls. In waste treatment systems little absorption onto the solids would be expected and unbiodegraded nonionics would be an integral part of the discharged effluent.

Generally, the lower a surfactant's HLB (hydrophilic/lipophilic balance), the more toxic it is to aquatic organisms. HLBs for the cationics TAM-15 and TAM-150 are reported to be 14.3 and 17.8, respectively. In this study, the aquatic LC_{50} for TAM-15 was 4.10 ppm and 66.09 ppm for TAM-150. Although their basic chemical structures are similar, the moles of ethylene oxide per mole of hydrophobe critically affected their aquatic toxicities.

Both anionic and cationic surfactants can be affected by oppositely charged particles as can their toxicity, which is a result of ion pairing and absorption effects (*7*). In this study, the strongly cationic compound NADBAC was mixed with an equal molar ratio of SLS, an anionic surfactant. The 48-hour acute static LC_{50} of the complex was 230 ppm, whereas the NADBAC alone had an LC_{50} of < 0.5 ppm. Similar results have been observed for other complexes (*5*). This neutralization by oppositely charged surfactant types can have direct application in textile effluent treatment operations. For example, if a quaternary compound such as BTMAC is used in a particular dyehouse operation, judicious use of a strong anionic compound in another operation that is discharging to the same waste treatment plant would offer ion pairing and therefore lessen the quaternary toxic effects. The anionic and cationic compounds react to form a nonsurface active complex that is very biodegradable and much less toxic than either of the compounds used alone.

A different treatment strategy was applied for another surfactant in this study that demonstrated a high level of toxicity. The ethoxylated thioether, TTE-7, had an acute LC_{50} of 17.28 ppm. A 500 mL volume of a 10,000 ppm solution of TTE-7 was mixed with an equal volume of a 66,667 ppm solution of chlorine bleach. The bioassay conducted with this mixture yielded an LC_{50} of 380.95 ppm, a 22 fold improvement in toxicity, after chlorine removal with sodium thiosulfate. Application of this treatment in dyehouse operations would allow the use of surfactants for wetting out fabrics followed by the elimination of those same wetting out properties *in situ* in the dyebath without affecting bleaching or fabric properties. This same strategy could be applied to many sulfated esters that are sensitive to hydrolysis.

Surfactant aquatic toxicity information is not yet routinely available on product Material Safety Data Sheets (MSDS). An indication of aquatic toxicity can be obtained, however, from information regarding oral, skin and eye toxicities for laboratory animals. These data are more widely available for chemical products. In this study, CPP had the lowest aquatic toxicity of the compounds tested with a LC_{50} of 159.11 ppm. According to MSDS information for CPP, this material causes moderate skin and eye irritation and is lethal to laboratory rabbits at an oral dosage of 20 g/kg (*18*). Conversely, LAE, which had one of the lowest LC_{50} values (5.36 ppm) of the 12 surfactants investigated, is a severe skin and eye irritant and is lethal to laboratory rats at 2.5 g/kg (*19*).

Table II. Chronic Static Bioassay NOEC[a] (7 day, *Ceriodaphnia dubia/affinis*) and Corresponding Acute Static LC_{50} for Selected Industrial Surfactants

Surfactant	NOEC[a] (ppm)	LC_{50}[b] (ppm)
Nonionic		
LAE	1.0	5.36
Anionic		
DDBSA	4.0	19.87
Cationic		
TAM-150	20.0	66.09
Amphoteric		
CPP	10.0	159.11

[a]No effect concentration. [b]Lethal concentration, 50%.

Conclusions

The following points can be made regarding the nonbiodegraded surfactants in this study:

- The less water soluble and more lipophilic the surfactants the more toxic they are, regardless of the charge type.
- Molecules with more ethoxylation have lower aquatic toxicities.
- Anionic surfactants are generally less toxic than nonionics because of their decreased lipophilic character.
- Very small amounts of surfactants in aquatic systems (1.0 ppm) will cause chronic toxicity problems to *Ceriodaphnia dubia/affinis* and could upset food chains based on this and similar aquatic fauna.

Nonionic surfactants are less toxic when sulfated, as demonstrated by the mean LC_{50} of 5.36 ppm for LAE and 20.21 ppm for AES. This is believed to be the result of liposolubility, the degree to which the surfactant can dissolve fatty materials, which is much greater in nonionic surfactants than the more polar anionic types.

There is a decrease in toxicity from TAM-15 to TAM-150. As ethylene oxide is added to a fatty amine, the amine number, or the measure of its basic character, grows smaller. This indicates a lessening in cationic nature and, therefore, less affinity for tissues and membranes of the test organism. As ethylene oxide is added, however, the liposolubility of the molecule lessens and the toxicity decreases. Surfactants soluble in oil—i.e., those surfactants with low hydrophilic/lipophilic balance values—render a greater toxic effect on aquatic organisms because of their ability to leach fats and oils from living tissues.

