BIOGEOCHEMICAL BEHAVIOUR OF ALKYLPHENOL POLYETHOXYLATES IN THE AQUATIC ENVIRONMENT

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To my sons Ivan, Tvrtko, Jakov, and Juraj

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Table of Contents

PROBLEM STATEMENT AND SCOPE OF THE WORK 1

1. INTRODUCTION 2

1.1. Ecological Acceptability of Surfactants 2
1.1.1. Definition, Classification and Characteristics of Surfactants 2
1.1.2. Manufacture and Usage of Surfactants 3
1.1.3. Input, Behaviour and Harmful Effects on the Environment 4
1.1.4. Biodegradability of Surfactants 5

1.2. Nonionic Surfactants 6
1.2.1. Types, Production and Usage 6
1.2.2. Physico-chemical Properties 8
1.2.3. Analytical Determination 10
1.2.4. Biological Degradation 14
1.2.5. Occurrence in the Environment and Harmful Effects 17

2. EXPERIMENTAL 19

2.1. Materials 19
2.1.1. Chemicals 19
2.1.2. Solutions and Reagents 20
2.1.3. Equipment 22

2.2. Analytical Procedures for the Determination of Alkylphenol Polyethoxylates and Their Metabolites 23
2.2.1. Extraction and Purification of Extracts 23
2.2.1.1. Alkylphenol Polyethoxylates 23
2.2.1.2. Lipophilic Alkylphenol Ethoxylates and Alkylphenols 25
2.2.1.3. Alkylphenoxy Carboxylic Acids 26
2.2.2. Preparative Separation and Determination of Response Factors 28
2.2.2.1. Alkylphenol Ethoxylates 28
2.2.2.2. Alkylphenoxy Carboxylic Acids 29
2.2.3. Instrumental Methods 29
2.2.3.1. High-Performance Liquid Chromatography (HPLC) 29
2.2.3.2. High-Resolution Gas Chromatography (HRGC) 31
2.2.3.3. High-Resolution Gas Chromatography/Mass Spectrometry (HRGC/MS) 31
2.2.3.4. Other Instruments 32

2.3. Determination of Solubility in Water 32

2.4. Determination of Partition Coefficients between Water and Organic Solvents 33

2.5. Determination of Biodegradability 34

2.6. Determination of Photochemical Degradability 36

2.7. Sampling 38

3. RESULTS AND DISCUSSION 39

3.1. Determination of Alkylphenol Polyethoxylates and Their Metabolites 39
3.1.1. Determination of Alkylphenol Ethoxylates and Alkylphenols 39
3.1.1.1. Chromatographic Separation 39
3.1.1.2. Response Factors of Alkylphenol and Alkylphenol Ethoxylates 45
3.1.1.3. Extraction and Purification of Extracts 47
3.1.1.4. Accuracy, Precision and Sensitivity 50
3.1.1.5. Application 52
3.1.2. Determination of Alkylphenoxy Carboxylic Acids 60
3.1.2.1. Chromatographic Separation and Identification of Alkylphenoxy Carboxylic Acids 60
3.1.2.2. Chromatographic Separation and Identification of Methyl Esters of Alkylphenoxy Carboxylic Acids 63
3.1.2.3. Response Factors 68
3.1.2.4. Extraction, Extract Purification and Derivatization 69
3.1.2.5. Application 73

3.2. Physico-chemical and Biological Behaviour of Alkylphenol Polyethoxylates and Their Degradation Products 78
3.2.1. Solubility in Water 78
3.2.1.1. Solubility of Pure APEO Oligomers 78
3.2.1.2. Dependence of Solubility upon Temperature 80
3.2.1.3. Solubility of APEO in Mixtures 82
3.2.2. Partition between Water and Organic Solvents 84
3.2.3. Biological Degradation 89
3.2.3.1. Biological Degradation of Alkylphenol Polyethoxylates 89
3.2.3.2. Biodegradation of APEO and AP in Synthetic Sewage Using Shake Culture Test 90
3.2.3.3. Biodegradation of APEO and AP in Mineral Medium Using Shake Culture Test 94
3.2.3.4. Biodegradation of APEO and AP in River Water Test 97
3.2.3.5. Biodegradation of APEO and AP in Modified Closed Bottle Test 100
3.2.3.6. Degradation Products of APEO 102
3.2.4. Photochemical Degradation 104
3.2.4.1. Direct Photolysis 104
3.2.4.2. Sensitized Photolysis 105
3.2.4.3. Photolysis in the Presence of Hydrogen Peroxide 109
3.2.4.4. Photolysis by Sunlight 111

