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European Oilfield Speciality Chemicals Association

Bioaccumulation Potential of Surfactants: A Review

This report was commissioned by the European Oilfield Specialty Chemical Association (EOSCA).

EOSCA was founded in 1990 and has grown to an organisation comprising 40 full members and 7 associate members. As it stands today it represents almost all of the chemical manufacturers and chemical services companies involved in the supply and application of chemicals to Oil and Gas Operations in Europe.

The primary function is to act as a focus of interest and concern on issues relating to Environmental and Safety Regulation. To this end it is recognised by government and operators as a first point of contact for chemical issues and is a fully recognised Non-Governmental Organisation within the OSPAR framework. It has the intention of acting as an advocacy group with regulatory and governmental bodies.

EOSCA provides an opportunity for members to network with Health, Safety and Environmental Affairs professionals in the field of Oilfield Chemicals.

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EUROPEAN OILFIELD SPECIALITY CHEMICALS ASSOCIATION

SUMMARY REPORT

SURFACTANT BIOACCUMULATION REVIEW PROJECT

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The work performed in collating and evaluating the data on surfactant bioaccumulation reviewed in this report was funded entirely by EOSCA. The work was carried out over the period September 1999 to July 2000. The data reviewed was obtained through database and literature searches of material available in the public domain. The conclusions presented in this report are pertinent to the data reviewed, but may need to be modified as more information becomes available.

All contributions to this review project by member companies and individuals within EOSCA are gratefully acknowledged.

Phil McWilliams, *Project Manager*

Bergen, August 2000

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List of Abbreviations and Definitions

APE	Alkyl phenol ethoxylate
BCF	Bioconcentration factor
CHARM	Chemical Hazard and Risk Management
CMC	Critical micelle concentration
CR	Concentration ratio
DMT	Diffusive mass transfer
EO	Ethylene oxide
HOCNF	Harmonised Offshore Chemical Notification Format
HPLC	High-pressure liquid chromatography
K_{oc}	Sediment partition coefficient
LAS	Linear alkylbenzene sulphonate
MECC	Micellar elektrokinetic capillary chromatography
MEEKC	Microemulsion elektrokinetic capillary chromatography
MEKC	Micellar elektrokinetic chromatography
OSPARCOM	Oslo and Paris Commissions
PEC	Predicted environmental concentration
PNEC	Predicted no observed effect concentration
P_{ow}	Octanol-water partition coefficient
QSAR	Quantitative structure-activity relationship
SEBA	OSPAR Working Group on Sea-based Activities
SPMD	Semi-permeable membrane device

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Chapter

1

INTRODUCTION

Surfactant Bioaccumulation Review Project

Background

Surfactants are a chemical group for which it is difficult to obtain reliable partitioning (log P_{ow}) or bioconcentration factor (BCF) data for inclusion in current models used in performing environmental risk assessments. The difficulties revolve largely around the intrinsic property of surface-active substances to adsorb to surfaces and to accumulate at phase interfaces. Surrogate techniques for estimating bioaccumulation potential (e.g. OECD 107 Shake Flask and OECD 117 HPLC) are therefore unsuitable for determining a log P_{ow} for a surfactant. In a shake-flask test it is likely that the bulk concentrations of a surfactant would not be in equilibrium between the water and octanol phases, but in equilibrium with the octanol-water interface concentration. The experimental procedures used in this test will generally produce fine emulsions with large total surface area. In addition, partitioning of complex mixtures in this test requires substance-specific analysis of all the components in the mixture to obtain realistic results. The OECD 117 (HPLC) test is only applicable for non-ionic, non-surface active chemicals. Normally, retention times in the HPLC column are determined by a chemical's relative affinity for the mobile (usually methanol:water) phase and the immobile (lipophilic) phase. The affinity of surfactants for surfaces (mobile/immobile phase interfaces and substrate/immobile phase) will invalidate this method for this group of chemicals.

Despite the apparent limitations of this surrogate analytical approach to estimation of bioaccumulation potential for a surfactant, regulatory authorities have, with few exceptions, insisted on the submission of log P_{ow} data for surfactants for the purposes of environmental risk assessments (OSPAR HOCNF 1995). The alternative approaches – experimental determination of a BCF, or derivation of a log P_{ow} using quantitative structure-activity relationships (QSARs) – would appear to be equally unreliable for surfactants. Reported BCF determinations for surfactants are in many instances considered to be overestimates of true values, and QSARs for estimating a surfactant BCF are necessarily based on unreliable log P_{ow} data. Since this project was initiated in September 1999, it has been proposed (Summary Record SEBA 2000) that *n*-octanol/water partitioning data should no longer be required for substances with surface-active properties, rather that a measured organic carbon adsorption coefficient (K_{oc}) in a marine sediment should be mandatory. Whether this will provide a more reliable data set upon which to base environmental risk assessments of surfactants is uncertain at present, particularly since there are currently no standardised test methods available and no inter-laboratory comparisons (ring tests) on which to formulate test validity criteria. However, this change in approach to the problem of surfactants in the marine environment has effectively 'moved the goal-posts' of this review project somewhat, in relation to the original project aims. There is apparently a move away from an acceptance of the non-reliability of log P_{ow} determinations for surfactants obtained from currently used surrogate analytical techniques, towards a sediment-seawater partitioning approach, even though there is no established relationship between a derived P_{ow} and K_{oc} for surfactants.

A wide range of surfactants is used offshore, for a number of different purposes, although the quantities of each class of surfactant used are difficult to estimate. It is considered that the most important environmental issues in relation to surfactant use/discharge offshore are whether the surfactants pose a risk as a result of direct toxicity in the aqueous environment, or whether biodegradation, bioaccumulation and biomagnification of surfactants poses a greater risk to the marine environment. The purpose of this review is to collate and assess currently available data on bioaccumulation potential of surfactants (log P_{ow} and BCF) in order to address the following issues:

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- What are the relevant environmental issues with regard to use and discharge of surfactants in the North Sea? Are there significant issues regarding the behaviour and fate of surfactants in the marine environment as opposed to the freshwater environment?

- Is a log P_{ow} or BCF relevant to a surfactant? What is more important/relevant - environmental exposure (direct toxicity) or bioaccumulation/biomagnification? If the latter, is it sufficiently high for oilfield surfactants to be of concern?

- What can be achieved from existing data? Are available analytical data and QSARs reliable? Can new QSARs be developed and validated?

- Do current developments in analytical techniques offer a better alternative to existing methodologies? How practical or relevant are current analytical techniques to existing surfactant chemistries? Are surrogates to live animal testing a reliable alternative?

- What is the likelihood of current or new methodologies being suitable for development of standard (surrogate) tests?

List of Contributors

The Surfactant Bioaccumulation Review Project was presented for funding to EOSCA by the Associate Members of EOSCA. The project consisted of two phases: a data search and collection phase (phase 1), and a review and evaluation phase (phase 2). The following Associate Members participated in the project:

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The available information obtained and presented in this report is representative of the current state of knowledge of the impact, fate and behaviour of surfactants in the aquatic environment. It is clear that much of the work reported here has been conducted on surfactants in freshwater environments, and certain assumptions must be made when extrapolating to the marine environment. Despite this limitation, the data provide a rational basis upon which to base further investigations and evaluations of the environmental impact of surfactants discharged to the marine environment.

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Chapter

2

OILFIELD SURFACTANTS

Introduction

Many offshore chemicals used in the North Sea contain surface-active substances or are surfactants. These surfactants can be divided into several categories or classes (see Table 1 below). Surfactants are molecules having a 'hydrophobic' tail, usually an aliphatic chain and/or aromatic group, and a 'hydrophilic' head. They are generally classified by their ionic properties in water: anionic (negative charge, usually sulphate or phosphate in the 'hydrophilic' head), non-ionic (no charge, usually polyethoxylates and/or polypropoxylates in the head), cationic (positive charge, usually nitrogen in the head) and amphoteric (either positive or negative charge depending on the pH of the water) (SDA 1999).

The HOCNF (Harmonised Offshore Chemical Notification Format; OSPAR 1995) requires operators to state whether a chemical preparation (or substance) to be used/discharged offshore has surface-active properties. A partition coefficient (n-octanol/water; log P_{ow}), which is generally accepted as not being a relevant parameter for surfactants, is a mandatory requirement of the HOCNF. However, the Summary Record SEBA 2000 proposes that *n*-octanol/water partitioning data should be required for all organic substances *with the exception of those with surface-active properties*. It is further proposed that for surface-active substances, a measured sediment partition coefficient (K_{oc}) should be mandatory, although no existing methodology for determining this parameter in marine sediments has been identified and accepted as an OSPAR standard, or subject to inter-laboratory testing.

However, there is a need for general agreement on the definition of a surfactant before regulatory requirements for a test regime for this type of chemical can be applied in a rational manner. The surface activity can be measured in terms of surface tension of a solution of a substance in water. There are various definitions currently in use. Francke et al. (1994) recommended that if a substance has a surface tension   50 mN m^{-1} at a concentration of   1 g l^{-1}, it be considered to be surface active. An EU definition of a surface active agent refers to a substance that gives a clear aqueous solution at a concentration of 1% at 40°C, and which reduces the surface tension to 60 mN m^{-1} or less. In the context of the revision of Detergents Directive, industry is arguing for a definition that allows a maximum concentration of 5 g l^{-1} at 20°C, and reduces the surface tension below 45 mN m^{-1} (Hugh Thomas, personal communication). Surface tension could therefore be used to assess whether determination of a log P_{ow} for a substance is relevant in the context of an environmental risk assessment. This approach may not be applicable in all cases, particularly for surfactants that are not readily soluble in water. In addition, solubility in seawater may also be lower than in freshwater for many surfactants, so separate definitions may be needed for freshwater and marine environments.

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Existing Oilfield Surfactant Chemistry and Classification

Table 1. Summary classification of currently used/discharged oilfield surfactants and their general applications in the North Sea.

SURFACTANT CATEGORY	TYPE	USED IN PRODUCTS OF TYPE*	CURRENTLY IN USE IN NORTH SEA
Alkyl aryl sulfonates	Anionic	EB, CI	Yes
Alkyl sulfates	Anionic	AF	Yes
Alkyl ethoxylate sulfates	Anionic	AF	Yes
Phosphate esters	Anionic	CI	Yes
Quaternary ammonium compounds	Cationic	CI, BC	Yes
Fatty amine salts	Cationic	CI	Yes
Fatty acid amides	Cationic	EB	Yes
Imidazolines	Cationic	CI	Yes
Alkyl phenol ethoxylates	Non-ionic	CI, BC, EB	No
Alkyl poly glycosides	Non-ionic	CI	Yes
Ethoxylate-Propoxylate polymers	Non-ionic	EB	Yes
Fatty alcohol ethoxylates	Non-ionic	BC, CI, EB	Yes
Betaines	Amphoteric	CI	Yes

*Key: AF, antifoam; BC, biocide; CI, corrosion inhibitor; EB, emulsion breaker

Current Use, Discharge and Future Trends

Use

Information on current levels of use of the various surfactants commonly found in offshore production and drilling chemicals is difficult to obtain. In 1993 the North Sea Quality Status Report (OSPARCOM North Sea Task Force) estimated the total quantity of surfactants/detergents discharged to the North Sea in 1991 at 376 tonnes, but this figure did not include surfactant components of production and drilling chemicals, so that actual consumption/discharge would be much higher.

Discharge

For standard production chemicals, the discharge fractions can be estimated from the P_{ow} and the production volumes. The CIN report (Thatcher et al. 1999) contains default values for fraction released with produced water of certain surfactant categories, as log P_{ow} data are not applicable (see Table 2). However, fraction released values are generally considered to give extreme overestimations

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of the actual amounts released to water; i.e. the CHARM default values are considered to be too conservative. This is illustrated by the few results available from field validation studies given in Table 2 (Statoil: Sæten et al. 1999; TNO: Fokema et al. 1998). The default values in Table 2 are, however, the best currently available.

Table 2. Default values (from Thatcher et al. 1999) and results from field validation studies for the fraction released of surface-active production chemicals.

Type of surfactant	Default fraction released	Fraction released in field validation studies
Primary amines (cationic type C>12)	0.1 (10%)	0.038 (3.8 %)[1]
Quaternary amines	1.0 (100%)	
Ethoxylate-Propoxylate (Eo-Po) Block polymer demulsifier	0.4 (40%)	
Imidazolines	0.1 (10%)	0.01 (1.0 %)[2]
Amines	0.1 (10%)	
Phosphate esters (anionic type C>13)	0.1 (10%)	0.002 (0.2 %)[1]
Other	1.0 (100%)	

[1] TNO: Fokema et al. (1998)
[2] Statoil: Sæten et al. (1999)

It should be noted that the values in Table 2 are constants, and therefore independent of offshore production rates which change throughout the lifetime of a field, while the fraction released for standard production chemicals in CHARM is a function of P_{ow} and the water-cut. This should perhaps also be taken into consideration for surfactants. Table 2 illustrates the need for more comprehensive information for surfactants.

Future Trends

The produced water discharges from the Norwegian sector in the North Sea are expected to peak in 2001 (OLF 1998). As the volume of produced water increases, more chemicals will be needed, and hence more surfactants will probably be used. Due to reduced exploration activities and smaller fields (satellites etc.), more chemicals are expected to be used in pipelines to prevent corrosion etc. Residuals from these chemicals will enter refineries and the residual water will be treated onshore. A similar trend is expected for the UK sector.

Development of New Chemistries

Of the surfactant categories listed in Table 1, EOSCA is committed to phasing out the use of alkyl phenol ethoxylates in the North Sea. Alkyl phenol ethoxylates can be replaced by fatty alcohol ethoxylates. Nonyl and octyl phenol ethoxylates have been defined as priority pollutants by the Norwegian authorities (SFT), meaning that these discharges should be significantly reduced by the end of 2000, and usage stopped by 2005 (The Norwegian Parliament White Paper no. 58, 1996-1997).

Information on new surfactant chemistry under development was not available for the purposes of this review, as this is largely industrially sensitive and confidential information. Generally, the main emphasis in developing new chemistry is towards more environmental friendly surfactants (and

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chemicals in general). The most important properties determining the acceptability of new chemistries are:

- log P_{ow}<3 or BCF<100
- Ready biodegradability (>60% in standard tests)
- Acute toxicity >10 mg/l.

Aspects Important to Environmental Risk Assessment

The following partition coefficients are used as input in environmental risk assessments: log P_{ow}, P_{sw}/K_{oc}, and BCF.

Oil/water Partitioning (P_{ow}/OWDF)

The n-octanol/water partition coefficient (log P_{ow}) is a central parameter in environmental risk assessment; e.g. the CHARM model, for determining partitioning factors and calculating the concentrations of chemicals in produced water, sediment and biota (see Fig. 1; Vik et al. 1998). OECD Guideline 117 (HPLC method; 1989) and OECD Guideline 107 (Shake Flask method; 1981) for determining the log P_{ow} are, however, not applicable for surface-active chemicals. This is because surfactants cannot, based on their intrinsic properties, have a true log P_{ow}. An alternative approach is therefore needed to estimate the partitioning of surfactants. The approach illustrated in Fig. 2 was adopted for use in CHARM when estimating a PEC/PNEC ratio for surfactants.

Figures 1 and 2 illustrate that partitioning is a critical input parameter in environmental risk assessment.

