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NONIONIC SURFACTANTS IN PERSPECTIVE*

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ABSTRACT

The emergence of hard synthetic organic compounds in water has added a new dimension to public health-related problems. During the last thirty years, the chemical industry has demonstrated a gradual and steady growth. Industrial growth has generated nondegradable and slowly degradable chemicals. Tracing the fate of hard chemicals in a stream of water is sometimes difficult because of their identification and quantification, because the techniques for their identification are not fully developed, and/or their concentration may be extremely low, making it rather difficult to measure. Some of these compounds when disseminated into the environment as waste cause a variety of health effects including carcinogenicity.

SURFACTANTS

In recent years society has witnessed changes in cleansing agents, from soap to highly complex synthetic detergents. The recent chemical on the scene is 4-nonylphenol (NP)—a metabolite of nonionic surfactants. It has been detected in sewage sludges and river waters. Limited health-related studies show that it is a toxic compound.

In 1982 a total of 66 billion pounds of soaps and detergent products were used worldwide [1]. Of these, 40 billion pounds of detergents were annually employed (worldwide) for laundry, dishwashing, industrial, institutional

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cleaning, and other industrial process aids [2]. In 1982 the total end use of surfactants in the United States was about 5.58 billion pounds [3].

Seven types of surfactants comprise the majority of commercial detergent formulations presently in use [4]. They are:

1. Alkylphenol ethoxylates (APEO) – nonionic
2. Alcohol ethoxylates (AE) – nonionic
3. Linear alkylbenzene sulfonates (LAS) – anionic
4. Alkyl sulfates (AS) – anionic
5. Alcohol ethoxy sulfates (AES) – anionic
6. Alpha olefin sulfates (AOS) – anionic
7. Secondary alkane sulfonates (SAS) – anionic

Synthetic nonionic surfactants were introduced in 1962. Since then, they have gained recognition for their remarkable properties as compared to anionic surfactants. Nonionic surfactants are not adversely affected by hard waters because they do not ionize in solution. Nonionic surfactants also perform well in hard waters containing a high concentration of salts. In addition, they are stable at high temperatures and extremes of pH.

Nonionic, anionic, and/or cationic surfactants are sometimes mixed together in predetermined proportions that provide a wide range of adaptability. For example, in a preformulated combination of anionic and nonionic surfactants, the washing power of anionic surfactants can be specifically directed to the removal of the polar fibers (such as cotton) from the mixture. A simple anionic surfactant will not perform as well. Additionally, these surfactants are particularly well suited for cleaning synthetic fibers that have troublesome oily soils attached to them [3].

Nonionic surfactants do not contain phosphate builders, thereby reducing the eutrophication in the receiving waters. Because of the recent ban of phosphate-based detergents in certain states, the phosphorous concentration in the wastewater has dramatically decreased. Jones and Hubbard report that the phosphorous reductions in the Washington, D.C. area ranged from 18 to 38 percent [5]. Considering the shortcomings of phosphorous in the detergents, it is likely that nonionic surfactants will be more widely used in the future.

APEOs are increasingly popular nonionic surfactants, which in 1974 had an estimated market share of 18 percent of the total synthetic surfactants in Europe [6]. In 1975 the total production of APEO surfactants in the United States and Europe reached 793 million pounds [7]. In 1982 the end use of these surfactants in the United States alone reached 308.7 million pounds (89% for industrial use and 11% for household products), which was approximately 8 percent of the total surfactants used in the United States [3].

Alkylphenols are reacted with varying amounts of ethylene oxide to provide a wide variety of APEOs that have a wide range of applications. 4-nonylphenol ethoxylates (NPEOs) are prepared by reacting 4-nonylphenol (NP) with ethylene oxide (EO). In the formulation of NPEOs, the molar ratio of hydrophilic (EO) to hydrophobic (NP) may vary from 4 to 30. The amount of EO added to the NP may be controlled to give a large variety of products that are useful in many industrial applications. NPEOs offer a broad range of properties such as oil solubilizing and emulsification characteristics. Because of their versatility, they are used in a number of industries and in a multitude of products.