3.3. Occurrence and Behaviour of Alkylphenol Polyethoxylates and Their Degradation Products in Sewage Treatment Plants 115
3.3.1. Characteristics of Investigated Sewage Treatment Plants 115
3.3.2. Occurrence and Distribution in Raw Wastewaters and Effluents 116
3.3.3. Diurnal and Daily Variations 122
3.3.4. Elimination of Alkylphenol Polyethoxylates and Their Metabolites During Biological Treatment 125
3.3.5. Role of Nonbiological Processes 132

3.4. Occurrence and Behaviour of Alkylphenol Polyethoxylates and Their Degradation Products in Natural Waters 136
3.4.1. Glatt River 136
3.4.1.1. Characteristics of the Investigated Area 136
3.4.1.2. Statistical Distribution of Concentrations 136
3.4.1.3. Diurnal Dynamics of Concentration Variations 138
3.4.1.4. Distribution of Concentrations and Mass Flows on the Longitudinal Profile and Seasonal Variations 142
3.4.1.5. Analysis of Input and Output Mass Fluxes 147
3.4.1.6. Sediments 150
3.4.2. Comparison of Swiss Rivers 151
3.4.2.1. Characteristics of Investigated Rivers 151
3.3.2.2. Distribution of Concentrations 154
2.4.2.3. Influence of Hydrological and Seasonal Conditions 160
3.4.3. Lake Geneva 164
3.4.3.1. Estimation of Input 164
3.4.3.2. Distribution of Concentrations 165
3.4.4. Infiltration of Riverwater into Groundwater 168
3.4.4.1. Characteristics of Investigated Locations 168
3.4.4.2. Elimination of Nonylphenol Ethoxylates and Nonylphenol 168
3.4.4.3. Elimination of Alkylphenoxy Carboxylic Acids 173
3.4.5. Bioaccumulation in Freshwater Organisms 175

4. CONCLUSIONS 179

5. REFERENCES 185

7. ABSTRACT 199

Curriculum Vitae 200

PROBLEM STATEMENT AND SCOPE OF THE WORK

Alkylphenol polyethoxylates (APnEO) are complex mixtures of oligomers, isomers, and homologues which are manufactured by addition of ethylene oxide to alkylphenols. Owing to their excellent surface active properties they are widely used as ingredients in many detergent formulations for household use, but have an even greater importance in various industrial applications.
It has been well known that alkylphenol polyethoxylates are comparatively less biodegradable than the linear alcohol polyethoxylates. However, a decisive impulse for the revival of discussions on their environmental acceptability has been given just recently. Namely, newer investigations have certainly shown that biodegradation of alkylphenol polyethoxylates can lead to the formation of persistent metabolites, some of them being more toxic than the parent compounds itself.

The scope of this work was to develop analytical procedures for the determination of alkylphenol polyethoxylates and their degradation products using highly specific techniques such as high-performance liquid chromatography, high-resolution gas chromatography, and high-resolution gas chromatography/mass spectrometry and to apply them to studies of biogeochemical behaviour of these compounds in the aquatic environment.
In order to achieve a better understanding of the behaviour and fate of alkylphenol polyethoxylates in the environment, laboratory investigations on their physicochemical and biological properties will be combined with extensive field observations of these compounds in various environmental compartments. The results of this study should finally provide a basis for an assesment of the environmental acceptability of alkylphenol polyethoxylate surfactants.

1. INTRODUCTION

1.1. Ecological Acceptability of Surfactants

The basic element for an assessment of the ecological acceptability of a certain substance is its chemical structure. Namely, all physico-chemical and biological properties which determine the behaviour of a substance in the environment are determined by that structure. The investigations of the relationships between chemical structure and harmful effects upon the living world allowed the predictions of harmful behaviour of so far uninvestigated compounds (1). Besides the characteristics derived from the chemical structure, important criteria for the environmental assesment of a chemical are the data about the amounts produced, usage pattern and ways by which surfactants are introduced into environment.

1.1.1. Definition, Classification and Characteristics of Surfactants

Surfactants represent highly variable and numerous groups of chemical substances. Their common structural characteristics is the presence of both hydrophobic and hydrophilic groups. The hydrophobic part of the surfactant molecule is usually an alkyl chain or alkylbenzene, while hydrophilic part can be very different. Surfactants are classified as anionic, cationic and amphotheric, depending on whether hydrophilic part of the molecule is neutral, negatively or positively charged. The consequence of the amphiphatic structure is the characteristic behaviour of surfactants in solutions and at interfaces between different phases (2, 3, 4).