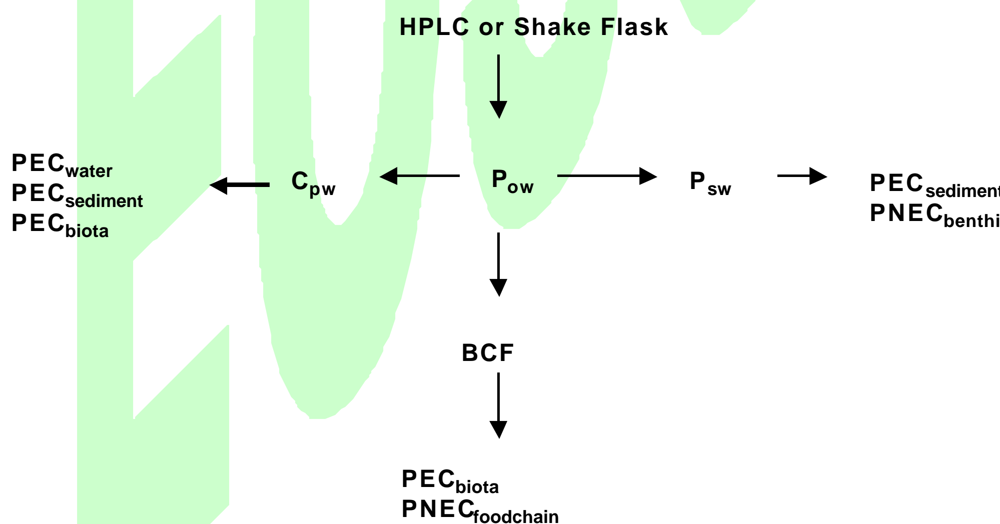

Fig. 1. The central role of log P_{ow} as an input parameter in environmental risk assessment (CHARM).

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Key to Fig. 1: ***P_{ow}*** **=** ***octanol/water partition coefficient***
C_{pw} **=** ***concentration in produced water***
P_{sw} **=** ***sediment/water partition coefficient***
BCF **=** ***bioconcentration factor***
PEC **=** ***predicted environmental concentration***
PNEC **=** ***predicted no observed effect concentration***

Figure 1 shows that the concentration of standard production chemicals in produced water is determined from the P_{ow}, while for surfactants it is preferably based on an experimental OWDF (oil/water distribution factor) test; alternatively, the default fraction released values given in Table 2 are used. The quantity of surfactants entering the oil fraction can also be determined:

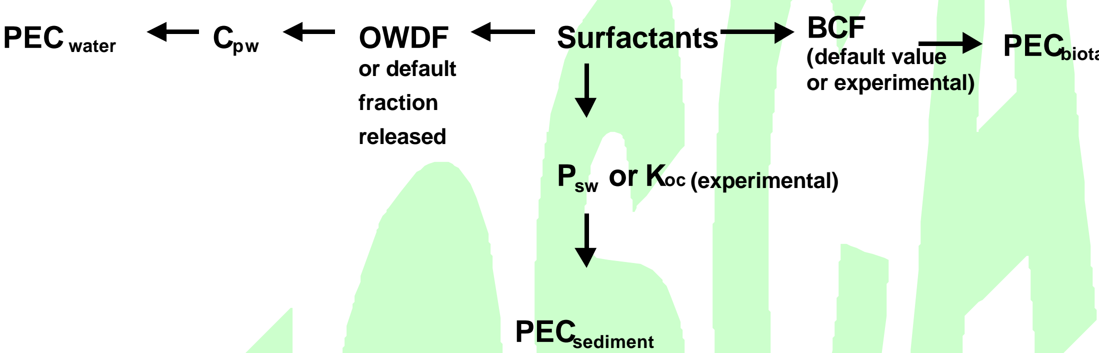

Fig. 2. Determination of surfactant partitioning in CHARM (OWDF = oil/water distribution factor).

Regulatory authorities have, until recently, insisted on determination of log P_{ow} for all deliberately added organic substances in a formulation regardless of whether the test is applicable or not. There are, however, published studies on surfactants claiming that there is a good correlation between retention on a C_{18} – HPLC column and the hydrophobic properties of the compounds (Tolls and Sijm 1995). Whether one chooses to use the term log P_{ow} (a contradiction in terms for surfactants) or simply retention time compared to other known compounds is really irrelevant, as the same principles apply for both. Based on experience, the OECD 117 method seems suitable for estimating a substance's (alleged) log P_{ow} most of the time; however, for substances such as surfactants no valid results can be obtained using this method, although the data are still reported in HOCNF submissions and used for subsequent CHARM evaluations (Bakke et al. 1997).

The relationship between the measured log P_{ow} of a substance and its partitioning to produced water, sediments or biota has, however, not been verified for surfactants. This is likely to differ from that for standard production chemicals not showing surface-active properties.

Sediment/water Partitioning (P_{sw}/K_{oc})

Figure 1 shows that the sediment/water partition coefficient (P_{sw}) for a standard production chemical can be estimated from its P_{ow}. During development of the CHARM model, several corrosion inhibitors were tested with respect to P_{sw} and P_{ow}. A non-correlation between these two parameters was observed (Vik et. al. 1996). Figure 2 shows that experimentally determined sediment/water partition coefficients (P_{sw} or K_{oc} data; e.g. based on OECD 106

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"Adsorption/Desorption", 1997) are needed for surfactants in CHARM. Such data are, however, presently not required by OSPAR (1995), i.e. they are currently conditional data in the HOCNF. There is a consensus of opinion that these should be mandatory data for surfactants. The parameter P_{sw} cannot, however, be regarded as being better suited for evaluations of environmental parameters for hydrophobic substances than data generated by the OECD 117 or OECD 107 analytical methods. Whether the adsorbance of a surface-active substance to sediment is a function of sediment organic carbon content, or is also influenced by other factors such as cation exchange, is largely unknown. For non-polar organics it has been established that partitioning is primarily dependent on the organic carbon content of the sediment (OECD 1992), whereas for polar organics both organic carbon and cation exchange capacity are equally important parameters (Orth et al. 1994). Determination of a sediment/water partition coefficient requires a suitable analytical method for the two phases, water and sediment, which is often problematic for many surfactants.

Some experimentally determined K_{oc} data for one of the surfactant categories in Table 1 gave a range of 300-5000 (source confidential). Whether such a wide range of values can be ascribed to the intrinsic behavioural properties of surfactants in sediment-seawater systems, or to current uncertainties in the available test methods is unknown. There is clearly a need for a standardised adsorption test for surfactants in order to eliminate the causes of such seemingly high variability in test results. However, in tests designed to determine BCFs for surfactants, it has been reported that between-test variability using the same test species was unexpectedly high despite apparently similar test conditions (Tolls et al. 1994). In sediment adsorption tests the binding of surfactants to sediments may be a function of parameters other than organic carbon, such as cationic exchange capacity (CEC). K_{oc} data for detergent surfactants can be found in EU (1995), some of which are also used offshore. Mechanisms of sorption of surfactants to sediment are discussed more fully in Chapter 4 of this review.

Table 3. Representative data from the Detergent Ingredients Database showing log P_{ow} and log K_{oc} data for a selection of surfactants

Anionic Surfactants	**log P_{ow}**	**log K_{oc}**
$C_{10/12}$ LAS Na O 11	3.2	2.82
$C_{10/13}$ LAS Na O 11,5	3.47	3.09
$C_{11,8}$ LAS Na	3.63	3.24
C_{13} LAS Na	4.28	3.89
C_{16} LAS Na	5.9	>5
C_{13} alk. sulphonate, linear	1.5	1.14
C_{15} alk. sulphonate, linear	2.58	2.21
C_{18} alk. sulphonate, linear	4.2	3.81
$C_{12/14}$ fatty alc. sulphate	2.14	1.77
$C_{14/16}$ alpha olefine sulphonate	1.81	1.44
$C_{15/18}$ alpha olefine sulphonate	2.62	2.25
Na-laurate	1.1	0.74
Cationic Surfactants		
$C_{12/14}$ TMAC	1.56	1.20
C_{16} TMAC	3.18	2.80
C_{18} TMAC	4.26	3.87
Imidazolinium methosulphate deriv.	2.15	1.70

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Table 3. Contd.

Non-ionic Surfactants	**log P_{ow}**	**log K_{oc}**
$C_{9/11}$ A 2,5EO	4.38	3.99
$C_{9/11}$ A 5EO	4.61	4.21
$C_{9/11}$ A,6EO	4.70	4.30
$C_{9/11}$ A 7EO	4.79	4.39
$C_{9/11}$ A 8EO	4.88	4.48
$C_{9/11}$ A 10EO	5.06	4.66
Lauryl alcohol 7, 6EO	5.92	5.51
Isotridecanol 6, 5EO	5.49	5.08
Amphoteric Surfactants		
15EO $C_{12/14}$ amine	6.83	6.41
15EO $C_{16/18}$ amine	7.49	7.06
15EO $C_{16/18}$ hydrotallow amine	7.49	7.06
15EO C_{18} oleyl amine	9.11	8.66

Partitioning Between Biota and Water (BCF)

Figure 1 shows that a BCF for standard production chemicals can be estimated from P_{ow}. However, a comparison of experimental P_{ow} and BCF data for two surfactants during the development of the CHARM model indicated that the BCF-P_{ow} correlation was not valid for surfactants (Bakke et al. 1997; Vik et al. 1998). It is therefore likely that the only reliable way to predict the bioaccumulation potential of surfactants will be to experimentally determine the BCF. This is, however, a very expensive and time-consuming approach. In a previous version of the CHARM model this was avoided by using a default value of log BCF = 4 for surfactants (Karman et al. 1996). Tolls recommended using the CMC (critical micelle concentration) to determine the BCF rather than to use a default value as applied in CHARM (Vik et al. 1996). In the study performed by Tolls and Sijm (1995), the CMC was selected as a measure of surfactant hydrophobicity, since the log P_{ow} was inappropriate. The hydrophobicity increased with decreasing CMC. The biota compartment is, however, no longer included in the CHARM model, since the PEC/PNEC$_{biota}$ contribution in most cases was negligible compared to the PEC/PNEC values of the water column and the sediment (Thatcher et al. 1999). In the context of evaluating potential long-term risk, the BCF is, however, an important parameter.

Francke et al. (1994) have reported that surfactants may have a bioaccumulation potential even if their estimated log P_{ow} values are <3. Adsorption onto biological (epithelial membrane) surfaces (e.g. gills, skin) has also been proposed as an indicator of bioaccumulation potential, although the intrinsic properties of many surface-active substances may severely limit their ability to cross biological membranes (see Chapter 7). Without further work, high adsorptive capacity should not be regarded as a reliable indicator of bioaccumulation and biomagnification potential. Bioaccumulation and biomagnification potential of surfactants is critically reviewed and discussed in Chapter 7 of this report.

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Chapter

3

TOXICITY OF SURFACTANTS TO AQUATIC ORGANISMS

Introduction

The aim of this section of the review is to provide an overview of the current understanding of surfactant toxicity in the marine environment. Most ecotoxicity studies reported in the literature have been concerned with effects of surfactants on freshwater species and toxicity data for marine organisms is noticeably lacking. Of the studies that have been published, most have been carried out on anionic surfactants, particularly LAS. There is some information on the toxicity of non-ionic surfactants, but data on cationic surfactants is severely limited and no information was obtained on amphoteric surfactants. However, many studies have examined the effects of oil dispersants and detergents, of which surfactants are the major component, and data from these experiments have also been included in this report.

Surfactant Toxicity in the Marine Environment

The oil-dispersing ability of surfactants is derived from their ability to lower interfacial tension, which facilitates phase mixing, micelle formation and surface slick dispersion. These surface-active properties are non-specific and act equally well on the lipid-bilayer membranes of living cells (Singer et al. 1994). Surfactants generally impact on aquatic animals through respiratory surfaces, since destabilisation of these membranes results in altered membrane permeability, membrane lysis and interrupted cellular respiration. Death usually arises through asphyxiation.

Taxonomic groups

Algae

Pybus (1973) observed that exposure of *Laminara saccharina* to a detergent containing several anionic surfactants significantly reduced zoospore motility. This was attributed either to direct attack on the proteinaceous flagella and/or disruption of the zoospore membrane. The inhibited growth of *Macrocystis* spores observed by Singer et al. (1994) was thought to be caused by an initial imbalance of membrane permeability (affecting nutrient transport, osmotic control and electrochemical gradients), followed by physical disruption of the cell wall and membrane.

Crustaceans

In mysids, the immediate effect of surfactant exposure is asphyxiation due to disruption of the respiratory membranes (Singer et al. 1993). The exact mode of action has not been examined in as much detail as that in fish, but is likely to be similar, although crustaceans may be less vulnerable to surfactants because of the (relatively) impermeable cuticle on their gill epithelium. Nonetheless, the Crustacea generally are sensitive to sub-lethal concentrations of surfactants, with Swedmark et al. (1971) reporting severely affected swimming activity of both larvae and adults of *Balanus balanoides* and *Hyas araneus* after exposure to surfactant concentrations around 1-10 mg/l.

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Molluscs

Changes in larval growth and development of oysters and clams have been observed at surfactant concentrations between 0.05 and 2.5 mg l^{-1} and 0.009 and 5.8 mg l^{-1}, respectively (Lewis 1991, and references therein), while effects on fertilisation and spawning in mussels were observed at surfactant concentrations exceeding 0.05 mg l^{-1}. Swedmark et al. (1971) found that exposure to LAS affected byssal thread formation and valve-closing ability in *Mytilus edulis* and siphon retraction in *Cardium edule* and *Mya arenaria*.

Singer et al. (1990) reported loss of cilia, disruption of microvilli, increased mucus production, increased lysosomal activity and vacuolation of mitochondria in limpet gill tissue exposed to oil-dispersant surfactants. Experiments on the mode of action of surfactants on molluscs have generally been carried out on early life-stages, e.g. Singer et al. (1993), where it was observed that mortality was due to rupture of the embryonic membrane. In this study, the few larvae that developed had abnormal shells, thought to be a result of chelation of calcium by the surfactant within the test medium, causing nutrient depletion and abnormality.

Fish

Reported effects of surfactants on fish include reduction of epithelium, loss of mucosal cells from gill membranes, haematomas, swelling, leukocyte abundance in pharyngeal walls, and swelling and thickening of gill epithelium. These are general reactions to toxicants and not necessarily specific to surfactants. Several levels of gill damage have been reported in the literature but the immediate cause of rapid death is usually asphyxiation due to impaired oxygen diffusion.

Reviewing the literature on chronic and sub-lethal surfactant toxicity, Lewis (1991) noted that the physiological responses of exposed fish generally occurred at anionic surfactant concentrations greater than 0.1 mg l^{-1}. Nonionic surfactants exert similar effects at concentrations greater that 0.5 mg l^{-1}. Such responses included changes in adrenergic control mechanisms, olfactory response and gill vasodilation. Other reported non-lethal effects include changes in serum glucose and sodium levels, enzymatic inhibition in liver and kidneys and haematological changes (Singer et al. 1994 and references therein). Avoidance reactions have been observed in fish exposed to anionic surfactant concentrations between 0.002 and 0.40 mg l^{-1} (Lewis 1990, and references therein). These reactions manifested as increased swimming activity and changes in feeding. At lower concentrations, ability to recover after exposure may be retained (Swedmark et al. 1971). At higher exposure concentrations, swimming activity becomes impaired and post-exposure recovery is precluded. Other sub-lethal effects include loss of equilibrium, spasms and paralysis (Swedmark et al. 1971).

Although surfactants are thought to impact on aquatic animals through this common mechanism, the susceptibility of an organism is affected by both internal and external factors and may vary 100-fold across different phyla (Singer et al. 1990). The action of membrane disruption means that less organised (developed) organisms may be more susceptible than more ontogenetically developed ones. A taxonomic cross-comparison of the surfactant toxicity data in this review (Tables 4-10) highlights the difficulties in identifying trends in surfactant toxicity. For acute toxicity studies with anionic surfactants (see Table 4), the algae and fish species tested appear to be most sensitive, with the molluscs showing an intermediate sensitivity and crustaceans being the least sensitive. However, larval stages of crustacean species appear to show significantly higher sensitivity to this class of surfactant than adults. The exception is the stage I zoea larva of the spider crab *Hyas* araneus, with a 96 h LC_{50} of >1000 mg l^{-1} compared to >100 mg l^{-1} for the adult when exposed to lauryl ether sulphate (LES 3EO), and 9 mg l^{-1} compared to >100 mg l^{-1}, respectively, when exposed to linear alkyl benzenesolphonate (LAS). Corresponding 96 h LC_{50} values for barnacle *Balanus balanoides*

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adults and larvae exposed to LAS are 50 mg l^{-1} and 3 mg l^{-1}, respectively (Table 4; Swedmark et al. 1971).