NP

NP is manufactured by the alkylation of phenol with an appropriate olefin. Typically, the reaction can be represented as

$$C_6H_5OH + C_9H_{18} \rightarrow \underset{\substack{\text{4-nonylphenol} \\ \text{75-80\% yield}}}{HOC_6H_4C_9H_{19}} + \text{dinonylphenols}$$

The reactive hydroxyl group in the NP molecule permits a multiplicity of reactions. These include ethoxylation, etherification, esterification, halogenation, mercuration, nitration, polymerization, salt formation, and sulfonation. NP is colorless, insoluble in water, and has mild phenolic odor.

About 70 percent of the NP manufactured is consumed in making surfactants. NP is incorporated into surfactants by ethoxylation or sulfonation. These surfactants have a wide variety of uses such as in the manufacture of emulsifiers, toxicants, metal cleaners, latex stabilizers, and tanning assistants. The second largest use of NP is in the plastics and rubber industry, where it is used as an intermediate in the manufacture of anti-oxidants. It is predicted that this use will continue to grow. In addition to the use of NP in formulating APEOs, NP is also used as an emulsifier in pesticide formulations, for example, Matacil.

APEO surfactants are discharged into the environment through the municipal collection systems. Recently, it was discovered that APEO-based surfactants, during their degradation by aerobic and anaerobic pathways, product toxic metabolites such as NP, which has many isomers [8].

NP in Wastewater

Giger, et al. tested thirty anaerobically stabilized sludge samples from European wastewater treatment plants and found that the NP concentration ranged from 450 to 2,530 mg/kg [8-12]. This concentration of NP is several-fold higher than many priority organic pollutants in sludge, such as polychlorinated biphenyls (PCBs), which were found in concentrations ranging from 0.35 to 23 mg/kg in sewage sludge [13]. NP is not listed in the priority pollutant classification [14].

Furthermore, NP concentrations in eight aerobically stabilized sludge samples were significantly lower (it varied from 80 to 500 mg/kg). Activated sludge and mixed primary and secondary sludge also showed low concentrations of NP (90 to 150 and 40 to 140 mg/kg, respectively). Giger, et al., mixed raw and anerobically stabilized sludge in equal parts [10]. The mixed sludge was anerobically digested for up to forty days. In this laboratory experiment, they observed a four to eight fold increase in the concentration of NP (related to the content already present in the raw sludge). However, in aerobic experimentation, NP concentrations increased by a factor of only two. NP concentrations did not increase in sterile controls.

Field investigations of full-scale sewage treatment plants and rivers in Switzerland revealed that 4-nonylphenol monoethoxylates (NP1EOs) and 4-nonylphenol di-ethoxylates (NP2EOs), together with NP, are major refractory constituents in mechanically/biologically treated sewage effluents [10, 11], and in the water of the Glatt River [12].

Garrison, et al. reported increased concentrations of NP in industrial wastewater after anaerobic treatment [15]. Jones, et al. reported short chain alkylphenol ethoxylates in treated sewage effluents, but did not provide precise structural information on the chemicals detected [16].

In their study, Sheldon and Hites identified nearly 100 compounds in Delaware River water samples using Gas Chromatography/Mass Spectrometry (GC/MS) [17]. One of these compounds was NP, which ranged from 1 ug/L to 40 ug/l in summer, and from 1 ug/L to 2 ug/L in winter.

Jungclaus, et al. studied organic constituents present in the effluents from two tire manufacturing plants in the United States using GC/MS analysis [18]. Their objective was to determine if tire plants are potential point sources of hazardous organic compounds in the environment. The authors identified several toxic compounds, including NP.

Dietrich, et al. identified NP among other organic pollutants in the Haw River, located in North Carolina [19].

The presence of NP has been detected by the U.S. Environmental Protection Agency (U.S. EPA) in raw water at the Rome and Calhoun plants in Georgia [20].

Varma, et al. have detected NP at two local sewage plants, with the concentration in the sludge varying from 23 to 134 mg/kg of dry solid [21].

BIODEGRADABILITY

Studies described earlier indicate that NP, a toxic metabolite of nonionic surfactants, has been detected in municipal wastewater effluents, sludges, and surface waters in Europe and in the United States.

