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D. BARCELÓ

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ANALYSIS AND FATE OF SURFACTANTS IN THE AQUATIC ENVIRONMENT

BY

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Series Editor's Preface

Obviously this is not just another book in the series: my involvement as co-editor of the book, together with my two old friends, Thomas Knepper and Pim de Voogt, makes this book rather special to me. Everything started in 1996 when I first met separately with Thomas and afterwards with Pim and we decided to establish a consortium covering the analysis, behaviour and toxicity of surfactants in the aquatic environment.

Our basic idea was to prepare a project proposal to be submitted to the European Union for funding. Surfactants were selected as the main pollutants as there was no project at that time that comprehensively covered the topic. There were many projects dealing with pesticides, phenols, persistent organic pollutants but none targeted surfactants. The project acronym, PRISTINE, is explained in the Foreword to this volume. Clearly the project was a big success and will undoubtedly be known for many years as the European Union surfactant project. I should add as well that the scientific officer involved in the development of the project, Dr Juergen Buesing, played an extremely active role. He was always constructive and communicative, so this book is also partly due to his efforts and I would like to acknowledge here his full support of the initiative. He was responsible for our accomplishing the objectives of the submitted proposal. With this book we even exceeded the objectives. We believe that this is an ideal situation for European Union project management: to have not only the work done at the laboratory level, with the various primary literature publications that are a result of the project, the associated conferences and the technology transfer between the different research institutions, and the bringing together of policy makers, industry representatives and end users, but also to have a final summation of the project in the form of a book from which the larger community can benefit.

In addition to a general introduction to surfactants, the book comprises a comprehensive variety of analytical techniques, including sample handling, for the analysis of surfactants in the aquatic environment. Sample preparation includes automated solid phase extraction and pressurised liquid extraction for water and solid samples, respectively. Analytical determinations of surfactants are based either on gas chromatography-mass spectrometry or liquid chromatography-mass spectrometry. Readers will find all the necessary information for analysing the different groups of surfactants, with special emphasis on transformation products. Quality assurance is also reported on in detail; it is obviously a necessary practice in order to ensure good quality data. One point that needs to be mentioned is the lack of reference materials on surfactants, which makes it even more difficult to ensure the reliability of inter-laboratory data in surfactant analysis. Chapters on toxicity and risk assessment are also included and give a complete perspective on the surfactants problem in the aquatic environment. Overall this book gives an extensive coverage of surfactant analysis in the aquatic environment and I am convinced that it will become the "surfactants book" for the analytical and environmental chemistry community.

Finally, I would like to thank not only my co-editors but also the various authors, most of whom are good friends and co-workers for several years, for their contributions to this comprehensive work on surfactants.

D. Barceló

Editor's Preface

Commercial mixtures of surfactants comprise several tens to hundreds of homologues, oligomers and isomers of anionic, nonionic, cationic and amphoteric compounds. Therefore, their identification and quantification in the environment is complicated and cumbersome. The requirement of more specific analytical methods has prompted a replacement of many of the separate steps in traditional methods of analysis, usually non-chromatographic, by chromatographic tools.

Detection, identification and quantification of these compounds in aqueous solutions, even in the form of matrix-free standards, present the analyst with considerable challenges. Even today, the standardised analysis of surfactants is not performed by substance-specific methods, but by sum parameter analysis on spectrophotometric and titrimetric bases. These substance-class-specific determination methods are not only very insensitive, but also very unspecific and therefore can be influenced by interference from other compounds of similar structure. Additionally, these determination methods also often fail to provide information regarding primary degradation products, including those with only marginal modifications in the molecule, and strongly modified metabolites.

High polarity is one of the reasons why both the ionic and amphoteric surfactants, and especially their metabolites, are difficult to detect. This property, however, is important for the application tasks of surface-active compounds, but is also the reason for their high water solubility. Due to this fact, their extraction and concentration from the water phase, which can be carried out in a number of very different ways, is not always straightforward. Furthermore, they are often not volatile without decomposition, which thus prevents application of gas chromatographic (GC) separation techniques combined with appropriate detection. This very effective separation method in environmental analysis is thus applicable only for short-chain surfactants and their metabolites following derivatisation of the various polar groups in order to improve their volatility.

Derivatisation is often substance-specific, and thus although volatile derivatives of the expected compounds will be produced according to the procedure adopted, discrimination of other surfactants that are simultaneously present but differ in structure – and thereby do not react with the derivatisation reagent – can occur, preventing simultaneous detection.

Many separation and detection methods applied in combination with liquid chromatography (LC) that are described in the literature for the determination of surfactants are not specific to the detection of these compounds at trace levels. Even ultraviolet (UV) spectra obtained from diode array detectors often give only limited information. Furthermore, non-reproducible retention behaviour as well as coelution interference effects are frequently observed during the separation of surfactant-containing extracts. This is recognised, however, only in those cases where specific detection methods such as mass spectrometry (MS) are applied.

In order to study simultaneously the behaviour of parent priority surfactants and their degradation products, it is essential to have accurate and sensitive analytical methods that enable the determination of the low concentrations generally occurring in the aquatic environment. As a result of an exhaustive review of the analytical methods used for the quantification within the framework of the three-year research project *Priority surfactants and their toxic metabolites in wastewater effluents: An integrated study* (PRISTINE), it is concluded that the most appropriate procedure for this purpose is high-performance (HP) LC in reversed phase (RP), associated with preliminary techniques of concentration and purification by solid phase extraction (SPE). However, the complex mixtures of metabolites and a lack of reference standards currently limit the applicability of HPLC with UV- or fluorescence (FL-) detection methods.