In highly diluted aqueous solutions, surfactants occur as real solutions. After reaching a certain concentration in solution, monomer surfactant molecules merge to form aggregates usually called micelles. The concentration at which micelles are formed is called critical micellar concentration (cmc). With ageing of the solutions, the water-air interface is enriched with surfactants forming monomolecular films whose hydrophilic part is solution oriented and the hydrophobic part is air oriented. Specific orientation of surfactant molecules is also retained in micelles, where hydrophilic parts are oriented towards solution and hydrophobic parts towards the center of micelle. Micelles are in constant dynamic equilibrium with the solution, and their size depends on the surfactant type (aggregation number). If the concentration of surfactant in the solution is increased even more, surfactants

form colloid solutions, while in highly concentrated solutions structural gels are formed (liquid crystals).

The consequence of surfactant adsorption on interfaces (liquid-gas or liquid-solid) is a decrease in surface tension and formation of an electric double layer. Such behaviour is the basis for many practical applications of surfactants (wetting, foaming, solubilization of slightly soluble substances, emulsifying, stabilizing of suspensions and colloids, dispersion, etc.). However, many important molecules in living organisms display also typical amphyphatic properties and can be considered natural surfactants (5). The most significant example is perhaps the lipoprotein cell membrane which allows exchange of the matter between the cell and its surroundings (6).

1.1.2. Manufacture and Usage of Surfactants

Washing and cleaning agents (detergents) are one of the most characteristic and most numerous products of modern civilization. In 1982 there were over 30 million tons of detergents produced globally for various industrial and domestic uses. There are significant differences in per capita consumption of detergents between specific geographical areas of the world. Consumption in developed countries of Western Europe and North America is several times greater than in Asian and African countries. With the annual consumption figure of 142.000 tons or 22.4 kg per year Switzerland is in the upper part of the consumption scale, somewhat higher than the West European average (21 6 kg per capita) (8). Production and consumption of detergents in Yugoslavia is experiencing fast growth (8.8 % per year). The estimated yearly production for 1985 is 496.000 tons which gives a significant consumption figure of 18.9 kg per capita per annum (9).

Modern detergents contain a great number of components which play different roles in the washing process (10), but the essential components are synthetic surface-active substances, so called surfactants.Total world production of surfactants for 1982 was 5 million tons (11, 12) and the majority (42 %) was used in the production of washing and cleaning agents. According to some authors (13) 60 % of the total world quantity of surfactants is anionic, 10 % cationic and about 30 % nonionic.

1.1.3. Input, Behaviour and Harmful Effects on the Environment

Surfactants are most often introduced to the environment through wastewaters. Scheme in Fig. 1 shows the ways of surfactant introduction into the environment, their distribution, and possible paths of harmful effects on living organisms.