In the evaluation of the acceptability of a surfactant, the rate of bio-oxidation in water is of utmost importance. The biodegradation of a chemical compound is achieved biochemically by the interaction of enzymes (endo and exo) and microbial population. Primary degradation is brought about by exoenzymes. These enzymes reduce the compounds to simpler structures that can permeate through the cellular wall. Once inside the protoplasm, the compound is attached to the endo-enzyme, thereby increasing its molecular structure and thus preventing its flow back from the cell. Once inside the cell, the compound is biodegraded to end products—ultimate conversion. Slowly degraded refractory organics are usually exotic in characteristics, and their residual components may have adverse health effects.

Many studies have been conducted on the biodegradation of surfactants, both in the laboratory and in full-scale sewage treatment plants, and these studies have been summarized by Swisher [22] and Leidner [23]. The intrinsic microbial transformation of nonionic surfactants is a recent phenomena, consequently only a few scientists have studied this subject [23-26]. In the studies conducted by Schoberl, et al., [24], and by Geiser [25], metabolites containing one or two residual oxyethylene groups were found to accumulate in the effluents of laboratory-scale activated sludge systems. Therefore, the occurrence of NP1EO and NP2EO in secondary sewage effluents (as identified by Giger, et al. [8]) can be explained by the refractory nature of these metabolites.

Schoberl, et al., in their study into the microbial metabolism of NP9EO (NP ethoxylates containing nine moles of EO), found that NP9EO is primarily attacked from the EO chain [24]. They also demonstrate the decomposition paths for the NPEO studied.

The rate of degradation of APEO is influenced by the degree of branching, the number of EO units/mole, and the position of attachment of the benzene ring to the alkyl chain [4]. Less branching results in a faster rate of degradation; an increase in the number of EO units slows degradation. In addition, the benzene ring configuration in a chemical structure generally slows the biodegradation; however, the attachment of the benzene ring to a primary carbon in the alkyl chain may result in faster biodegradation [27].

It has been postulated that the major degradative pathways of APEOs seem to shorten the ethoxylate chain and causes carboxylation of the alkyl chain, perhaps by omega-oxidation [22]. Omega-oxidation breaks free the alkylphenol mono- and di-ethoxylates (AP1EOs and AP2EOs), which are resistant to biodegradation. Because these metabolites have lost their hydrophilic moieties, they become less soluble in water. These AP1EOs and AP2EOs are further degraded to alkylphenols, such as NP, which accumulate in the effluents, digested sludge, and surface waters [8].

Gaffney reported biodegradation of NP at 1.0 mg/L. [28, 29]. He found that in adapted sewage, there was no biodegradation in twenty-four hours; however, 45 percent was metabolized in 135 hours. NP was stable up to 135 hours in the nonacclimatized experiments, indicating that NP may be very stable and resistant to degradation while residing in normal digested sludge and effluent.

Rudling and Solymon reported similar results on the decomposition of branched chain NPEOs [26] (such as NP8EO, NP10EO, and NP14EP). In certain cases, the first degradation product was NP2EO, and 50 percent of this product was degraded. In the activated sludge system, all of the investigated NP derivatives were biologically degraded and the degradation exceeded 90 percent. It is generally accepted that APEO surfactants undergo primary biodegradation in a variety of test systems, provided sufficient acclimatization time is allowed [30, 31]. Apparently the biodegradation of NPEOs takes place via a series of microbial transformations of the ethoxylate chain.

TOXICITY

In the last five to ten years, some progress has been made in assessing the toxic effects of surfactants and their degradation products. Acute toxicity to aquatic life forms has been studied, and the scientists generally contend that toxicity occurs in adult vertebrate and invertebrate species at surfactant concentrations between 1 and 20 mg/L. Juvenile and development stages of these species show adverse effects at somewhat lower concentrations [26]. Invertebrates appear to be generally susceptible to surfactants in the same range as vertebrates, although toxicity to some marine bivalves and crustaceans occurs at high concentrations–greater than 100 mg/L [27]. Typical LC_{50} values (range of most frequently reported 24 to 96 hours) for APEO type of surfactants range from 4 to 12 mg/L for fish.