For non-ionic surfactants the data available (Table 6) generally supports this trend in sensitivity (fish most sensitive, molluscs intermediate and crustaceans (adults) showing low sensitivity), although there are no data for algal species exposed to non-ionic surfactants. The larval stages of crustacean species again show higher sensitivities than the adults, although larval *Hyas areneus* is once more the exception (96 h LC_{50} >100 mg l^{-1} for the adult compared to 800 mg l^{-1} for the stage I zoea larva exposed to tallow alcohol ethoxylate (TAE 10 EO; Swedmark et al. 1971). There is insufficient data for cationic surfactants to be able to identify cross-taxonomic trends in sensitivity (Table 5). The data available for acute toxicity studies using mixtures of surfactants (Table 7), as might perhaps be expected, show no identifiable trends in sensitivity, although LC_{50}s generally appear to span a greater range of concentrations within each taxonomic group. This may possibly indicate that mixtures of different classes of surfactants could act synergistically to exacerbate toxic effects, or that certain surfactant types may reduce the toxic effects of another type. However, there is insufficient data to draw any firm conclusions.

These trends in acute surfactant toxicity have previously been noted (for instance, Swedmark et al. 1971; Singer et al. 1993) and are likely to be a result of morphological and physiological factors. For example, Singer et al. (1995) noted that while most *Atherinops* (topsmelt) mortalities occurred within the first 24 hours of exposure, *Holmesimysis* (mysid) juveniles were more able to survive the initial exposure. This was explained by the fact that *Atherinops* have no physical barrier to absorption of toxicants across their gills, whereas *Holmesimysis* juveniles have a protective exoskeleton and accompanying structures to protect gill lamellae. *Holmesimysis* juveniles may also lessen the impact of toxicant exposure through cuticular respiration. Similarly, Lewis (1990) attributed variations in effect concentrations for algae to differences in physiology. Surfactants denature and bind protein in the cell wall and alter the permeability of the cell membrane to nutrients. Cell wall thickness and chemical composition differs between algal species and a thicker cell wall will reduce the surfactant's impact, while a higher cell wall lipid and protein content will allow greater surfactant penetration. It should be noted, however, that variations in life-stage, test methods and end-point considerations would also result in interspecies variation in surfactant tolerance - these factors will be discussed later. Swedmark et al. (1971) also noted that the most active species in their experiments were the most susceptible to surfactant toxicity, probably as a result of increased exposure.

The available data also illustrates the effect of life-stage on susceptibility to surfactants. Singer et al. (1990) estimated that this may vary 1000-fold with different developmental stages. On the whole, information on the susceptibility of organisms at various points in their life cycle is limited and somewhat conflicting. Swedmark et al. (1971) found that eggs and larvae of fish, crustaceans and molluscs were considerably more sensitive to surfactant toxicity than adult stages. However, Scott Hall et al. (1989) found no significant difference in the sensitivity of the crustacean *Mysidopsis bahia* at ages 3-8 days and 28 days. Swedmark et al. (1971) pointed out that any assessment of surfactant toxicity to crustaceans must take into account the phases of the moulting cycle. In their experiments, crustaceans in the intermoult stage were generally very resistant to surfactants and lethal concentrations could only be determined in a few instances. However, resistance was considerably reduced during the 15-hour period after moulting (ecdysis). This was attributed to the absence of a thick protective cuticle and increased respiration that accompanies moulting.

Although only a limited range of surfactants have been investigated for aquatic toxicity, a few studies have illustrated a difference in toxicity between different surfactant classes. Lewis (1990) noted that the toxicity of different surfactants on the same algal test species may vary over four orders of magnitude. Charged surfactants (anionic and cationic) have been reported to have a greater denaturing effect than neutral chemicals, and cationic surfactants are generally considered to be most toxic to both freshwater and marine algae, invertebrates and fish (Ukeles 1965; Lewis 1991).

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Toxicity data on marine phytoplankton and animal test species suggest a moderate sensitivity to several major anionic and nonionic surfactants (Ukeles 1965; Lewis 1991). These are only generalisations, however, since Kutt and Martin (1974) found that the red tide algae *Gymnodium breve* was most affected by anionic LAS, followed by non-ionic and then cationic surfactants.

Chronic toxicity data for surfactants collected and presented in Tables 8, 9 and 10 are more difficult to interpret, since in the majority of cases there is no information given for the test conditions employed. As a broad generalisation, algae appear to be the least sensitive, in as much as growth inhibition is documented at higher concentration ranges of anionic, cationic and non-ionic surfactants than those inducing effects on either molluscs or fish. Non-ionic surfactants appear to be significantly less toxic to algae than either anionic or cationic surfactants (EC_{50}s in the range 10 – 1000 mg l^{-1} for non-ionics, compared to 2 – 54 mg l^{-1} and 0.1 – 10 mg l^{-1} for anionics and cationics, respectively), although molluscs appear to be equally sensitive to both. Data for fish is only available for anionic surfactants so no comparison can be made. Chronic effects of surfactant exposure in molluscs and fish are largely limited to inhibition of larval growth and development in the studies documented (Tables 8 – 10). Without a more complete understanding of the toxic mechanisms involved during long-term (chronic) exposure of aquatic organisms to surfactants, only very broad generalisations are possible. The following sections of this chapter, and Chapter 5 of this review discuss some of the possible mechanisms of toxicity relevant to long-term exposures.

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Table 4. Acute Toxicity Data for Anionic Surfactants

Surfactant Type	Species	Test Conditions	Exposure Effects	Reference
LAS (Na dodecylbenzene sulphonate)	*Phaeodactylum tricornutum* (marine diatom, exponential growth phase) Marine.	48 h exposure to 0.5-20 mg/l	48 h LC50: 1.94 mg/l	Aider et al. (1997
LAS (Na dodecylbenzene sulphonate)	*Phaeodactylum tricornutum* (marine diatom, exponential growth phase) Marine.	96 h exposure to 0.5-20 mg/l	96 h LC50: 1.9 mg/l	Aider et al. (1997)
Na dodecylbenzene sulphonate, Na lauryl-ether sulphate and lauric diethanolamide mixture	*Laminaria saccharina* (benthic coastal algae, zoospores) Marine.	30 min exposure to 5.10^{-5} - 5.10^{4} mg/l	Exposure to 50 mg/l prevented swimming after 7 minutes	Pybus (1973)
C-13 linear alkyl benzene sulfonate	*Gymnodium breve* (green algae) Marine.	No information	Mortality at 0.025 mg/l	Lewis (1990) and references therein
LAS (linear dodecylbenzene sulphonate)	*Leander adspersus* (shrimp) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: 50mg/l	Swedmark et al. (1971)
LAS (linear dodecylbenzene sulphonate)	*Leander squilla* (shrimp) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >100 mg/l	Swedmark et al. (1971)
LAS (linear dodecylbenzene sulphonate)	*Eupagrurus bernhardus* (hermit crab) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >100 mg/l	Swedmark et al. (1971)
LAS (linear dodecylbenzene sulphonate)	*Hyas araneus* (spider crab, adult) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >100 mg/l	Swedmark et al. (1971)
LAS (linear dodecylbenzene sulphonate)	*Hyas araneus* (spider crab, stage 1 zoea larvae) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: 9 mg/l	Swedmark et al. (1971)
LAS (linear dodecylbenzene sulphonate)	*Carcinus maenas* (shore crab) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >100 mg/l	Swedmark et al. (1971)

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Table 4. Contd.

Surfactant Type	Species	Test Conditions	Exposure Effects	Reference
LAS (linear dodecylbenzene sulphonate)	*Balanus balanoides* (barnacle, adult) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: 50 mg/l	Swedmark et al. (1971)
LAS (linear dodecylbenzene sulphonate)	*Balanus balanoides* (barnacle, stage II nauplius larvae) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: 3 mg/l	Swedmark et al. (1971)
ABS (tetrapropylene benzene sulphonate)	*Leander adspersus* (shrimp) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >100 mg/l	Swedmark et al. (1971)
ABS (tetrapropylene benzene sulphonate)	*Leander squilla* (shrimp) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >100 mg/l	Swedmark et al. (1971)
ABS (tetrapropylene benzene sulphonate)	*Eupagrurus bernhardus* (hermit crab) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >100 mg/l	Swedmark et al. (1971)
ABS (tetrapropylene benzene sulphonate)	*Hyas araneus* (spider crab, adult) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >100 mg/l	Swedmark et al. (1971)
ABS (tetrapropylene benzene sulphonate)	*Carcinus maenas* (shore crab) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >100 mg/l	Swedmark et al. (1971)
LES 3EO (lauryl ether sulphate with 3 mol ethylene oxide)	*Leander adspersus* (shrimp) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >100 mg/l	Swedmark et al. (1971)
LES 3EO (lauryl ether sulphate with 3 mol ethylene oxide)	*Leander squilla* (shrimp) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >100 mg/l	Swedmark et al. (1971)
LES 3EO (lauryl ether sulphate with 3 mol ethylene oxide)	*Eupagrurus bernhardus* (hermit crab) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >100 mg/l	Swedmark et al. (1971)
LES 3EO (lauryl ether sulphate with 3 mol ethylene oxide)	*Hyas araneus* (spider crab, adult) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >100 mg/l	Swedmark et al. (1971)

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Table 4. Contd.

Surfactant Type	Species	Test Conditions	Exposure Effects	Reference
LES 3EO (lauryl ether sulphate with 3 mol ethylene oxide)	*Hyas araneus* (spider crab, stage 1 zoea larvae) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >1000 mg/l	Swedmark et al. (1971)
LES 3EO (lauryl ether sulphate with 3 mol ethylene oxide)	*Carcinus maenas* (shore crab) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >100 mg/l	Swedmark et al. (1971)
LES 3EO (lauryl ether sulphate with 3 mol ethylene oxide)	*Balanus balanoides* (barnacle, stage II nauplius larvae) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: 5 mg/l	Swedmark et al. (1971)
LAS (linear dodecylbenzene sulphonate)	*Mytilus edulis* (mussel) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >100 mg/l	Swedmark et al. (1971)
LAS (linear dodecylbenzene sulphonate)	*Cardium edule* (cockle) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: 20 mg/l	Swedmark et al. (1971)
ABS (tetrapropylene benzene sulphonate)	*Mya arenaria* (clam) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: 50 mg/l	Swedmark et al. (1971)
ABS (tetrapropylene benzene sulphonate)	*Mytilus edulis* (mussel) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >100 mg/l	Swedmark et al. (1971)
ABS (tetrapropylene benzene sulphonate)	*Cardium edule* (cockle) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: 50 mg/l	Swedmark et al. (1971)
LES 3EO (lauryl ether sulphate with 3 mol ethylene oxide)	*Mya arenaria* (clam) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: 70 mg/l	Swedmark et al. (1971)
LES 3EO (lauryl ether sulphate with 3 mol ethylene oxide)	*Mytilus edulis* (mussel) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >100 mg/l	Swedmark et al. (1971)
LES 3EO (lauryl ether sulphate with 3 mol ethylene oxide)	*Cardium edule* (cockle) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: 15 mg/l	Swedmark et al. (1971)

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Table 4. Contd.

Surfactant Type	Species	Test Conditions	Exposure Effects	Reference
LES 3EO (lauryl ether sulphate with 3 mol ethylene oxide)	*Pecten maximus* (Scallop) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: <5 mg/l	Swedmark et al. (1971)
LAS (linear dodecylbenzene sulphonate)	*Gadus morrhua* (cod, 30cm) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: 1.0 mg/l	Swedmark et al. (1971)
LAS (linear dodecylbenzene sulphonate)	*Pleuronectes flesus* (flounder) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: 1.5 mg/l	Swedmark et al. (1971)
LAS (linear dodecylbenzene sulphonate)	*Pleuronectes platessa* (plaice) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >1.0<5.0 mg/l	Swedmark et al. (1971)
ABS (tetrapropylene benzene sulphonate)	*Gadus morrhua* (cod, 30cm) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: 3.5 mg/l	Swedmark et al. (1971)
ABS (tetrapropylene benzene sulphonate)	*Pleuronectes flesus* (flounder) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: 6.5 mg/l	Swedmark et al. (1971)
LES 3EO (lauryl ether sulphate with 3 mol ethylene oxide)	*Gadus morrhua* (cod, 30cm) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: <5 mg/l	Swedmark et al. (1971)
LES 3EO (lauryl ether sulphate with 3 mol ethylene oxide)	*Pleuronectes flesus* (flounder) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: <5 mg/l	Swedmark et al. (1971)

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Table 5. Acute Toxicity Data for Cationic Surfactants

Surfactant Type	Species	Test Conditions	Exposure Effects	Reference
Quaternary ammonium chloride (DTDMAC)	*Mysidopsis bahia* (mysid shrimp, 25-40 mm) Marine.	96 h exposure, unknown concentration	LC50: 36.0 mg/l	Lewis and Wee (1983)
Quaternary ammonium chloride (DTDMAC)	*Penaeus duorarum* (pink shrimp, 25-40 mm) Marine.	96 h exposure, unknown concentration	LC50: 0.22 mg/l	Lewis and Wee (1983)
Quaternary ammonium chloride (DTDMAC)	*Callinectes sapidus* (blue crab, 20-30 mm) Marine.	96 h exposure, unknown concentration	LC50: >50 mg/l	Lewis and Wee (1983)
Quaternary ammonium chloride (DTDMAC)	*Crassostrea virginica* (eastern oyster, larvae) Marine.	48 h exposure, unknown concentration	EC50: 2 mg/l	Lewis and Wee (1983)
Quaternary ammonium chloride (DTDMAC)	*Cyprinidon variegatus* (sheepshead minnow, 15-20 mm) Marine.	96 h exposure, unknown concentration	LC50: 24 mg/l	Lewis and Wee (1983)

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Table 6. Acute Toxicity Data for Non-ionic Surfactants

Surfactant Type	Species	Test Conditions	Exposure Effects	Reference
Alcohol ethoxylate (DAEO4)	*Mysidopsis bahia* (mysid shrimp, 3-8 D) Marine.	48 h exposure, unknown concentration	48 h LC50: 5.57 mg/l	Scott Hall et al. (1989)
Alcohol ethoxylate (TDAEO9.75)	*Mysidopsis bahia* (mysid shrimp, 3-8 D) Marine.	48 h exposure, unknown concentration	48 h LC50: 2.24 mg/l	Scott Hall et al. (1989)
Alcohol ethoxylate (TDAE10-Cl capped)	*Mysidopsis bahia* (mysid shrimp, 3-8 D) Marine.	48 h exposure, unknown concentration	48 h LC50: 0.71 mg/l	Scott Hall et al. (1989)
Caster oil ethoxylate	*Mysidopsis bahia* (mysid shrimp, 3-8 D) Marine.	48 h exposure, unknown concentration	48 h LC50: >50 mg/l	Scott Hall et al. (1989)
Methyl Oleoyl Taurate, sodium salt	*Mysidopsis bahia* (mysid shrimp, 3-8 D) Marine.	48 h exposure, unknown concentration	48 h LC50: 19.1 mg/l	Scott Hall et al. (1989)
Polyoxyethylene ether (polyoxyethylene (4) lauryl ether)	*Gammarus oceanicus* (skud, adult) Marine.	7 day exposure to 1-1000 mg/l	LT50 = 4h at 100 mg/l	Wildish (1972)
Polyoxyethylene ester (polyoxyethylene (14) monolaurate)	*Gammarus oceanicus* (skud, adult) Marine.	7 day exposure to 22.5-100000 mg/l	LT50 = 100h at 10000 mg/l	Wildish (1972)
Polyoxyethylene ester (polyoxyethylene (14) dilaurate)	*Gammarus oceanicus* (skud, adult) Marine.	7 day exposure to 25-100000 mg/l	LT50 = 200h at 10000 mg/l	Wildish (1972)
TAE 10 EO (tallow alcohol ethoxylate with 10 mol ethylene oxide)	*Leander adspersus* (shrimp) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >100 mg/l	Swedmark et al. (1971)

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Table 6. Contd.