In off-line coupling of LC and MS for the analysis of surfactants in water samples, the suitability of desorption techniques such as Fast Atom Bombardment (FAB) and Desorption Chemical Ionisation was well established early on. In rapid succession, new interfaces like Atmospheric Pressure Chemical Ionisation (APCI) and Electrospray Ionisation (ESI) were applied successfully to solve a large number of analytical problems with these substance classes. In order to perform structure analysis on the metabolites and to improve sensitivity for the detection of the various surfactants and their metabolites in the environment, the use of various MS-MS techniques has also proven very useful, if not necessary, and in some cases even high-resolution MS is required.

Following their use in aqueous systems as surface-active compounds, surfactants often reach wastewater treatment plants (WWTP). Although the legislator prescribes their biodegradability, they often cannot be completely mineralised because of short retention times in the WWTP. Therefore, together with their biochemical degradation products (metabolites), they arrive in surface waters serving as receiving water. In addition, relevant compounds adsorb to the biological sewage sludge in the WWTP, and then, in original or partly degraded form, are disposed of along with excess sludge when this is removed.

The particularly persistent compounds and their metabolites reach the raw water serving for drinking water treatment. Some of them are even found in drinking water. Today these effects are not observed as often as in the past, as the non-degradable compounds of the branched alkylbenzene sulfonate type (ABS), formerly widely applied, have been replaced by compounds that are more easily degradable. Nevertheless some surfactants can still be found in relatively remote, estuarine sediments across Western Europe and in relatively high concentrations in effluents of wastewater treatment plants. Therefore it is important that the fate of the corresponding metabolites should also be studied. The most widely used anionic and nonionic surfactants should have the highest priority.

The environmental behaviour of LAS, as one of the most widely-used xenobiotic organic compounds, has aroused considerable interest and study. As a result, it has been determined that, under certain conditions, LAS compounds are completely biodegradable; however, in the marine environment their degradation is known to be slower. The presence of metabolites of the anionic LAS surfactants, the long and short chain SPC derivatives, in the aqueous environment is well known, and as such these degradation intermediates needed to be monitored (and tested for their toxic effects).

Not only the extreme amounts of surfactants emitted into sewage plants and thereby into surface waters, but also the broad variety of the chemical structures combined with their excellent water solubility, their surface-active nature and the persistence of some of the known metabolites make them a group of environmental pollutants that need to be addressed with high priority. For some of the compounds, an enormous impact on the ecosystem, e.g. on fish, can be shown.

In this book, methods and data covering the state-of-the-art of modern analysis and environmental fate of the entire synthetic surfactant spectrum is provided. The first part deals with the analysis of surfactants and consists of three chapters. The chapter dealing with the unequivocal detection of surfactants is mainly devoted to highly sophisticated and established hyphenated mass spectrometric methods, such as LC–MS and LC–MS–MS. In addition, examples are given for the use of solid phase micro extraction (SPME) coupled to (GC)–MS and capillary electrophoresis (CE)–MS. Sample preparation methods have been thoroughly evaluated for all four groups of surfactants (anionic, nonionic, cationic and amphoteric) including their major metabolites. One chapter also addresses quality assurance and interlaboratory studies.

The second part, comprising four chapters, centers on an extensive set of data regarding the different environmental levels of all analyzed surfactants and their major degradation products in various countries. The aerobic biodegradation of surfactants is treated extensively, with emphasis on metabolic routes and novel and persistent metabolites formed. In addition, anaerobic degradation and sorption is also covered.

The presence of both surfactants and their degradation products in different aquatic matrices, such as wastewater, surface water and marine water besides biota is discussed and its importance for the environment evaluated.

By the nature of its content, with contributions from experienced practitioners, the book aims to serve as a practical reference for researchers, post docs, PhD-students and postgraduates as well as risk assessors working on surfactants in environmental laboratories, environmental agencies, the surfactant industry, the water industry and sewage treatment facilities. Each chapter includes extensive references to the literature and also contains detailed investigations. The broad spectrum of the book and its application to environmental priority compounds makes it unique in many ways.

We thank the authors for their time and effort in preparing their chapters. Without their co-operation and engagement this volume would certainly not have been possible.

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Foreword

An understanding of the fate and behaviour of organic chemicals, such as surfactants, in the environment is a prerequisite for the sustainable development of human health and ecosystems. Surfactants are important in daily life in households as well as in industrial cleansing processes. As they are being produced in huge amounts, it is important to have a detailed knowledge of their lifetime in the environment, their biodegradability in wastewater treatment plants and in natural waters, and their ecotoxicity. Parameters relevant for the assessment of the long-term behaviour, such as interactions with hormonal systems, also need to be understood in order to avoid unexpected adverse effects on future generations of people and the environment.

The EU-funded PRISTINE project (*Priority surfactants and their toxic metabolites in wastewater effluents: An integrated study; ENV4-CT97-0494*) brought together a critical mass of scientists and stakeholders from the field of analytical environmental chemistry, toxicology and industry in order to treat wastewater heavily contaminated with surfactants, and created a momentum which triggered new RTD activities in the following priority areas:

- Development of tools in order to trace and measure, in particular, extremely water-soluble and toxic chemicals as well as their degradation products
- Improvement to the functioning of Wastewater Treatment Plants
- Improved risk assessment methodologies regarding surfactants and their degradation products.

The project was one of five European research projects within the WASTEWATER CLUSTER of the EU Environment & Climate Programme, the result of a focused approach within the area of *Environmental Technologies*. The objective was to improve the understanding of the transformation, fate and toxicity of selected groups of industrial pollutants discharged into the water resources by using complementary sampling and advanced measuring techniques.