Studies have been conducted with respect to possible harmful effects of NP to the aquatic fauna. Stephanou, et al., summarized the available information on the toxicity of NPEOs to the aquatic fauna (Table 1) [11]. Table 1 reflects the fact that toxicities decrease with an increase in oxyethylene side chains. Pseudomonas showed highest resistivity (among the species tested) when the oxyethylene groups were low; however, the resistivity was reversed at higher (above 30) oxyethylene groups. Daphnia showed no effect, even at greater than 1,000 mg/L concentration.

The high toxicity of NP became evident in a study on the toxic effects of Matacil, a pesticide formulation in which NP is used as a major component [32]. The toxicity of NP in aquatic ecosystems has been studied at length by McLeese, et al., [33], and Bringmann, et al., [34]. McLeese, et al., tested NP with salmon in a flow-through system [33]. They found that the concentration of NP in water exponentially decreased during the lethality and uptake tests according to the equation:

$$C = ae^{-bt} \qquad (2)$$

where

C = relative concentration;
t = time in hours; and
a and b = empirical coefficients.

The numerical values of a and b coefficients for shrimp and salmon are listed in Table 2. Table 3 lists the 96-hour LC_{50} and lethal thresholds for NP as reported by McLeese, et al., [33], and by Armstrong and Kingsbury [34]. Toxicity tests with Daphnia magna show a median effective concentration

Table 1. Toxicity to Aquatic Fauna of Nonylphenol Ethoxylates [11]

Nonylphenol Ethoxylates[a]	*No Effect Level, mg/L*			
	Pseudomonas	*Scendesmus*	*Colpoda*	*Daphnia*
30	1,000	5,000	250	> 10,000
20	1,000	125	250	1,000
10	1,000	31	31	10
7	63-50	16	16	10
6	500	10	10	5
4	50	6	6	5

[a] Average numbers of oxyethylene groups.

Table 2. a and b Coefficients for Salmon and Shrimp [33]

			Salmon			
	Shrimp		*Lethality*		*Uptake*	
Compound	*a*	*b*	*a*	*b*	*a*	*b*
NP	0.709	0.011	0.649	0.030	0.765	0.020

Table 3. 96-h LC_{50} and Lethal Thresholds for Nonylphenol [33, 34]

	96-h LC_{50} and Lethal Thresholds for NP to Aquatic Organisms			
	Shrimp [33]	*Salmon [33]*	*Fingerling Brook Trout (Salvelinus Fontinalis) [34]*	*Fingerling Rainbow Trout (Salmo Gairdneri) [34]*
96-h LC_{50} (mg/L)	0.3	0.13-0.19	0.145	0.230
Lethal Thresholds (mg/L)	0.15-0.32	0.18-0.19	--------	--------

(EC_{50}) for NP of 0.18 mg/L [35]. The maximum permissible concentration in sludge for cadmium toxicity (EC_{50}, 0.35 mg/L) is set at about 30 mg/kg. Evidently, NP is two-fold more toxic than cadmium.

Gaworski, et al., tested a series of chemical compounds used by the United States Air Force, and these were then evaluated for acute toxicity effects to establish safe handling guidelines.[36]. Of the compounds tested, NP was found to cause a skin sensitization reaction in eighteen of the twenty-two animals dosed.

Alkylphenols, particularly those with alkyl chains ranging from six to twelve carbon atoms, are highly toxic to aquatic fauna. The latter also have relatively high bioconcentration factors [33].

Present day use of the major surfactants may not appear to represent a hazard to human health. The primary support for this view comes from the low order of acute mammalian toxicity. However, the data on chronic effects in mammalian toxicity and the data on chronic effects in mammalian test systems are not available. Focal cardiac necrosis was reported in dogs fed with 40 mg/kg/day of NP20EO (containing 20 EO moles/mole of NP) for ninety days; however, lesions was evident within five days at higher doses (1,000 mg/kg) [27].