Surfactant Type	Species	Test Conditions	Exposure Effects	Reference
TAE 10 EO (tallow alcohol ethoxylate with 10 mol ethylene oxide)	*Leander squilla* (shrimp) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >100 mg/l	Swedmark et al. (1971)
TAE 10 EO (tallow alcohol ethoxylate with 10 mol ethylene oxide)	*Eupagrurus bernhardus* (hermit crab) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >100 mg/l	Swedmark et al. (1971)
TAE 10 EO (tallow alcohol ethoxylate with 10 mol ethylene oxide)	*Hyas araneus* (spider crab, adult) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >100 mg/l	Swedmark et al. (1971)
TAE 10 EO (tallow alcohol ethoxylate with 10 mol ethylene oxide)	*Hyas araneus* (spider crab, stage I zoea larvae) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: 800 mg/l	Swedmark et al. (1971)
TAE 10 EO (tallow alcohol ethoxylate with 10 mol ethylene oxide)	*Carcinus maenas* (shore crab) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >100 mg/l	Swedmark et al. (1971)
TAE 10 EO (tallow alcohol ethoxylate with 10 mol ethylene oxide)	*Balanus balanoides* (barnacle, stage II nauplius larvae) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: 1.2 mg/l	Swedmark et al. (1971)
TAE 10 EO (tallow alcohol ethoxylate with 10 mol ethylene oxide)	*Mya arenaria* (clam) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: 100 mg/l	Swedmark et al. (1971)

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Table 6. Contd.

Surfactant Type	Species	Test Conditions	Exposure Effects	Reference
TAE 10 EO (tallow alcohol ethoxylate with 10 mol ethylene oxide)	*Mytilus edulis* (mussel) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: 50 mg/l	Swedmark et al. (1971)
TAE 10 EO (tallow alcohol ethoxylate with 10 mol ethylene oxide)	*Cardium edule* (cockle) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: <5 mg/l	Swedmark et al. (1971)
TAE 10 EO (tallow alcohol ethoxylate with 10 mol ethylene oxide)	*Gadus morrhua* (cod, 30 cm) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >0.5 <1.0 mg/l	Swedmark et al. (1971)
TAE 10 EO (tallow alcohol ethoxylate with 10 mol ethylene oxide)	*Pleuronectes flesus* (flounder) Marine.	>96 h exposure to 0.5-100 mg/l	96 h LC50: >0.5 <1.0 mg/l	Swedmark et al. (1971)

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Table 7. Acute Toxicity Data for Surfactant Mixtures

Surfactant Type	Species	Test Conditions	Exposure Effects	Reference
Anionic + Non-ionic (Slik-A-Way)	*Macrocystis pyrifera* (kelp, zoospores) Marine.	48 h exposure to 20-50 mg/l	NOEC: 8.4-<19.1 mg/l; IC50: 73-95.9 mg/l	Singer et al. (1994
Anionic + Non-ionic (Nokomis)	*Macrocystis pyrifera* (kelp, zoospores) Marine.	48 h exposure to 20-50 mg/l	NOEC: 29.7-47.2 mg/l; IC50: 73.0-79.4 mg/l	Singer et al. (1994)
Anionic + Non-ionic - typically larger ethoxylates (Corexit 9554)	*Macrocystis pyrifera* (kelp, zoospores) Marine.	48 h exposure to 10-160 mg/l	NOEC: 9.6-11.7 mg/l; IC50: 94.9-106.5 mg/l	Singer et al. (1995)
35% anionic + 48% non-ionic - major components include ethoxylated sorbitan mono- and trioleates, sorbitan monooleate and Na dioctylsulfosuccinate (Corexit 9527)	*Macrocystis pyrifera* (kelp, zoospores) Marine.	48 h exposure to 0.5-32 mg/l	NOEC: 1.32-<2.35 mg/l; gametophyte germ tube length inversely related to exposure concentration from 1-30 mg/l - at 30 mg/l, lengths were the minimum required to be considered germinated.	Singer et al. (1990)
Anionic + Non-ionic (Slik-A-Way)	*Holmesimysis costata* (kelp forest mysid, juveniles) Marine.	96 h exposure to 5-80 mg/l	NOEC: 9-10.4 mg/l; LC50: 16.8-23.9 mg/l	Singer et al. (1993)
Anionic + Non-ionic (Nokomis)	*Holmesimysis costata* (kelp forest mysid, juveniles) Marine.	96 h exposure to 5-80 mg/l	NOEC: 6.7-10.8 mg/l; LC50: 21-24 mg/l	Singer et al. (1993)
Anionic + Non-ionic - typically larger ethoxylates (Corexit 9554)	*Holmesimysis costata* (kelp forest mysid, juveniles - 3 D) Marine.	96 h exposure to 50-300 mg/l	NOEC: 80.6-125.5 mg/l; LC50: 162.1-184.3 mg/l	Singer et al. (1995)
35% anionic + 48% non-ionic - major components include ethoxylated sorbitan mono- and trioleates, sorbitan monooleate and Na dioctylsulfosuccinate (Corexit 9527)	*Holmesimysis costata* (kelp forest mysid, juveniles - 4 D) Marine.	96 h exposure to 2-32 mg/l	NOEC: 1.66-4.20 mg/l; LC50: 4.26-7.26 mg/l	Singer et al. (1990)

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Table 7. Contd.

Surfactant Type	Species	Test Conditions	Exposure Effects	Reference
Anionic + Non-ionic (Slik-A-Way)	*Haliotis rufescens* (red abalone embryos, 1 h post-fertilisation) Marine.	48 h exposure to 3-48 mg/l	NOEC: 15.7-24.7 mg/l; LC50: 31.3 mg/l	Singer et al. (1993)
Anionic + Non-ionic (Nokomis)	*Haliotis rufescens* (red abalone embryos, 1 h post-fertilisation) Marine.	48 h exposure to 3-48 mg/l	NOEC: 79.5-87.6 mg/l; LC50: 119.9 mg/l	Singer et al. (1993)
Anionic + Non-ionic - typically larger ethoxylates (Corexit 9554)	*Haliotis rufescens* (red abalone embryos, 1 h post-fertilisation) Marine.	48 h exposure to 3-48 mg/l	NOEC: 79.5-87.6 mg/l; LC50: 119.9 mg/l	Singer et al. (1995)
35% anionic + 48% non-ionic - major components include ethoxylated sorbitan mono- and trioleates, sorbitan monooleate and Na dioctylsulfosuccinate (Corexit 9527)	*Haliotis rufescens* (red abalone embryos) Marine.	48 h exposure to 1-10 mg/l	NOEC: 0.63-1.50 mg/l; EC50: 1.60-2.20 mg/l	Singer et al. 1990)
Anionic + Non-ionic (Slik-A-Way)	*Atherinops affinis* (topsmelt larvae) Marine.	96 h exposure to 20-50 mg/l	NOEC: 19.7-42.2 mg/l; LC50: 43.7-45.8 mg/l	Singer et al. (1994)
Anionic + Non-ionic (Nokomis)	*Atherinops affinis* (topsmelt larvae) Marine.	96 h exposure to 20-50 mg/l	NOEC: 46.3-52.3 mg/l; LC50: 48.2-72.9 mg/l	Singer et al. (1994)
Anionic + Non-ionic - typically larger ethoxylates (Corexit 9554)	*Atherinops affinis* (topsmelt larvae, 11D) Marine.	96 h exposure to 10-300 mg/l	NOEC: 48.5-148.1 mg/l; LC50: 111.1-159.2 mg/l	Singer et al. (1995)
35% anionic + 48% non-ionic - major components include ethoxylated sorbitan mono- and trioleates, sorbitan monooleate and Na dioctylsulfosuccinate (Corexit 9527)	*Atherinops affinis* (topsmelt larvae, 10 D) Marine.	96 h exposure to 8-132 mg/l	NOEC: 12.3-13.9 mg/l; LC50: 25.5-40.6 mg/l	Singer et al. (1990)

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Table 8. Chronic Toxicity Data for Anionic Surfactants

Surfactant Type	Species	Test Conditions	Exposure Effects	Reference
LAS (alkyl benzene sulfonate)	*Chlamydomonas* sp. (green flagellate algae)	No information	Growth at 12-14 days affected by 2-54 mg/l	Lewis (1990) and references therein
LAS (alkyl benzene sulfonate)	*Carteria* sp. (green algae)	No information	Growth at 12-14 days affected by 2-54 mg/l	Lewis (1990) and references therein
LAS (alkyl benzene sulfonate)	*Platymonas* sp. (green flagellate algae)	No information	Growth at 12-14 days affected by 2-54 mg/l	Lewis (1990) and references therein
LAS (alkyl benzene sulfonate)	*Dunaliella euchlora* (green algae) Marine.	No information	Growth at 12-14 days affected by 2-54 mg/l	Lewis (1990) and references therein
LAS (alkyl benzene sulfonate)	*D. primolecta* (green algae)	No information	Growth at 12-14 days affected by 2-54 mg/l	Lewis (1990) and references therein
LAS (alkyl benzene sulfonate)	*Pyramimonas grossi* (green algae)	No information	Growth at 12-14 days affected by 2-54 mg/l	Lewis (1990) and references therein
LAS (alkyl benzene sulfonate)	*Chlorella* sp. (green algae)	No information	Growth at 12-14 days affected by 2-54 mg/l	Lewis (1990) and references therein
LAS (alkyl benzene sulfonate)	*Chlorella stigmatophora* (green algae)	No information	Growth at 12-14 days affected by 2-54 mg/l	Lewis (1990) and references therein

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Table 8. Contd.

Surfactant Type	Species	Test Conditions	Exposure Effects	Reference
LAS (alkyl benzene sulfonate)	*Stichococcus* sp. (green algae)	No information	Growth at 12-14 days affected by 2-54 mg/l	Lewis (1990) and references therein
LAS (alkyl benzene sulfonate)	*Protococcus* sp. (green algae)	No information	Growth at 12-14 days affected by 2-54 mg/l	Lewis (1990) and references therein
LAS (alkyl benzene sulfonate)	*Nannochloris* sp. (green algae)	No information	Growth at 12-14 days affected by 2-54 mg/l	Lewis (1990) and references therein
LAS (C-13 alkyl benzene sulfonate)	*Gymnodium breve* (green algae) Marine.	No information	Growth at 9 days reduced by 69% after exposure to 0.003 mg/l	Lewis (1990) and references therein
LAS (C-13 alkyl benzene sulfonate)	*Gymnodium breve* (green algae) Marine.	No information	Mortality at 0.025 mg/l	Lewis (1990) and references therein
LAS	*Mytilus galloprovincialis* (mussel, 5.8cm main axis) Marine.	7 days exposure to 132 mg/kg on sediment	No significant effects on O2 consumption, NH3 excretion or filtration when compared to control	Marin et al (1994) Wat. Res. 28(1) p85
LAS	*Mytilus edulis* (mussel) Marine.	10 days, unknown concentration	Exposure concentrations of 0.05 mg/l affected fertilisation and larval growth	Lewis (1991) and references therein
LAS	*Mytilus edulis* (mussel) Marine.	10 days, unknown concentration	Exposure concentrations of 10.0 mg/l caused byssal thread formation, adductor muscle closing	Lewis (1991) and references therein

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Table 8. Contd.

Surfactant Type	Species	Test Conditions	Exposure Effects	Reference
LAS	*Crassostrea virginica* (oyster) Marine.	10 days, unknown concentration	Exposure concentrations of 0.05-0.10 mg/l affected larval growth and egg development	Lewis (1991) and references therein
ABS	*Mercenaria mercenaria* (clam) Marine.	14 days, unknown concentration	Exposure concentrations of 0.55-5.8 mg/l affected larval growth and egg development	Lewis (1991) and references therein
AS	*Crassostrea virginica* (oyster) Marine.	14 days, unknown concentration	Exposure concentrations of 0.14-1.63 mg/l affected larval growth and egg development	Lewis (1991) and references therein
AS	*Mercenaria mercenaria* (clam) Marine.	14 days, unknown concentration	Exposure concentrations of 0.47-1.46 mg/l affected larval growth and egg development	Lewis (1991) and references therein
LAS	*Limanda yokohamae* (flatfish) Marine.	30 days, unknown concentration	Exposure concentrations of 0.05-0.50 mg/l affected hatching	Lewis (1991) and references therein
LAS	*Paralichtys olivaceus* (flatfish) Marine.	30 days, unknown concentration	Exposure concentrations of 0.05-0.50 mg/l affected hatching	Lewis (1991) and references therein
LAS	*Gadus morrhua* (cod) Marine.	30 days, unknown concentration	Exposure concentrations of 0.5 mg/l affected swimming activity	Lewis (1991) and references therein

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Table 9. Chronic Toxicity Data for Cationic Surfactants

Surfactant Type	Species	Test Conditions	Exposure Effects	Reference
Quaternary ammonium chloride (DTDMAC)	*Dunaliella tertiolecta* (marine flagellate) Marine.	Exposure concentration 0.1-100 mg/l	Algistatic concentration: >0.5-1.0 mg/l; Algicidal concentration: >1.0-10 mg/l	Lewis and Wee (1983)
Quaternary ammonium chloride (DTDMAC)	*Gymnodium breve* (green algae) Marine.	No information	Growth at 9 days affected by 0.003 mg/l	Lewis (1990) and references therein
Lauryl pyridinium chloride	*Chlamydomonas* sp. (green flagellate algae)	No information	Growth at 12-14 days affected by 0.1 - 10.0 mg/l	Lewis (1990) and references therein
Lauryl pyridinium chloride	*Carteria* sp. (green algae)	No information	Growth at 12-14 days affected by 0.1 - 10.0 mg/l	Lewis (1990) and references therein
Lauryl pyridinium chloride	*Platymonas* sp. (green flagellate algae)	No information	Growth at 12-14 days affected by 0.1 - 10.0 mg/l	Lewis (1990) and references therein
Lauryl pyridinium chloride	*Dunaliella euchlora* (green algae) Marine.	No information	Growth at 12-14 days affected by 0.1 - 10.0 mg/l	Lewis (1990) and references therein
Lauryl pyridinium chloride	*D. primolecta* (green algae) Marine.	No information	Growth at 12-14 days affected by 0.1 - 10.0 mg/l	Lewis (1990) and references therein
Lauryl pyridinium chloride	*Pyramimonas grossi* (green algae) Marine.	No information	Growth at 12-14 days affected by 0.1 - 10.0 mg/l	Lewis (1990) and references therein
Lauryl pyridinium chloride	*Chlorella* sp. (green algae)	No information	Growth at 12-14 days affected by 0.1 - 10.0 mg/l	Lewis (1990) and references therein

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Table 9. Contd.