When test organisms are exposed to LC_{50} concentrations of anionic, cationic and nonionic surfactants, and removed before death occurs, they generally recover from exposure to the nonionic surfactants. Recovery from exposure to cationics and anionics is less successful. This may be explained by a proposed tighter salt bonding between anionic and cationic surfactants in the gill membrane.

Recommendations

Of maximum importance during the next decade is the utilization of detergents and surfactants in a manner which minimizes their acute and chronic toxic effects in the aquatic environment. To meet this goal the textile industry must eliminate the use of ethoxylated alkyl phenolic compounds. These compounds are produced by the disinfecting processes, usually involving the chlorine treatment of sludges. They can have genotoxic as well as acute toxic effects and, therefore, must be eliminated or their discharge curtailed to the lowest possible levels.

New surfactants are being developed with structures that are based on carbohydrates and linear alcohols. As improved biotechnology increases the availability of natural surface active compounds, the prudent dyehouse manager will give serious consideration to these alternatives. A product's environmental impact and ease of biodegradability need to be considered in conjunction with economic and performance factors.

The following questions should be asked when choosing surfactants for dyehouse use:

- Is the compound biodegradable?
- Is oral, skin and eye irritation low?
- Is the HLB high or low?
- Is the aquatic acute and/or chronic toxicity value known?

Answers to these questions should be known and affirming applications performed before incorporation of a surfactant product into textile processing. Using the physical and aquatic bioassay information for surfactants can aid textile operations in reducing pollution loading and minimize the acute and chronic toxicity to aquatic organisms in surface waters. Although most textile mill effluents can be adequately treated by biological water treatment plants before discharge, the surfactants chosen by the wet processor of textile goods can influence the efficiency and ultimate toxicity of that plant's effluent.

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References

(1) Giger, W. and P. H. Brunner, *Science,* Vol. 225, 1984, p623.

(2) Gottschaldt, N., *ACTA Hydrochimistri Hydrobiologia,* Vol. 10, 1982, p583.

(3) Holman, W. F. and K. J. Macek, *Transactions of the American Fisheries,* Vol. 109, 1980, p122.

(4) Huber, L. H., *Journal of the American Oil Chemist's Society,* Vol. 61, No. 2, 1984, p377.

(5) Lewis, M. A. and V. T. Wee, *Environmental Toxicology and Chemistry,* Vol. 2, 1983, p105.

(6) Lewis, M. A. and D. Suprenant, *Ecotoxicology and Environmental Safety,* Vol. 7, 1982, p313.

(7) Lewis, M. A. and R. L. Perry, *Aquatic Toxicology and Hazard Assessment: Fourth Conference,* American Society for Testing and Materials, STP 737, 1981, p402.

(8) Maki, A. W., *Journal of the Research Board of Canada,* Vol. 36, 1979, p411.

(9) Maki, A. W. and W. E. Bishop, *Environmental Contamination and Toxicology,* Vol. 8, 1979, p599.

(10) Seabaugh, Van M., Detergent survey toxicity testing report (1971-76), Bureau of Biomedical Science, U.S. Consumer Product Safety Commission, 1976, p38.

(11) Rosen, M. J., *Surfactants and Interfacial Phenomena,* Wiley-Interscience Publication, John Wiley & Sons, 1978, p304.

(12) Kravetz, L. et al., Technical Bulletin SC:321-78., Shell Chemical Co., 1978, p16.

(13) American Public Health Association, *Standard Methods for the Examination of Water and Wastewater,* 16th Edition, American Public Health Association, Washington, D. C., 1985, p689.

(14) Peltier, W. H. and C. W. Weber, EPA/600/4-85/013, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 1985, p216.

(15) Mount, D. I. and T. J. Norbert, *Environmental Toxicology and Chemistry,* Vol. 3, 1984, p425.

(16) Hamilton, M. A., R. C. Russo and R. V. Thurston, *Environmental Science and Technology,* Vol. 11, 1977, p714.

(17) United States Environmental Protection Agency, Bootstrap variance program for analysis of *Ceriodaphnia* reproductivity toxicity test. Programmed by Martin Hamilton, edited by John Rogers, Environmental Research Laboratory, Duluth, Minn., 1984.

(18) Burlington Chemical Co., Material Safety Data Sheet, Mirapon FBS, CAS#68919-41-5, p3.

(19) Shell Chemical Co., Material Safety Data Sheet, Neodol 25-3, CAS#68131-39-5, p3.