Laws forbidding the use of hard surfactants in Europe and the United States relate only to anionic surfactants. As a result, the nonionic surfactants are widely dispersed. The presence of nonionic surfactants in sewage and other effluents may create environmental problems such as those created by anionic surfactants (foaming at sewage treatment plants and on water bodies, such as rivers, into which effluents are disposed) [37].

Nonionic surfactants appear to be more toxic to fish and plant life. In light of the available toxicity data on NP, it can be assessed that NP poses a considerable threat to the aquatic fauna. However, in-depth animal toxicity data are lacking. APEO-type of surfactants get transformed in the biological treatment to daughter refractory metabolites, such as NP, that are more toxic than the parent APEO chemicals. Hence, the lethality and bioconcentration factors create a situation that warrants an in-depth study of the sources and the environmental fate and effects of APEOs in sewage treatment and in natural waters.

REFERENCES

1. R. Schneider, Umschau: Weltproduktion undverbrauch un Scifen, Wasch -und Reinigung smitteln 1980, 1981, and 1982, *Tenside Detergents, 21,* pp. 212-215, 1984.
2. P. L. Layman, Brisk Detergent Activity Changes Picture for Chemical Suppliers, *Chemical and Engineering News,* pp. 17-49, January 23, 1984.
3. D. E. Haupt, U.S. Detergents/Surfactant Trends—1980's, *Tenside Detergents, 20,* pp. 332-337, 1983.
4. M. M. Goyer, J. H. Perwak, A. Sivak, and P. S. Thayer, Human Safety and Environmental Aspects of Major Surfactants, Report to the Soap and Detergent Association, Arthur D. Little, Inc., Cambridge, MA, 1981.

5. E. R. Jones and S. D. Hubbard, Maryland's Phosphate Ban—History and Early Results, *Water Pollution Control Federation, 58,* pp. 816-822, 1986.
6. Environmental Resources Limited, *Cleaning and Conditioning Agents: Their Impact on the Environment,* Graham and Trotman, London, 1977.
7. W. Wirth, Nichtionische Tenside: Bedeutung, Herstellungsverfahren, Eigenschaften und Einsatzmolichkeiten, *Tenside Detergents, 12,* p. 245, 1975.
8. W. Giger, P. H. Brunner, and C. Schaffner, 4-nonylphenol in Sewage Sludge: Accumulation of Toxic Metabolites from Nonionic Surfactants, *Science, 225,* pp. 623-625, 1984.
9. W. Giger and M. Ahel, Determination of Alkylphenols and Alkylphenol Mono- and Di-ethoxylates in Environmental Samples by High Performance Liquid Chromatography, *Analytical Chemistry, 57,* pp. 1577-1583, 1985.
10. W. Giger, E. Stephanou, and C. Schaffner, Persistent Organic Chemicals in Sewage Sludge Effluents: 1. Identifications of Nonylphenols and Nonylphenolethoxylates by Glass Capillary Gas Chromatography/Mass Spectrometry, *Chemosphere, 10,* pp. 1253-1263, 1981.
11. W. Giger and E. Stephanou, Persistent Organic Chemicals in Sewage Sludge Effluents: 2. Quantitative Determinations of Nonylphenols and Nonylphenolethoxylates by Glass Capillary Chromatography, *Environmental Science and Technology, 16,* pp. 800-805, 1982.
12. M. Ahel, W. Giger, E. Molnar-Kubica, and C. Schaffner, in *Analysis of Organic Water Pollutants,* G. Angeletti and A. Bjorseth (eds.), Reidel, Dordrecht, Holland, pp. 280-288, 1984.
13. A. K. Furr, et al., Multielement and Chlorinated Hydrocarbon Analysis of Municipal Sewage Sludges of American Cities, *Environmental Science and Technology, 10,* p. 683, 1976.
14. M. M. Varma and W. W. Talbot, Organic Pollutants in Municipal Sludge—Health Risks, *Journal of Environmental Systems, 16*:4, p. 295, 1986-87.
15. A. Garrison and D. W. Hill, *American Dyestuff Reporter,* February 1972.
16. P. Jones and G. Nickless, Characterization of Nonionic Detergents of the Polyethoxylated Type from Water Systems. II. Isolation and Examination of Polyethoxylated Material Before and After Passage Through a Sewage Plant, *Journal of Chromatography, 156,* pp. 99-100, 1978.
17. R. Hites and L. Sheldon, Organic Compounds in the Delaware River, *Environmental Science and Technology, 12,* pp. 1188-1194, 1978.
18. G. Jungclaus, L. Games, and R. Hites, Identification of Trace Organic Compounds in Tire Manufacturing Plant Wastewaters, *Analytical Chemistry, 48*:13, pp. 1894-1896, 1976.
19. A. M. Dietrich, D. S. Millington, and R. F. Christman, *Specific Identification of Organic Pollutants in Haw River Using Gas Chromatography/Mass Spectrometry,* report of the Water Resources Research Institute, University of North Carolina, Raleigh, NC, *206,* p. 144, 1983.
20. Communication, United States Environmental Protection Agency to Georgia Water Quality Control Board, October 6, 1972.
21. M. M. Varma, et al., Quantitative Analysis of 4-Nonylphenol in Wastewater Sludges, presented at the American Water Works Association Water Quality Technology Conference, Portland, OR, November 16-20, 1986.