Surfactant Type	Species	Test Conditions	Exposure Effects	Reference
Lauryl pyridinium chloride	*Chlorella stigmatophora* (green algae)	No information	Growth at 12-14 days affected by 0.1 - 10.0 mg/l	Lewis (1990) and references therein
Lauryl pyridinium chloride	*Stichococcus* sp. (green algae)	No information	Growth at 12-14 days affected by 0.1 - 10.0 mg/l	Lewis (1990) and references therein
Lauryl pyridinium chloride	*Protococcus* sp. (green algae)	No information	Growth at 12-14 days affected by 0.1 - 10.0 mg/l	Lewis (1990) and references therein
Lauryl pyridinium chloride	*Nannochloris* sp. (green algae)	No information	Growth at 12-14 days affected by 0.1 - 10.0 mg/l	Lewis (1990) and references therein
Lauryl pyridinium chloride	*Mercenaria mercenaria* (clam) Marine.	14 days, unknown concentration	Exposure concentrations of 0.009-0.05 mg/l affected larval growth and development	Lewis (1991) and references therein
Lauryl pyridinium chloride	*Crassostrea virginica* (eastern oyster) Marine.	14 days, unknown concentration	Exposure concentrations of 0.05-0.09 mg/l affected larval growth and development	Lewis (1991) and references therein
Ethyl dimethyl benzyl ammonium chloride	*Mercenaria mercenaria* (clam) Marine.	14 days, unknown concentration	Exposure concentrations of 0.25-1.27 mg/l affected larval growth and development	Lewis (1991) and references therein
Ethyl dimethyl benzyl ammonium chloride	*Crassostrea virginica* (eastern oyster) Marine.	14 days, unknown concentration	Exposure concentrations of 0.10-0.49 mg/l affected larval growth and development	Lewis (1991) and references therein

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Table 10. Chronic Toxicity Data for Non-ionic Surfactants

Surfactant Type	Species	Test Conditions	Exposure Effects	Reference
Polyether alcohols	*Chlamydomonas* sp. (green algae)	No information	Growth at 14 days affected by exposure to 10-1000 mg/l	Lewis (1990) and references therein
Polyether alcohols	*Carteria* sp. (green flagellate algae)	No information	Growth at 14 days affected by exposure to 10-1000 mg/l	Lewis (1990) and references therein
Polyether alcohols	*Platymonas* sp. (green flagellate algae)	No information	Growth at 14 days affected by exposure to 10-1000 mg/l	Lewis (1990) and references therein
Polyether alcohols	*Dunaliella euchlora* (green algae) Marine.	No information	Growth at 14 days affected by exposure to 10-1000 mg/l	Lewis (1990) and references therein
Polyether alcohols	*D. primolecta* (green algae) Marine.	No information	Growth at 14 days affected by exposure to 10-1000 mg/l	Lewis (1990) and references therein
Polyether alcohols	*Pyramimonas grossi* (green algae)	No information	Growth at 14 days affected by exposure to 10-1000 mg/l	Lewis (1990) and references therein
Polyether alcohols	*Chlorella* sp. (green algae)	No information	Growth at 14 days affected by exposure to 10-1000 mg/l	Lewis (1990) and references therein
Polyether alcohols	*Chlorella stigmatophora* (green algae)	No information	Growth at 14 days affected by exposure to 10-1000 mg/l	Lewis (1990) and references therein

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Table 10. Contd.

Surfactant Type	Species	Test Conditions	Exposure Effects	Reference
Polyether alcohols	*Stichococcus* sp. (green algae)	No information	Growth at 14 days affected by exposure to 10-1000 mg/l	Lewis (1990) and references therein
Polyether alcohols	*Protococcus* sp. (green algae)	No information	Growth at 14 days affected by exposure to 10-1000 mg/l	Lewis (1990) and references therein
Polyether alcohols	*Nannochloris* sp. (green algae) Marine.	No information	Growth at 14 days affected by exposure to 10-1000 mg/l	Lewis (1990) and references therein
TAE10	*Mytilus edulis* (mussel) Marine.	5 months	Exposure concentrations of <0.1-20 mg/l affected fertilisation and spawning	Lewis (1991) and references therein
Alkyl polyether alcohol	*Crassostrea virginica* (eastern oyster) Marine.	14 days, unknown concentration	Exposure concentrations of 1.6-2.5 mg/l affected larval growth and egg development	Lewis (1991) and references therein
Alkyl polyether alcohol	*Mercenaria mercenaria* (clam) Marine.	14 days, unknown concentration	Exposure concentrations of 1.75-2.5 mg/l affected larval growth and egg development	Lewis (1991) and references therein
Iso-octyl phenoxy polyethoxy ethanol	*Crassostrea virginica* (eastern oyster) Marine.	14 days, unknown concentration	Exposure concentrations of 0.86-1.0 mg/l affected larval growth and egg development	Lewis (1991) and references therein
Iso-octyl phenoxy polyethoxy ethanol	*Mercenaria mercenaria* (clam) Marine.	14 days, unknown concentration	Exposure concentrations of 0.77-2.5 mg/l affected larval growth and egg development	Lewis (1991) and references therein

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Structural considerations of surfactant toxicity

Toxicity has also been found to vary between homologues within a given surfactant type and can depend upon chemical structure. LAS toxicity is modified by increasing the length of the alkyl chain, while the toxicity of nonionic ethoxylated surfactants depends upon the length of the ethoxylate chain (Lewis 1991 and references therein). Scott Hall et al. (1989) found that the general structure of a surfactant, be it highly branched, linear, aromatic or aliphatic, did not determine toxicity to the mysid shrimp *Mysidopsis bahia*, but observed that toxicity could be predicted by calculating the surfactant's ethylene oxide (EO) molar ratio. An EO ratio of ≤15 was common to the most toxic surfactants, while those chemicals with an EO ratio of 30-50 were consistently of very low toxicity. This observation applied both for a given series of homologues and across various surfactant types. Wildish (1974) suggested a number of possible explanations for the longer-chain/lower toxicity observation: for example, uptake rate across biological membranes is the limiting factor in the ultimate toxic mechanism of longer chain, less lipid-soluble surfactants. Alternatively, the number of surfactant molecules at the same weight per unit volume decreases with increasing chain length. If a critical number of molecules must accumulate at the active site for lethal poisoning to occur, then surfactants with a longer chain will exhibit less toxic effects. Another possible explanation is that surfactant binding to proteins may be less efficient when the chain is longer, resulting in a slower-acting toxic mechanism. Wildish (1972) also noted that polyoxyethylene ethers are generally more toxic than analogous polyoxyethylene esters, and attributed this difference to the relative ease of cleavage of the ester linkage by lipid-metabolising enzymes in comparison with the more resistant ether linkage.

Environmental considerations of surfactant toxicity

Sediments

Generalisations about surfactant toxicity in sediments are difficult to make due to the variety of experimental methods and end-points in the literature. For instance, studies on marine fish, molluscs and crustaceans have shown toxicity to increase with increasing temperature (Swedmark et al. 1971). However, this effect is not well understood and would appear to be dependent upon the test species, since Nyberg (1976) showed a certain diatom to be more sensitive to three surfactants at lower temperatures. Singer et al. (1990) estimated that susceptibility to surfactant toxicity may vary by as much as 10-fold over a range of temperatures.

Salinity

The effects of salinity on surfactant toxicity have been investigated in only a few studies. Lewis (1992) reports experiments in which the toxicity of alkyl benzene sulphonates to juvenile eels and mummichogs increased with increasing salinity, and the effects of an anionic surfactant on a marine copepod were more severe at higher salinities. This may be an important consideration when extrapolating results of toxicity tests on freshwater organisms to the marine environment.

Physical phase

The physical phase of a toxicant will also modify its effect. For example, Marin et al. (1994) found that LAS did not cause a toxic effect on the physiological activities of *Mytilus galloprovincialis* when

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sorbed onto sediments. The absence of toxicity contrasts with data reporting adverse effects from water-column LAS concentrations 1/3 to 1/10 of those used in this experiment. Casellato and Negrisolo (1989) observed similar results in experiments on tubificid oligochaetes, where no toxic effects were detected after exposure to sediment LAS concentrations five times the 96 hour LC_{50}. Likewise, the midge *Chironomus riparius* showed no effects on pupae development or emergence as winged adults when exposed to sediment LAS concentrations of 319 mg/kg; the 72-hour LC_{50} for this species is between 1 and 4.7 mg/l (Pittinger et al. 1989).

Conclusions

The range of surfactants, test species and experimental methods reported in the literature mean that generalisations on surfactant toxicity to marine organisms are difficult to make. Current scientific understanding of the effects of surfactants is based mainly on laboratory experiments for a few freshwater species. Also, most surfactants appear to be less toxic in the environment than would be inferred from laboratory tests (Lewis 1990). As a result, extrapolation of laboratory data to the marine environment is problematic. Field exposure will vary depending on solution strength, application method and rate, the degree of dilution and dispersion and meteorological conditions. Biodegradation of surfactants will affect exposure concentration and duration, and the toxicity of surfactant metabolites is an issue on which no studies were found. Lewis (1991) notes that although comprehensive data on effect and exposure exists for LAS, comparable information is not available for other surfactants, especially in the marine environment. Consequently, existing risk assessments should be considered to be limited since they are based on extrapolated data and may be inapplicable to all marine species and all surfactant classes without extensive validation.

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Chapter

4

ENVIRONMENTAL FATE AND BEHAVIOUR OF SURFACTANTS

Introduction

Surfactants may be classified into several groups, depending on their molecular structure (see Tables 1 and 3). Quantitatively, anionic surfactants are the most important, representing 60-70% of surfactants currently in use. Non-ionic compounds constitute around 30% but their use is increasing, while cationic and amphoteric products make up the smallest proportion.

Table 11. Surfactant classes and some examples

Surfactant Class	Examples
Anionic	Linear alkylbenzene sulfonate (LAS) (sulfonated aromatic HCs) Secondary alkanesulfonates/paraffin sulphonates (sulfonated aliphatic HCs) α-olefinesulfonate Sulfated fatty alcohol (e.g. sodium lauryl sulphate, sodium lauryl polyglycol) Ethoxylate (e.g. ether-sulfate) Sulfonated fatty acid Methyl ester (e.g. acid methyl ester) Sulfonated maleic ester Alcohol ethoxylates (AE) Phosphated alcohol
Cationic	Benzildodecyl-dimethylammonium chloride
Nonionic	Fatty alcohol ethoxylate Alkylphenol ethoxylate Fatty acid ethoxylate Fatty acid alkanolamide Fatty acid alkanolamide ethoxylate Fatty amine ethoxylate Polyalkylene glycol (ethylene oxide/propylene oxide addition products)
Amphoterics	Alkylbetaines

The majority of studies on the fate of surfactants have been carried out on LAS and alcohol ethoxylates, and although there have been numerous studies of surfactant fate in freshwater, only a small proportion are concerned with their behaviour in seawater. Surfactants may be removed from the marine environment via one or more mechanisms: volatilisation across the sea/air interface, abiotic degradation (i.e. photolysis or hydrolysis), adsorption to particles, microbial degradation and uptake by marine organisms. This section of the review summarises the information available on the first four these mechanisms and provides an overview of the current understanding of the fate of surfactants in the marine environment. Biological uptake (bioaccumulation/biomagnification) is discussed in detail in Chapter 5 of this report.

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Mechanisms of removal from the marine environment

Volatilisation

Surfactants do not volatilise to a significant extent due to their relatively high aqueous solubility combined with low to unmeasurable vapour pressures. Consequently, their environmental fate is restricted largely to aqueous environmental compartments (Tolls 1998).

Sorption/Desorption

Surfactants may accumulate in sediments via adsorption to particles, which sink and become incorporated into the sediment bed. Sorption of surfactants on marine sediments has received limited attention, despite the fact that the concentrations in sediments, especially those from coastal areas, may be high as high as 10-30 $\mu g\ l^{-1}$ (Quiroga et al. 1992). However, some experiments have demonstrated that LAS sorption is a rapid process with equilibrium being attained within 4 hours of contact (Rubio et al. 1996; Fytianos et al. 1998).

Several studies, for example Rubio et al. (1996) and Fytianos et al. (1998) have found that LAS sorption onto marine sediments can be fitted to a linear Freundlich isotherm of the type:

$$\log X = \log K + n \log C_e \quad (1)$$

where X is the amount of LAS adsorbed per unit of adsorbent ($\mu g\ g^{-1}$);
C_e is the equilibrium constant of LAS in solution ($mg\ l^{-1}$);
K is a constant relating to the bounding energy (defined as the distribution or sorption coefficient, representing the amount of surfactant adsorbed per unit of equilibrium concentration ($\mu g\ g^{-1}$);
n denotes sorption intensity.

This is consistent with sorption characteristics in freshwater, as described by Urano et al. (1984). While LAS sorption onto riverine sediments is generally considered to be reversible, desorption occurs much less readily in marine sediments. Rubio et al. (1996) observed that LAS recovery from marine sediments was less than 6%¸ and attributed this to one of two possible factors. (1) The sorption constant increases with the ionic strength of the medium, or (2) the experiments were conduced at low LAS concentrations, with sediments of high specific surface and organic content in comparison to previous work. Desorption is dependent upon changes in ambient conditions, and since the seawater/sediment sink is assumed to be in a steady-state, it is assumed that sorption of surfactants to marine sediments is in effect irreversible.

The extent to which surfactants adsorb to sediments is determined by the chemical nature of the surfactant and environmental conditions. In a study using surfactants of similar hydrocarbon chain length, Brownawell et al. (1991) found that, consistent with the negative charge of sediments at the pH used, sediment affinity increased in the order anionic – nonionic – cationic. The length of the aliphatic hydrocarbon chain also affects the sorption process. Rubio et al. (1996) carried out

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sorption experiments using LAS homologues from C_{10}-LAS to C_{13}-LAS and found that *K* increased with the length of the aliphatic chain. This observation supports the surfactant sorption mechanism proposed by Di Toro et al. (1990), whereby competitive and co-operative processes coexist during sorption. Competitive processes occur via hydrophobic interactions with the various homologues vying for preferential adsorption sites. The value of *n* was observed to decrease as the length of the aliphatic chain increased, suggesting that chain length may also affect the co-operative sorption mechanism.

Several studies have shown surfactant adsorption to be dependent on sediment organic carbon content. This has been observed for LAS adsorption in both freshwater and marine systems (Urano et al. 1984; Fytianos et al. 1998) and nonionic AE and APE in freshwater (Urano et al. 1984). Brownawell et al. (1997) also observed an increase in AE absorption with increasing organic content, but noted that the effect was perturbed by appreciable quantities of swelling clays such as montmorillonite in sediment samples.

In experiments over a wide range of salinities, Rubio et al. (1996) found that *K* varied by more than 300%, and concluded that where factors such as degradation and dispersion were absent, increasing salinity would lead to greater LAS accumulation in sediments. In comparison, Brownalow et al. (1997) observed that addition of sodium azide (NaN_3) affected sorption both positively and negatively, depending on the homologue. The increased sorption was explained by a “salting-out” effect, while reduced sorption was attributed to the addition of supporting electrolytes blocking sorption sites. Addition of Ca^{2+} to solutions of AE homologues and sediment (i.e. increasing hardness) had little effect on sorption. (Brownawell et al. 1997).

Finally, pH was found to have a “small but measurable” effect on AE adsorption (Brownawell et al. 1997), the magnitude of which decreased with decreasing oxyethylene chain length. A decrease in APE adsorption with increasing pH was also observed where the adsorbents have a pH-dependent surface charge.

Abiotic Degradation

No information was found on abiotic degradation of surfactants in the marine environment. However, Pelizzetti et al. (1990) summarised data from laboratory studies and concluded that the following surfactants could be at least partially mineralised via photolysis: dodecylbenzene sulphonate and dodecylsulphate (anionic), benzildodecyl-dimethylammonium chloride (cationic), and NPEO (non-ionic).