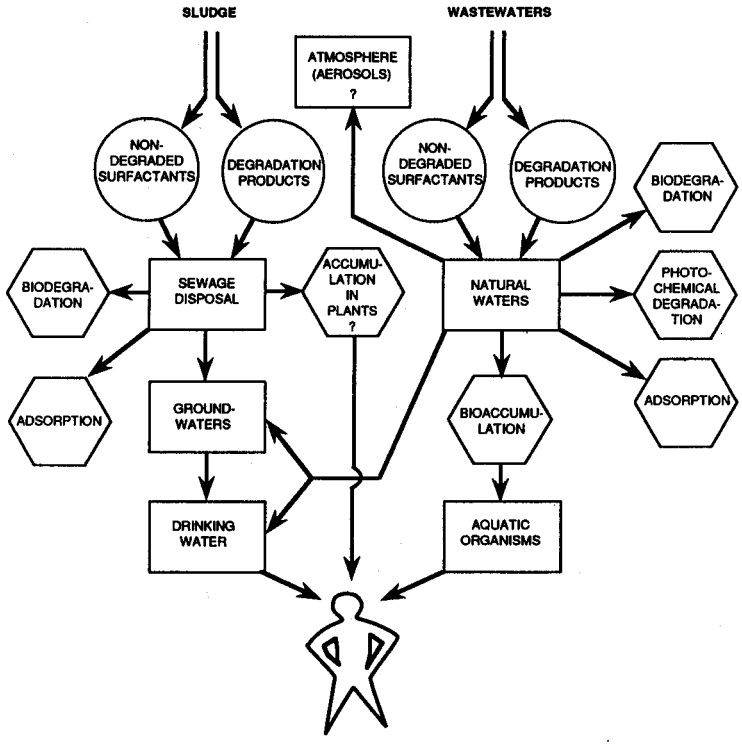


Figure 1. *Inputs, distribution and behaviour of surfactants in the environment*

If wastewaters enter the environment via sewage treatment plants the surfactants can be significantly eliminated before they enter natural waters due to the action of microorganisms. However, biological breakdown is not complete even in highly effective plants, leaving a certain quantity of surfactants undergraded. Moreover, microbial degradation proceeds not always to ultimate products, carbon dioxide and water, and can result in the formation of various degradation products which are more resistant to further microbial attack (14). Due to their biorefractory nature such degradation products can accumulate in the environment. The behaviour of surfactants and their degradation products is affected by various physico-chemical processes, primarily adsorption onto solid particles which can result in very high concentrations of surfactants in sludge (15). The disposal of sludge onto fields as

fertilizer introduces surfactants and their degradation products into arrable land. From there they can be taken up by the crop plants or they can reach ground water through soil leaching. In addition, wastewaters which usually contain surfactants are in some cases deliberately introduced into the groundwater. Namely, due to water shortages, there are efforts in many parts of the world to recycle treated wastewater; often it is firstly kept in accumulation ponds or underground (16) expecting spontaneous die-away of the present chemicals.

Following their introduction into natural waters surfactants can be further degraded by the present microorganisms, adsorbed onto solid particles and photochemically degraded.
The surfactants present in natural waters influence numerous physico-chemical processes of organic (17) and inorganic compounds (18).

Because of the use of surfactants as washing and cleaning agents, and especially in personal care products, it is of the highest importance that they should not be harmful to human health. Generally, it can be stated that surfactant toxicity is relatively low for mammals, but can be considerable for aquatic organisms (11, 19, 20). Biorefractory degradation products, which can be even more toxic than surfactant itself, can reach the human population through polluted drinking water, or through bioaccumulation in edible water organisms.

1.1.4. Biodegradability of Surfactants

Biodegradation of surfactants, i.e. breaking down of complex molecules into simpler ones through the action of microorganisms, is one of the basic prerequisites of their environmental acceptability. The first negative consequences of surfactant application were already observed in the 1950's, through the use of the synthetic anionic surfactant tetrapropylenebenzene sulphonate (TBS). Foaming was observed in wastewater treatment facilities as well as in natural waters, which was the consequence of the surfactant resistance towards biodegradability (21). That was the reason for substitution of TBS with biodegradable linear alkylbenzene sulphonates. Fast and complete degradation of a certain surfactant simplifies the assessment of its environmental acceptability because it means that it will degrade considerably in the wastewater treatment facilities. Furthermore, it means that its concentration in natural waters will be lower than expected from the figures on their discharge via nontreated wastewaters. The law regulations which deal

with the environmental acceptability of surfactants are actually based on the requirement that applied surfactants must be at least 80 % biodegradable (22-26).

From the numerous methods for testing of the biodegradability (21) the most often used are the shake bottle test, the river water test and the method with activated sludge. The last method was officially accepted by all members of the Organization for Economic and Development (OECD) (27). According to that method, concentration of anionic surfactants is measured by the complex formation with methylene blue (MBAS method) (28), and concentration of nonionic surfactants by the method of complex formation with Dragendorff reagent (BiAS method) (29). Since the above mentioned analytical methods measure only the original surfactants and not their degradation products, these methods give insight only into the initial biodegradation. Recently there prevails the opinion that in the detergent formulations for wide use only those surfactants that can be degraded down to carbon dioxide and water should be applied. Therefore, valid law regulations on 80 % degradability, which are based on MBAS and BiAS measurements, are no longer satisfactory.

1.2. Nonionic Surfactants

1.2.1. Types, Production and Usage

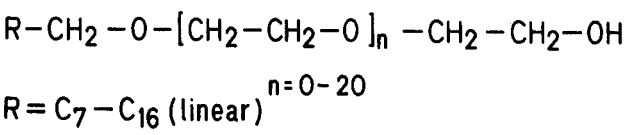
Nonionic surfactants are, together with anionic ones, the most important surfactants. While some older reports estimated that their share in the whole production and consumption was only 30 % (13), according to more recent reports (30) the usage of nonionic surfactants is strongly increasing and it is expected that they will soon become the dominant group. Nonionic surfactants today represent the most important group of surfactants for industrial applications (31). The increased use of nonionic surfactants is the consequence of their excellent surface-active (surface wetting, emulgation) and some special properties (weaker foaming) which make them acceptable for a number of applications other than as washing and cleaning agents. They are used in the textile, leather and paper industries, for the preparation of colours, varnishes and pesticides, as well as for flotation and for crude oil processing (32).