22. R. D. Swisher, *Surfactant Biodegradation,* Marcel Decker, New York, NY, 1970.
23. H. Leidner, G. Bringmann, and R. Kuhn, Abbaukinelik Linearer Alkylbenzene Sulfonate, *Tenside Detergents, 12,* pp. 122-130, 1976.
24. P. Schoberl, E. Kunkel, and K. Espeter, Comparative Investigations into the Metabolism of a Nonylphenol and an Oxyalcohol Ethoxylate, *Tenside Detergents, 18,* pp. 64-72, 1981.
25. R. Geiser, Microbial Degradation of a Nonionic Detergent in the Presence of Activated Carbon, Ph.D. thesis, ETH-Zurich, Switzerland (Diss. ETH Nr. 6678, in German), 1980.
26. L. Rudling and P. Solymon, The Investigation of Biodegradability of Branched Nonylphenol Ethoxylates, *Water Research, 8,* pp. 115-119, 1974.
27. Arthur D. Little, Inc., *Human Safety and Environmental Aspects of Major Surfactants,* National Technical Information Service, Document PB 301 193/9ST, Springfield, VA, 1977.
28. P. E. Gaffney, Carpet and Rug Industry Case Study II: Biological Effects, *Journal of Water Pollution Control Federation, 48*:12, pp. 2731-2737, 1976.
29. ———, Carpet and Rug Industry Case Study I: Water and Wastewater Treatment Plant Operation, *Journal of Water Pollution Control Federation, 48*:11, pp. 2590-2598, 1976.
30. E. S. Lashen and K. A. Booman, Water and Sewage Works, J., R155, 1967.
31. R. C. Allred and R. L. Huddleston, *Southwest Water Works Journal, 49,* p. 26, 1967.
32. D. W. McLeese, V. Zitco, C. D. Metcalfe, and D. B. Seargent, *Chemosphere, 9,* p. 79, 1980.
33. D. W. McLeese, V. Zitco, D. B. Seargent, L. Burridge, and C. D. Metcalfe, Lethality and Accumulation of Alkylphenols in Aquatic Fauna, *Chemosphere, 10,* pp. 23-730, 1981.
34. G. Bringmann and R. Kuhn, Results of Toxic Action of Water Pollutants on Daphania Magna Straus by an Improved Standardized Procedure, *Zeitschrift fur Wasser -und Abwasser -Forschung, 15,* p. 1, 1982.
35. J. A. Armstrong and P. D. Kingsbury, Interim Progress Report, Forest Pest Management Institute, Canadian Forestry Service, p. 63, 1979.
36. C. L. Gaworski, E. R. Kinkead, and R. L. Doyle, Acute Toxicity of a Number of Chemicals of Interest to the Air Force, Report: AMRL–TR-79-11, Order No. AD-A067313, p. 32, 1979.
37. M. Horowitz, Specific Phototoxicity of Surfactants, proceedings of the E.W.R.S. Symposium, Methods Weed Control and Their Integration, pp. 79-86, 1977.

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