Biotic Degradation

Considerable research has been carried out on surfactant biodegradation in freshwater, but their fate in the marine environment has received much less attention. Swisher (1987) listed studies showing surfactant degradation in seawater; those found to undergo biodegradation include LAS, SDS, AOS, SAS, primary alkyl sulphates and NPE_9. Vives-Rego et al. (1987) demonstrated that the anionic surfactants sodium dodecyl sulphate (SDS) and LAS, and the cationic surfactant cetyl trimethyl ammonium bromide (CTAB) undergo rapid primary degradation in the marine environment, with half-lives of 0.26-0.34, 6-9, and 4-9 days, respectively. It should be noted however, that this experiment was conducted using concentrations of surfactants (20 mg l^{-1}) much higher than those observed in the environment, and did not measure complete mineralisation.

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Degradation Pathway (LAS)

Knowledge of the degradation pathway of LAS is still incomplete, but is thought to begin with ω-oxidation of a methyl group at the end of the alkyl chain, which gives rise to an acid. The chain then undergoes further oxidations to generate new sulfophenylcarboxylic acids whose chain length shortens each time by two carbon atoms (β-oxidation) or one carbon atom (α-oxidation). This is followed by oxidative ring splitting and cleavage of the carbon sulphur bond, thus liberating sulphate.

Salinity Effects

Degradation of LAS in the marine environment is slower than in freshwater, and a half-life 2-3 times greater in seawater has been reported (Vives-Rego et al. 1987). This may be explained by microbial communities in the marine environment being less active towards xenobiotic chemicals than freshwater bacteria (Shimp 1989), or the fact that complexation of LAS with calcium and magnesium ions results in reduced bioavailability, particularly at low concentrations (González-Mazo et al. 1997). Quiroga and Sales (1990) found that the extent of surfactant biodegradation after 21 days was similar over a range of salinities, but the induction period was shorter for higher salinities (50-65 ppt) than for lower ones (16 and 32 ppt). This could be an artefact of bacterial culture dilution and the accompanying reduction in culture numbers.

Temperature Effects

Quiroga and Sales (1989) found that LAS degradation failed to occur at temperatures of 5-10°C, occurred to only a limited extent at 15°C, and was almost complete after 15 days at 25°C. Also, the acclimation period was significantly reduced at higher temperatures. This is consistent with enhanced microbial activity at higher temperatures and according to the authors, implies that marine contamination with LAS could be more serious in winter. Quiroga and Sales (1990) found that the rate of surfactant degradation also increased with aeration and luminescence, which again was probably a result of increased microbial activity.

At temperatures up to 15°C, degradation followed a zero-order kinetic equation, i.e. microbial activity is the rate-determining step. At 20 - 25°C degradation was best modelled using a second-degree polynomial, interpreted in terms of a bacterial adaptation phase, a phase of exponential development during which degradation occurs, and a phase where the residual surfactant concentration approaches zero which coincides with a plateau in micro-organism growth.

Sediment Effects

Studies on surfactant biodegradation in the presence of sediment have produced contradictory results. Shimp (1989) assessed the mineralisation of LAS to CO_2 at realistic environmental concentrations (20 $\mu g\,l^{-1}$) and found that addition of 1000 $mg\,l^{-1}$ sediment to water samples increased the extent of degradation, but not the rate. This was attributed to the presence of additional microbial biomass, organic matter or nutrients. In a similar set of experiments, Quiroga and Sales (1989) observed an increase in the rate of biodegradation, and pointed out that addition of marine sludge would provide a greater surface area over which the surfactant could be adsorbed, thus facilitating biodegradation. The presence of proteolytic enzymes in marine sediments may also enhance surfactant degradation (Quiroga and Sales 1991b).

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In contrast, Quiroga et al. (1992) explained enhanced biodegradation of LAS in sandy sediments by the lower capacity of sand, compared to clay, to adsorb LAS. Meanwhile, in a study of NPEO persistence in marine sediments, Shang et al. (1999) found no relationship between surfactant concentration and sediment depth that could be interpreted as enhancement of the rate of degradation. There was also no evidence of a shift from higher to lower NPEOs with increasing depth in the sediment, which would have indicated sequential breakdown of ethoxy groups with time. The low temperature of marine sediments makes them an ideal environment in which to preserve NPEOs, and since they comprise a minute and relatively refractive proportion of the organic carbon in sediments, once they become incorporated neither primary degradation or mineralisation occur rapidly, if at all. Taking these factors and the effects of sediment mixing into account, Shang et al. (1999) estimated a conservative half-life of 60 years for NPEOs in marine sediments.

Chain Length and Isomer Effects

Terzic et al. (1992a) found that for LAS homologues, biodegradation increased with increasing aliphatic chain length for all bacterial cultures and/or temperatures investigated. It was also noted that chain branching had a significantly stronger effect on biodegradation than chain length. Degradation of isomers with a sulphophenyl group positioned in the middle of the alkyl chain was slower than degradation of 2-phenyl isomers.

Effect of Initial Surfactant Concentration

Terzic et al. (1992b) found that the primary LAS biodegradation efficiency of coastal bacteria was significantly higher at an initial surfactant concentration of 2 mg l^{-1} than 20 mg l^{-1}. This relationship has also been observed for degradation of SDS (Quiroga and Sales 1991a) and was attributed either to reduced oxygen solubility in the medium or toxic effects of the surfactant.

Effect of Heavy Metals

Quiroga et al. (1992) found no relationship between sediment heavy metal concentration and surfactant degradation, suggesting that heavy metals did not have an inhibitory effect on the bacterial community.

Bacteria Type

Terzic et al. (1992b) attempted to isolate and identify the bacterial strain responsible for LAS degradation by a mixed culture. Identification was not possible, but data suggested that the strain was terrestrial in origin. Shimp (1989) and Quiroga et al. (1992) found that LAS biodegradation proceeded more readily in a site exposed to industrial effluents than in a pristine site, and suggested that degradation efficiency is dependent upon exposure history of the microbial population.

Anaerobic Degradation

Field studies on anaerobic degradation of LAS are limited but the available data suggests that degradation is poor in anoxic conditions (Quiroga et al. 1992; Rubio et al. 1996) and is controlled by the same factors that dictate anaerobic degradation of other aliphatic hydrocarbons lacking oxidised substituents (Larson et al. 1993). Quiroga et al. (1992) found that degradation in anoxic environments could be fitted to a zero-order kinetic which implies degradation by facultative

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anaerobic bacteria. This observation was supported by studies using laboratory microcosms, which show that anaerobic degradation may be enhanced if preceded by a period of aerobic exposure (Larson et al. 1993). Although it is feasible that such conditions could occur in marine sediments, the environmental compartments exposed to surfactants are usually aerobic and environmental concentrations of LAS are comparable to other detergent chemicals that are known to undergo rapid anaerobic degradation.

AISE (1999) summarised laboratory studies to evaluate the anaerobic degradability of several surfactant groups. Sulphonated anionic surfactants such as LAS, SAS and MES, and mono- or di-alkyl quaternary compounds were considered poorly biodegradable, alkylphenol ethoxylates were considered partially degradable, and AEs, sulphated anionic surfactants, sugar-based surfactants and esterified mono- or di-alkyl quaternary surfactants were classed as easily biodegradable.

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Table 12. Summary of currently available information on surfactant degradation in the marine environment.

Surfactant	Class	Experimental conditions	Half-life (days)	Percentage degradation	Reference
LAS	Anionic	20 μg l^{-1} LAS added to effluent-exposed seawater (27-30°C, 34 ppt)	6.9	42.3% after 60 days incubation	Shimp (1989)
LAS	Anionic	20 μg l^{-1} LAS added to effluent-exposed seawater (27-30°C, 34 ppt), plus 1000 mg l^{-1} sediment	6.9	60.4% after 60 days incubation	Shimp (1989)
LAS	Anionic	20 μg l^{-1} LAS added to effluent-exposed/pristine seawater (at in situ temperature)	ca. 7	Approx. 40% (effluent exposed) and 10% (non-exposed) after 40 days incubation	Larson et al. (1993)
SDS	Anionic	4 mg l^{-1} added to seawater (33 ppt, pH = 8.35, [O_2] = 4.3 mg l^{-1}, [micro-organisms] = 6700 colonies ml^{-1})	-	90% after 17 days incubation	Quiroga and Sales (1991b)
SDS	Anionic	15 mg l^{-1} added to seawater (33 ppt, pH = 8.35, [O_2] = 4.3 mg l^{-1}, [micro-organisms] = 6700 colonies ml^{-1})	-	90% after 21 days incubation	Quiroga and Sales (1991b)
SDS	Anionic	20 mg l^{-1} added to seawater (33 ppt, pH = 8.35, [O_2] = 4.3 mg l^{-1}, Type B micro-organisms (enterobacteriaceae), [micro-organisms] = 12,500 colonies ml^{-1}).	-	100% after 21 days incubation	Quiroga and Sales (1991a)
SDS	Anionic	20 mg l^{-1} added to seawater (33 ppt, pH = 8.35, [O_2] = 4.3 mg l^{-1}, Type D micro-organisms (micrococcaceae), [micro-organisms] = 12,500 colonies ml^{-1}).	-	75% after 21 days incubation	Quiroga and Sales (1991a)
LAS	Anionic	90 μg l^{-1} added to seawater (25°C, 33.8 ppt, pH = 8.1, [O_2] = 7.1 mg l^{-1}, [micro-organisms] = 6.1-8.1 x 10^3 colonies ml^{-1}) plus 250 g l^{-1} sediment.	-	10-90% after 15 days incubation, depending on composition of sediment added.	Quiroga et al. (1992)

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Table 12. Continued

C_{10}-LAS	Anionic	1 mg l^{-1} added to non-filtered estuarine water (23°C, 36-36.5 ppt)	6.9	-	Terzic et al. (1992a)
C_{11}-LAS	Anionic	1 mg l^{-1} added to non-filtered estuarine water (23°C, 36-36.5 ppt)	6.1	-	Terzic et al. (1992a)
C_{12}-LAS	Anionic	1 mg l^{-1} added to non-filtered estuarine water (23°C, 36-36.5 ppt)	4.5	-	Terzic et al. (1992a)
C_{13}-LAS	Anionic	1 mg l^{-1} added to non-filtered estuarine water (23°C, 36-36.5 ppt)	3.6	-	Terzic et al. (1992a)
LAS	Anionic	1 mg l^{-1} added to non-filtered estuarine water (23°C, 36-36.5 ppt)	4.4	-	Terzic et al. (1992a)
SDS	Anionic	20 mg l^{-1} added to non-filtered seawater (22°C)	0.26-0.34	-	Vives-Rego et al. (1987)
LAS	Anionic	20 mg l^{-1} added to non-filtered seawater (22°C)	6-9	-	Vives-Rego et al. (1987)
LAS	Anionic	62.7 µg DSN l^{-1} added to seawater (20-25°C, 33.3 ppt, $[O_2]$ = 6.78 mg l^{-1}, [micro-organisms] = 17,100 colonies ml^{-1})	-	90% after 15 days	Quiroga and Sales (1989)
LAS	Anionic	62.7 µg DSN l^{-1} added to seawater (20-25°C, 33.3 ppt, $[O_2]$ = 6.78 mg l^{-1}, [micro-organisms] = 17,100 colonies ml^{-1}) plus 250 g l^{-1} sediment	-	90% after 10 days	Quiroga and Sales (1989)
CTBA	Cationic	20 mg l^{-1} added to non-filtered seawater (22°C)	4-9	-	Vives-Rego et al. (1987)

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Chapter

5

BIOACCUMULATION AND BIOMAGNIFICATION OF SURFACTANTS

Mechanisms and routes

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Introduction

Bioaccumulation factors

Bioaccumulation is primarily of concern in relation to chemicals which are not acutely toxic, and which, if they persist in living tissue, have the potential to cause increasingly serious effects as they are passed from one trophic level to another. Historically, the chemicals that have been of greatest concern are those which are also highly environmentally persistent, and which accumulate to significant concentrations in tissue even at low environmental exposure concentrations. For such chemicals, the most severe consequences might be observed only after many decades and in organisms many trophic levels removed from direct environmental exposure. It is, however, important to recognise that it is not bioaccumulation *per se* which is of concern; it has been an environmental issue primarily when it is associated with harmful chemicals which are environmentally persistent and which are metabolised poorly or not at all. It is also important to recognise that (at whichever trophic level effects are expressed) the critical condition for effect is attained when a chemical substance exceeds a tolerable tissue burden threshold, and that this condition can be “satisfied” by any environmental exposure scenario which sustains chemical uptake at a sufficient rate.

It is, however, historically the case that most attention in relation to bioaccumulation has focused on highly lipophilic chemicals that are poorly metabolised and depurated, and that can therefore accumulate over time to high and damaging tissue concentrations even from very low exposure concentrations. For such chemicals, experimental measures of bioaccumulation and bioconcentration potential have provided a useful basis for risk assessment. Some caution is required, however, in the blanket application of this philosophy to all chemicals. While there is empirical evidence that bioaccumulation and harm are closely linked for specific types of chemical, the observed fact that some classes of harmful chemical are bioaccumulative does not automatically imply the corollary that all bioaccumulative chemicals are harmful, or are harmful in the same way.

A wide variety of approaches have been taken in the study of bioaccumulation, ranging from simple “black box” studies of whole-body accumulation to more sophisticated tracing of individual compounds and metabolites through organs and tissues. Since bioaccumulation studies are often complex and expensive in terms of time and resource, a common approach is to develop some form of quantitative structure-activity relationship (QSAR), by means of which bioaccumulation potential can be estimated from a comparatively simple, quick and inexpensive measurement of some physical, chemical or structural property of the substance in question. The commonest QSAR measurement in routine use is the octanol-water partition coefficient, usually reported as log P_{ow} and often estimated indirectly by HPLC methods (e.g. OECD 117). This measurement has been established as a standard for all oilfield chemicals (HOCNF 1995), although there is little evidence that its applicability to such chemicals received careful consideration prior to its adoption. Strictly speaking, this QSAR is valid only for the classes of chemical from which the relationship was derived; for other chemicals, even when it is technically feasible to make the measurements, it is not always clear that the established assessment criteria are valid. In particular, there is no reason to believe that lipophilicity or hydrophobicity automatically or invariably imply either harm, persistence in tissue, or food-chain biomagnification.

As noted above, the primary concern about bioaccumulation has arisen in relation to chemicals that can accumulate to critical concentrations in organisms towards the top of the food chain. This implies a combination of limited metabolism and limited depuration. Partial metabolism can either mitigate or exacerbate the effects of the chemical; in some instances, metabolism can reduce the tissue burden of the harmful molecule, while in other instances the metabolites can be more harmful

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and more persistent than the parent compound. Where studies have only addressed the whole-body burden of the parent compound, low bioaccumulation rates do not therefore necessarily indicate a lack of potential for harm. For this reason, it is difficult to justify any "black box" regulatory approach that relies on a single and often arbitrary measurement. Any assessment of bioaccumulation potential should, realistically, take into account as much information as possible on the chemistry, metabolism, degradability and potential breakdown products of the chemical. With oilfield chemicals, this can be difficult, since

a) they are often quite complex mixtures
b) their chemistry is often very poorly described
c) few, if any, are classed as priority chemicals and have therefore not been the subject of detailed biological and environmental fate studies

Environmental variables

The uptake processes and degree of overall bioaccumulation of chemicals can be significantly influenced by environmental conditions; in water, factors such as the ionic strength of the aqueous phase, the presence of dissolved organic matter and/or other surfactants can be important (Tolls et. al. 1994). In sediments, particulate composition, structure, and adsorptive capacity will have a considerable influence on exposure and uptake.

Surfactant types

All major surfactant groups (anionic, cationic, nonionic and amphoteric) are currently used to some extent by the offshore oil industry. Nonionic surfactants are the most widely used, with perhaps the greatest concern focusing on the bioaccumulation potential of alkylphenol ethoxylates, for some of which there is tentative evidence of weak endocrine disruption activity.