Nonionic surfactants are the molecules whose hydrophilic group can not dissociate to form ions, but it has to be sufficiently polar to ensure good solubility in water. There exists a considerable number of nonionic surfactant types (33), but the most important are those produced by the addition of ethylene oxide to different

hydrophobic molecules like long-chain alcohols, alkylphenols and fatty acids (34, 35). It should be pointed out that linear alcohol polyethoxylates (LAEO, Figure 2a) and alkylphenol polyethoxylates (APEO, Figure 2b) represent 80 % of all produced nonionic surfactants (13). The consumption of those nonionic surfactants in Western Europa, USA and Japan in 1982 was 500.000 tons of LAEO and 310.000 tons of APEO. The consumption for Switzerland can be estimated at about 5.000 tons/year (8).

During the synthesis of LAEO and APEO the oxygen atom of ethylen oxide transfers to hydroxyl group resulting in an electrophilic alkylation or more precisely in hydroxyethylation. The products thus formed should be consistently called oxethylates and not ethoxylates, commonly found in literature. However, in order to avoid confusion of the alternative use of different names for the same compounds, in this work the educts of ethylene oxide will be named ethoxylates.
Oxethylation can be conducted with the use of acidic or basic catalysis which influences the composition of the formed reaction products; with basically catalysed synthesis the anion (alcoholate or phenolate) is formed first, which reacts subsequently with ethylene oxide through the nucleophilic reaction.

Linear Alcohol Polyethoxylates (LAEO)



Alkylphenol Polyethoxylates (APEO)

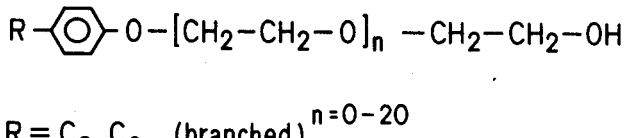


Figure 2. *Structures, names, and abbreviations of the most important nonionic surfactants*

The distribution of oligomeres formed by oxethylation should theoretically follow the Poisson statistical distribution, but due to the uneven reaction rate of resulting oligomeric compounds deviations from the ideal curve occur (3).

1.2.2. Physico-chemical Properties

Lower molecular weight oligomers of LAEO and APEO are viscous liquids. With the increase of molecular weight they change to semisolid state (pastes).

The solubility of surfactants is thermodynamically determined by the value of free energy (ΔG_0) neccessary for the transfer of molecules from the pure phase to the water solution. The value of ΔG_0 is obtained from the combination of contributions for hydrophilic (ΔG_{e0}) and hydrophobic (ΔG_{h0}) part of the molecule. These two contributions differ strongly:ΔG_{h0} is positive (determined by the negative value of enthropy ΔS_{h0}) and ΔG_{e0} is negative and generally larger than ΔG_{h0}.
Since the solubility depends on the characteristics of the hydrophilic group of the surfactant, it is considerably different for ionic and nonionic surfactants; for non-ionic surfactants it obviously depends on the number of polar groups forming the hydrophilic part of the molecule. It should be kept in mind that nonionic surfactants are as a rule complex mixtures of oligomers, isomers and homologues, so that their solubility is never considered as the solubility of pure chemical compounds. This is probably the reason why the exact data on the solubility of particular oligomers could not be found in literature. According to the manufacturers technical data (32) the lower oligomers of alkylphenol ethoxylates (nEO < 5) are described as "water insoluble", while higher oligomers form at 20 °C clear solutions; the behaviour in nonpolar organic solvents is quite opposite. Neither the concentrations nor the type of solutions for which these observations were made are stated.
Some information about the solubility of the surfactants can be obtained from the data on their critical micellar concentration (cmc). The nonionic surfactants have much lower cmc than ionic surfactants with the same hydrophobic group. If non-ionic surfactants alone are compared, it can be seen that cmc depends on both the hydrophilic and hydrophobic part of the molecule. Of decisive influence on cmc is the size of the hydrophobic part of the molecule, i.e. cmc decreases sharply with the increase of alkyl chain length. For example, cmc for OPEO (nEO=10) is 3.3×10^{-4} mol/L, and for NPEO with the same average number of EO groups is 7.5×10^{-5} mol/L (36, 37). The introduction of aromatic ring into the hydrophobic part of the molecule has approximately the same effect as the increase