The following properties are common to surfactants:

- They all have a combined lipophilic/hydrophilic structure which gives them a tendency to collect at aqueous/organic-phase boundaries
- Most surfactants are susceptible to biodegradation, metabolism and other breakdown reactions that may lead to metabolites with significantly different chemical properties.
- They will form micelles in water when present above critical levels.

Evidence of bioaccumulation

The bioaccumulation potential of a wide range of hydrophobic organic chemicals and their subsequent effects on the environment have been extensively studied over many years. Interest in the bioaccumulation of surfactants has increased over recent years due to the large quantities of these materials manufactured and the relatively high proportion discharged to the environment.

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Considerable evidence of surfactant bioaccumulation has been collected and published. See Chapter 6 of this review for a summary of existing surfactant bioaccumulation data.

As indicated by Tolls et. al. (1995) much of the available data can only be used tentatively since it has been derived from experiments using radiolabelled compounds. Very few such studies can differentiate between parent compounds and metabolites or other breakdown products. Because of this limitation, many reported concentration factors are probably significant overestimates.

In general, bioconcentration factors for surfactants are reported as being comparatively low, and are generally below the conventional criteria for concern (i.e. log P_{ow} value of 3 - 4).

Trends and relationships between bioaccumulation data and chemical structure of surfactants

In evaluating the possible mechanisms of interaction between surfactants and organisms it is important to try to identify the factors that have the greatest influence on overall accumulation potential. The following surfactant properties have been examined:

- Increased hydrophobicity
- Decreased hydrophobicity
- Increased size leading to steric effects

Increasing the hydrophobicity of the surfactant molecule

The effect of increasing alkyl chain length (and hence hydrophobicity) has been studied for a number of different surfactant classes.

In studies of the bioaccumulation potential of different radioactively labelled LAS anionic surfactants (cited in Tolls et. al. 1994), Comotto et. al. (1979) calculated concentration ratios (CRs) for *Pimephales promelas* of 551 and 1223 expressed as a dry weight for C_{12}-LAS and C_{13}-LAS, respectively. Similar ratios were obtained by Kimerle et. al. (1975) where CR values of 173 and 385, expressed as wet weight, were recorded for the same species and surfactants. These studies suggest that a slight increase in the length of the alkyl chain (from C_{12} to C_{13}) significantly increases the bioaccumulation potential of the compound.

A more detailed investigation of the bioaccumulation potential of specific LAS compounds and isomers present in industrial mixtures (again using *Pimephales promelas*) was carried out by Tolls et. al. (1997). The same trend of increasing BCF with alkyl chain length was found with values ranging from 6.0 to 987.2 for C_{10}- to C_{13}-LAS. In addition, the effect of the position of the *p*-sulfophenyl group was also investigated. The data indicated that BCF increased the closer the *p*-sulfophenyl group was positioned to the terminal carbon of the alkyl chain.

Versteeg and Shorter (1992; cited in Tolls et.al. 1994) studied the accumulation of various TMAC cationic surfactants in *Pimephales promelas*. Concentration ratios of 2.4, 35, and 1962 were recorded for C_8-TMAC, C_{12}-TMAC, and $C_{16/18}$TMAC, respectively.

Tolls et. al. (2000) produced data that allowed the comparison of alcohol ethoxylate components containing different alkyl chain lengths. In all cases an increase in the length of the alkyl group led to an increase in measured bioaccumulation (Table 13).

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Table 13. Effect of increasing alkyl chain length on BCF (example: alcohol ethoxylate - C_nEO_8)

n	BCF
12	12.7
13	49.9
14	56.7
16	387.5

Decreasing the hydrophobicity of the surfactant molecule

Increasing the length of the hydrophilic section of the molecule has the effect of decreasing the overall hydrophobicity of a non-ionic surfactant:

The bioconcentration potential of ethoxylated alkylphenols (widely used non-ionic surfactants now being gradually phased out due to concerns regarding the biological effects of alkylphenol) and their breakdown products have been studied extensively over recent years. Staples et. al. (1998) reviewed the available data and collated a useful database of bioconcentration and toxicity values for these compounds. A number of the studies referenced investigated the effect of the length of the ethoxylate chain on bioaccumulation potential. In all but one study the degree of overall bioconcentration decreased as the length of the hydrophilic ethoxylate chain increased; for example, bioaccumulation factors for caged mussels in a field study decreased from 340 for nonylphenol (NP) to 60 for NPEO3 (Grammo et. al. 1990). This property has been also been observed in alcohol ethoxylate surfactants by Wakabayashi et. al. (1987, cited in Tolls et.al. 1994) and Tolls et. al. (2000).

Steric effects

There is evidence that, that in some cases, the size and shape of a surfactant molecule can influence uptake and therefore bioaccumulation.

Versteeg and Shorter (1992, cited in Tolls et. al. 1994) studied the effect of alkyl chain length on a range of alkyl ammonium cationic surfactants. A general increase in bioaccumulation was observed as alkyl chain increased; however, for C_{18} (2)-DMAC a sharp decrease in CR was observed. Tolls et. al. (1994) hypothesised that the presence of two long alkyl chains could lead to the molecules being stabilised in the lipid bilayer of membranes thereby hindering transport.

Tolls and Sijm (1995) noted that the uptake rate, k_1, and hence the overall bioaccumulation, of both C_{18}-DMAC and $C_{12}EO_{16}$ were considerably lower than would be expected from compounds exhibiting their degree of hydrophobicity. A possible explanation for these observations can be found in a review of bioaccumulation kinetics of organic micropollutants by Opperhuizen (1991),

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where it was proposed that hydrophobic chemicals of greater width than 0.95 nm or length 5.3 nm will have great difficulty passing through biological membranes. Examples of calculated molecular lengths for various surfactants are shown in Table 14:

Table 14. Calculated molecular lengths for various surfactants (from Tolls and Sjim 1995)

Surfactant	Length (nm)
$C_{12}EO_4$	3.8
$C_{12}EO_8$	5.6
$C_{12}EO_{16}$	7.9
$C_{14}EO7$	5.4
$C_{18}DMAC$	5.8

Summary of trends

In all studies increased alkyl chain length led to an *increase* in bioaccumulation, whereas increasing the length of the hydrophilic moiety of the surfactant molecule leads to an overall *decrease* in bioaccumulation potential. There is a strong possibility that the bioaccumulation of many surfactants (especially non-polar types containing long EO chains) may be significantly inhibited due to steric factors.

Mechanisms of bioaccumulation

As stated previously the majority of bioaccumulation studies have been carried out on various species of freshwater and marine fish using radiolabelled surfactants. Despite the limitations of this type of study , they do, however, offer a relatively easy way of monitoring the mechanism of uptake. Whole-body radiograms of fish exposed to dissolved surfactants demonstrated that most surfactants are rapidly taken up and distributed within the fish. More focused studies showed that an initial rapid increase in radioactivity in the gills was followed by steady increase in the bloodstream. This indicates that the gills are an important uptake site for dissolved surfactants from the aqueous phase (Tolls et. al. 1994).

Tolls et. al. (1995) tested the applicability of the diffusive mass transfer (DMT) concept using a first-order, single-compartment model for evaluating the relationship between bioaccumulation potential and hydrophobicity for surfactants. The theoretical relationship between bioconcentration, uptake and elimination rates and hydrophobicity shown below had previously been shown to be applicable for hydrophobic compounds such as polychlorinated biphenyls (PCBs):

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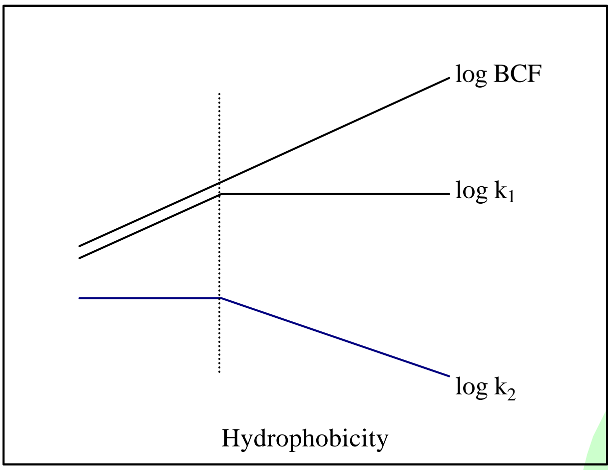

Figure 3. Theoretical relationship between bioconcentration, uptake and elimination rates, and hydrophobicity (k_1 uptake constant; k_2 elimination constant).

To the left of the dotted line (*compounds of relatively low hydrophobicity*) mass transfer is limited by diffusion through the lipid phase.

To the right of the dotted line (*compounds of relatively high hydrophobicity*) mass transfer is limited by diffusion through the aqueous phase.

It should be noted that measurements of k_2 often include non-diffusive sources of elimination (such as growth and biotransformation), and where these processes are significant the DMT model may not fully apply. In addition, it has been shown that the bioaccumulation of very small or very large molecules is not covered by the concept.

Overall, the DMT concept agreed with the empirical data studied. It was found that as hydrophobicity of different surfactants (estimated using CMCs) increased the rate of uptake (log k_1) also increased. Therefore, assuming DMT, this suggests that surfactant bioaccumulation is dependant on diffusion of the surfactant through the lipid phase. Since the source data used for this study did not differentiate between parent and biotransformation compounds the elimination rate constants calculated could not be used to confirm diffusive elimination process of the DMT concept.

In more recent work Tolls et. al. (1997) calculated k_1, k_2 and BCF data for various C_{10}-C_{13} LAS constituents in *Pimephales promelas* using compound-specific methods. The data obtained from this study agreed with the DMT concept, with BCF and k_1 values increasing with increased hydrophobicity, while k_2 remained fairly constant. A similar study looking at AE surfactants (Tolls et. al. 2000) again found increasing uptake rates and bioaccumulation factors with increased hydrophobicity; however, the elimination rate also varied and was found to decrease with increasing hydrophobicity. This observation may be explained by the increased hydrophobicity of AE surfactants compared with the LAS surfactants tested.

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Biotransformation

As indicated previously the overall rate of elimination can be affected by more than one factor (diffusive losses, biotransformation, growth, etc). Preliminary information suggesting that biotransformation processes were occurring in fish exposed to surfactants was obtained during radiolabel studies. Metabolism of surfactant components was suggested by increased radioactivity levels in gall bladder. Tolls et. al. (1994) proposed that this accumulation may be explained by surfactant transformation in the liver followed by excretion into the gall bladder. Because the test fish were not fed during exposure this means the contents of the gall bladder were not emptied into the gut, thereby allowing the build up of high concentrations of metabolites.

More evidence of biotransformation can be obtained by comparing data from of radiolabel studies (which would include a significant proportion of metabolites) with compound-specific studies using very similar species and test environments.

Tolls and Sjim (1999) found that for $C_{14}EO_8$, the BCF calculated using a total radioactivity measurement was 224 l kg^{-1} compared with 31.4 l kg^{-1} for the parent compound only. A first-order, single-compartment model of bioconcentration was extended to allow for quantification of the in vivo rate constant of biotransformation, yielding an elimination rate constant of 10 day^{-1}. When compared with the overall elimination rate constant of 10.1 day^{-1} it was deduced that biotransformation was the dominant contributor in the elimination of the AE surfactant.

Similar data were obtained for C_{12} and C_{13}-LAS by Tolls et. al. (1997):

Table 15. Comparison of BCF for surfactants estimated from radiolabel studies with values obtained from parent compound measurements (from Tolls et al. 1997)

Surfactant	BCF (radioactivity measurements)	BCF (parent compound measurements)
C_{12}-LAS	173-245	62
C_{13}-LAS	291-345	182

Biomagnification potential of surfactants

Interest in the bioaccumulation potential of chemicals arises primarily from the observation that some substances with high bioaccumulation factors can be concentrated in successive transfers through the food chain and present significant hazard to organisms near the top of the chain. For such chemicals, the "out of sight, out of mind" philosophy proved disastrous, since it eventually became apparent that critical tissue concentrations could occur in top predators even when the environmental exposure concentrations were very low. In other words, for some contaminants there is effectively no biologically safe exposure threshold. A focus on bioaccumulation potential was intended, originally, to enable such chemicals to be identified and eliminated.

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While the bioaccumulation of a chemical can still present a problem where exposure levels and uptake rates are sufficiently high in relation to depuration and metabolism rates, a high bioaccumulation potential does not automatically imply the potential for biomagnification. Indeed, for some chemicals that are readily taken up by organisms near the bottom of the food chain, a capacity for metabolism is more likely in successively higher trophic levels.

Studies into the bioaccumulation and biomagnification of organic micropollutants have shown that uptake from the water column is the most significant pathway for the accumulation of relatively hydrophobic (log P_{ow} <4.5) organic compounds (Bartell et. al. 1998). This is due to the fact that the volume of water passed across the gills is usually several orders of magnitude higher than the quantities of food and particles ingested by most aquatic organisms (Opperhuizen 1991). Uptake via food and sediment sources, and therefore biomagnification, will only become significant for extremely hydrophobic compounds, e.g. polychlorinated biphenyls, which would be present at very low levels in the aqueous phase and relatively high levels in food and sediment.

In addition, in order for biomagnification to take place the compound must be stable in the environment for significant periods of time. Compounds which degrade relatively rapidly or which are readily metabolised will not be biomagnified within the food chain.

The information available indicates that most commonly used surfactants do not have the properties required to exhibit biomagnification, i.e. they have a tendency to be rapidly degraded and metabolised and are not highly hydrophobic.

Empirical data obtained for nonylphenol ethoxylate surfactant breakdown products (NP, $NPEO_1$ and $NPEO_2$) in a freshwater environment by Ahel et. al. (1993), showed no indication of biomagnification occurring via algae to fish. In fact, calculated BCF factors in fish (ranging from 3 to 330) were significantly lower than the levels found in the algae tested (BCF values of up to 10,000).

Conclusions

No evidence has been found to support concern with respect to the biomagnification of surfactants, although it is noted that most of the research effort has been devoted to a relatively small number of surfactant types. Bioconcentration factors in the aqueous phase are generally below the level of concern, and (for some nonionic surfactants at least) can be quantitatively related to the length of the hydrophobic and hydrophilic components. There is also evidence that overall molecular size may place constraints on biological uptake. The studies examined in this report raise no concerns with respect to long-term retention of accumulated surfactant material in tissue, and indeed they present considerable evidence that many surfactants are metabolised. The fate of metabolites has not been thoroughly studied, however, and there is consequently uncertainty as to the fate and longer-term effects of some hydrophobic components (such as some alkylphenols) following partial metabolism.

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Chapter

6

EXISTING DATA FOR SURFACTANTS

Introduction

This section of the report presents a summary of existing data for log P_{ow} and BCF values for surfactants that was found in the scientific literature. Data was obtained through searches by the Royal Society of Chemistry Library Services, searches of databases including Dialog, STN, US EPA Ecotox Aquire database, and Internet searches.

Several on-line databases were also searched, including the CAS Registry database (http://stneasy.cas.org); the US EPA Ecotox database (http://www.epa.gov/cgi.bin/ecotox); the LogK_{ow} Calculation Program (Syracuse Research Corporation) (http://www.esc_plaza.syres); and the CLOGP Database (Biobyte) (http://www.biobyte.com).

The data has been collated into two Tables (16 and 17). Table 16 shows BCFs and exposure concentrations (if known) of surfactants to various aquatic species, while Table 17 presents data on log P for various surfactants and indicates the method used to determine the value. Although the literature and database searches have been comprehensive, they are by no means exhaustive, and the data presented in Tables 16 and 17 should be regarded as representative only and not definitive.

Available Data

Definition of BCF

Bioconcentration is the result of uptake of a compound from the surrounding medium and elimination to the medium. Assuming that chemical uptake and elimination kinetics are first-order processes, the time-course of the concentration of a chemical in an organism can be expressed mathematically as:

$dC_f/dt = k_1 * C_w - k_2 * C_f$ (Branson et al. 1975). (2)

For steady-state conditions ($dC_f/dt = 0$) it follows that

$C_f/C_w = k_1/k_2 = \text{BCF}.$ (3)

The quantitative measure of bioconcentration is the bioconcentration factor (BCF).

From the above equations, two possible experimental approaches to determining the BCF are possible. In the first, the steady-state concentrations of a compound in the organism and water are measured and the BCF calculated as their ratio. The second approach is to measure the time-course of a compound's concentration in water and/or organism during an uptake and elimination experiment.

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Definition of Partition Coefficient

The partition coefficient (*P*) is defined as the ratio of the equilibrium concentrations of a dissolved substance in a two-phase system, consisting of two largely immiscible solvents. In the case of *n*-octanol and water:

$$P_{ow} = (C_{\text{n-octanol}})/(C_{\text{water}}). \qquad (4)$$

The partition coefficient, being the quotient of two concentrations, is dimensionless and is usually given in the form of its logarithm to base 10, i.e. log P_{ow}.

Comments on BCF data

There have been a number of reviews on the subject of surfactant bioconcentration in the aquatic environment, notably that by Tolls et al. (1994), in which much of the data presented here has been critically reviewed. It is not intended to repeat the work already done in the above-mentioned review, but the reader should have an opportunity to evaluate the available data in the context of the issues being addressed in this report.

The data set is relatively small, with the majority of data available being for anionic surfactants, particularly linear alkylbenzene sulphonate (LAS), with a smaller amount of data found for cationic and nonionic surfactants. No data was found for amphoteric surfactants.

A glance at the data in Table 16 shows that the vast majority of the available BCF data has been determined from studies on freshwater as opposed to marine species. In this respect, the data set is of less relevance to surfactants used offshore, and extrapolation to conditions in the marine environment should be made with caution.

Much of the data presented in Table 16 was obtained from studies in which liquid scintillation counting (LSC) was used to measure surfactant concentration. This method does not allow for the quantitation of individual compounds in either mixtures of radiolabelled isomers or homologues or mixtures of a parent compound from its biotransformation products. All of the data for LAS (including the data of Lewis and Wee 1983) was obtained by quantitating mixtures by LSC. This is also true for $C_{16/18}$-TMAC (Veersteg and Shorter 1992) and C_{12}-EO_{16} (Wakabayashi et al. 1987). These data are not specific for individual components and therefore do not fulfil the definition of BCF. Since evidence exists of biotransformation of surfactants (Comotto et al. 1979; Wakabayashi et al. 1987), it is likely that much of the existing data *overestimates* the extent of accumulation of intact surfactant molecules (see also Chapter 5 of this report).

The bioconcentration of alkyl sulphate surfactants (Wakabayashi et al. 1987) is difficult to interpret. These materials are readily hydrolysed in aquatic systems and the radiolabel used in this study was [^{35}S], thus hydrolysis would yield [^{35}S] sulphate as a second radiolabelled species.

Tolls et al. (1994) noted that the data for bioconcentration was obtained on a variety of fish species, using different exposure concentrations and feeding regimes. Between-species variation in the data is quite small, while within-species variation in data is considerable. For this reason it would appear that the data is not sufficiently good to identify interspecies differences.

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Comments on log *P* data

Experimentally derived log P (log K_{ow}) values were found for a small number of surfactants (Tolls et al. 1995). Tolls noted that the formation of emulsions was a serious experimental problem in determining the octanol/water partition coefficients for surfactants. He additionally noted that measurement of log K_{ow} for ionic surfactants would yield distribution ratios rather than partition coefficients. Surfactant molecules exist in the water phase almost exclusively as ions and must pair with a counterion in order to be solvated in octanol. For this reason K_{ow} does not characterize the partitioning of ionic surfactants.

The majority of surfactant log P (log K_{ow}) data have been derived by calculation, many using equations based on the fragment contribution methods of Leo and Hansch (1979). Calculation methods are based on the theoretical fragmentation of the molecule into suitable substructures for which reliable log P_{ow} values are known. The log P_{ow} is obtained by summing these fragment values and applying correction factors for bonding, branching etc.

Many surfactants have branched chains, in which the branches can be several carbon atoms long. It is well known that physical and toxicological properties vary depending on the branching position in the surfactant; however, the fragment method gives log P values that are independent of branch position. These data may therefore not give a true representation of the potential of these surfactants to accumulate.

Roberts (1991) commented that in practice there are several difficulties relating to the calculation of log P values for surfactants by the fragment method of Leo and Hansch. Surfactants tend to be mixtures rather than pure compounds, meaning that some of the fragment values appear to be unreliable and structural factors are inadequate to model effects on physical properties of isomerism in surfactant structure. Roberts (1991) gives various equations for the calculation of log P, in which a position dependent branching factor (PDBF) has been defined in an attempt to overcome these problems.

In order to generate comparative data, the log K_{ow} calculation program (Syracuse Research Corp., SRC) was used to calculate log P for a number of primary alcohol ethoxylates ($RO(EO)_nH$, where R is primary (predominantly linear). This calculation program uses an atom/fragment contribution method developed at SRC. The log P values were then compared to those given by Roberts (1991). These data show that in some cases the two methods of calculation give similar results, but that there are significant differences for some of the data.

The data from Schuurmann (1991) calculates log K_{ow} from the equation:

$$\log K_{ow} = \log K^{0}_{ow} + (-0.10)*(\#EO-1), \qquad (5)$$

where K^{0}_{ow} denotes the K_{ow} of the mono-ethoxylate parent compound according to the CLOGP program (Leo 1989), and #EO-1 specifies the number of non-terminal ethoxylate units. This data again relies upon the fragment calculation method discussed above.

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Reliability of calculated values

For simple molecules of low molecular weight with one or two functional groups, a deviation of 0.1 to 0.3 log P_{ow} units between the results of the different fragmentation methods and experimentally derived data can be expected. As the complexity of the molecule increases, the reliability of the various methods decreases.

The areas for error concern the reliability of the various fragments used, the worker's ability to recognise intramolecular interactions (e.g. hydrogen bonding) and the correct use of the various correction factors (e.g. branching factors, proximity effects). Ionic species may be determined provided that the charge and degree are considered.

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Table 16: Existing bioconcentration factor (BCF) data for surfactants

Surfactant name	Class of surfactant	Bioconcentration factor (BCF)	Aqueous exposure conc. (μmol l^{-1})	Organism	FW/M	Reference
CRUSTACEA						
C12-Linear alkyl benzene sulphonate	Anionic	103	1.26	Water flea *Daphnia magna*	FW	Comotto et al. (1979)
C12-Linear alkyl benzene sulphonate	Anionic	720	1.26	Water flea *Daphnia magna*	FW	Comotto et al. (1979)
C12-Linear alkyl benzene sulphonate	Anionic	173	0.3	Water flea *Daphnia magna*	FW	Comotto et al. (1979)
C12-Linear alkyl benzene sulphonate	Anionic	560	0.32	Water flea *Daphnia magna*	FW	Comotto et al. (1979)
C12-Linear alkyl benzene sulphonate	Anionic	168.4 l/kg	-	Brown shrimp *Crangon crangon*	M	Ekelund et al. (1990)
C12-Linear alkyl benzene sulphonate	Anionic	99.1 l/kg	-	Water flea *Daphnia magna*	FW	Comotto et al. (1979)
C12-Linear alkyl benzene sulphonate	Anionic	47.6 l/kg	-	Water flea *Daphnia magna*	FW	Comotto et al. (1979)
C13-Linear alkyl benzene sulphonate	Anionic	1250	0.25	Water flea *Daphnia magna*	FW	Kimerle et al. (1975)
C13-Linear alkyl benzene sulphonate	Anionic	293	0.31	Water flea *Daphnia magna*	FW	Kimerle et al. (1975)
C13-Linear alkyl benzene sulphonate	Anionic	1223	0.28	Water flea *Daphnia magna*	FW	Kimerle et al. (1975)
C13-Linear alkyl benzene sulphonate	Anionic	385	0.28	Water flea *Daphnia magna*	FW	Kimerle et al. (1975)
C13.1-Linear alkyl benzene sulphonate	Anionic	696	2.52	Water flea *Daphnia magna*	FW	Kimerle et al. (1975)
C13.1-Linear alkyl benzene sulphonate	Anionic	4100	2.53	Water flea *Daphnia magna*	FW	Kimerle et al. (1975)
C11.6-Linear alkyl benzene sulphonate	Anionic	480	2.68	Water flea *Daphnia magna*	FW	Comotto et al. (1979)
MOLLUSCA						
C12-Linear alkyl benzene sulphonate	Anionic	211.5 l/kg	-	Mussel *Mytilus edilus*	M	Ekelund et al. (1990)

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Table 16. Contd

Surfactant name	Class of surfactant	Bioconcentration factor (BCF)	Aqueous exposure conc. (µmol l^{-1})	Organism	FW/M	Reference
FISH						
C10-Linear alkyl benzene sulphonate	Anionic	1.7 l/kg	-	Fathead minnow *Pimephales promelas*	FW	Tolls et al. (1997)
C10-Linear alkyl benzene sulphonate	Anionic	6 l/kg	-	Fathead minnow *Pimephales promelas*	FW	Tolls et al. (1997)
C11-Linear alkyl benzene sulphonate	Anionic	5.8 l/kg	-	Fathead minnow *Pimephales promelas*	FW	Tolls et al. (1997)
C11-Linear alkyl benzene sulphonate	Anionic	6.1 l/kg	-	Fathead minnow *Pimephales promelas*	FW	Tolls et al. (1997)
C11.6-Linear alkyl benzene sulphonate	Anionic	50	2.63	Fathead minnow *Pimephales promelas*	FW	Kimerle et al. (1975)
C11.6-Linear alkyl benzene sulphonate	Anionic	269	0.79	Fathead minnow *Pimephales promelas*	FW	Comotto et al. (1979)
C11.7-Linear alkyl benzene sulphonate	Anionic	104	1.45	Bluegill sunfish *Lepomis macrochirus*	FW	Kimerle et al. (1975)
C12-Linear alkyl benzene sulphonate	Anionic	8	0.2	Water flea *Daphnia magna*	FW	Comotto et al. (1979)
C12-Linear alkyl benzene sulphonate	Anionic	58	0.46	Fathead minnow *Pimephales promelas*	FW	Comotto et al. (1979)
C12-Linear alkyl benzene sulphonate	Anionic	108	0.23	Bluegill sunfish *Lepomis macrochirus*	FW	Bishop and Maki (1980)
C12-Linear alkyl benzene sulphonate	Anionic	10.5 l/kg	-	Stickleback *Gasterosteus aculeatus*	FW	Ekelund et al. (1990)
C12-Linear alkyl benzene sulphonate	Anionic	145	0.23	Bluegill sunfish *Lepomis macrochirus*	FW	Bishop and Maki (1980)
C12-Linear alkyl benzene sulphonate	Anionic	490	0.2	Fathead minnow *Pimephales promelas*	FW	Comotto et al. (1979)
C12-Linear alkyl benzene sulphonate	Anionic	551	0.29	Zebra danio *Brachydanio rerio*	FW	Coenen (1988)
C12-Linear alkyl benzene sulphonate	Anionic	227	2.3	Bluegill sunfish *Lepomis macrochirus*	FW	Bishop and Maki (1980)
C12-Linear alkyl benzene sulphonate	Anionic	231	0.3	Bluegill sunfish *Lepomis macrochirus*	FW	Bishop and Maki (1980)
C12-Linear alkyl benzene sulphonate	Anionic	245	0.4	Fathead minnow *Pimephales promelas*	FW	Comotto et al. (1979)

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Table 16. Contd

Surfactant name	Class of surfactant	Bioconcentration factor (BCF)	Aqueous exposure conc. (µmol l-1)	Organism	FW/M	Reference
C12-Linear alkyl benzene sulphonate	Anionic	280	2.3	Bluegill sunfish *Lepomis macrochirus*	FW	Bishop and Maki (1980)
C12-Linear alkyl benzene sulphonate	Anionic	31.9 l/kg	-	Bluegill sunfish *Lepomis macrochirus*	FW	Gledhill et al. (1991)
C12-Linear alkyl benzene sulphonate	Anionic	42.1 l/kg		Calculated		Gledhill et al. (1991)
C13-Linear alkyl benzene sulphonate	Anionic	34.0 l/kg	-	Fathead minnow *Pimephales promelas*	FW	Tolls et al. (1997)
C13-Linear alkyl benzene sulphonate	Anionic	358.3 l/kg	-	Fathead minnow *Pimephales promelas*	FW	Tolls et al. (1997)
C13-Linear alkyl benzene sulphonate	Anionic	142	0.25	Bluegill sunfish *Lepomis macrochirus*	FW	Kimerle et al. (1981)
C13.1-Linear alkyl benzene sulphonate	Anionic	472	1.17	Fathead minnow *Pimephales promelas*	FW	Kimerle et al. (1975)
C13-Linear alkyl benzene sulphonate	Anionic	1050	0.3	Fathead minnow *Pimephales promelas*	FW	Kimerle et al. (1975)
C13-Linear alkyl benzene sulphonate	Anionic	1325	1.13	Fathead minnow *Pimephales promelas*	FW	Kimerle et al. (1975)
C13-Linear alkyl benzene sulphonate	Anionic	987.2 l/kg	-	Fathead minnow *Pimephales promelas*	FW	Tolls et al. (1997)
C12- Alkyl sulphate	Anionic	2.6	13.9	Bluegill sunfish *Lepomis macrochirus*	FW	Bishop and Maki (1980)
C12- Alkyl sulphate	Anionic	2.7	0.093	Bluegill sunfish *Lepomis macrochirus*	FW	Bishop and Maki (1980)
C12- Alkyl sulphate	Anionic	4.6	1.39	Bluegill sunfish *Lepomis macrochirus*	FW	Bishop and Maki (1980)
C12- Alkyl sulphate	Anionic	7.15	13.9	Bluegill sunfish *Lepomis macrochirus*	FW	Bishop and Maki (1980)
Linear alkyl benzene (LAB)	Parent To LAS	6250 - 6600	-	Fathead minnow *Pimephales promelas*	FW	Veersteg and Shorter (1992)
Linear alkyl benzene (LAB)	Parent To LAS	35	92	Fathead minnow *Pimephales promelas*	FW	Veersteg and Shorter (1992)
Linear alkyl benzene sulphonate	Anionic	94	0.680	Fathead minnow *Pimephales promelas*	FW	Veersteg and Shorter (1992)
Linear alkyl benzene sulphonate	Anionic	220	0.064	Fathead minnow *Pimephales promelas*	FW	Veersteg and Shorter (1992)
Linear alkyl benzene sulphonate (LAS)	Anionic	104	500	Fathead minnow *Pimephales promelas*	FW	Veersteg and Shorter (1992)

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Table 16. Contd

Surfactant name	Class of surfactant	Bioconcentration factor (BCF)	Aqueous exposure conc. (µmol l^{-1})	Organism	FW/M	Reference
C_8-Monoalkyltrimethyl ammonium compound	Cationic	2.4	n.a	Fathead minnow *Pimephales promelas*	FW	Tolls et al. (1997)
C_8-Monoalkyltrimethyl ammonium compound	Cationic	0.5	n.a	Fathead minnow *Pimephales promelas*	FW	Tolls et al. (1997)
C_{12}-Monoalkyltrimethyl ammonium compound	Cationic	41	n.a	Fathead minnow *Pimephales promelas*	FW	Kimerle et al. (1975)
C_{12}-Monoalkyltrimethyl ammonium compound	Cationic	35	n.a	Bluegill sunfish *Lepomis macrochirus*	FW	Huber (1984)
$C_{16/18}$-Monoalkyltrimethyl ammonium compound	Cationic	1962	n.a	Fathead minnow *Pimephales promelas*	FW	Tolls et al. (1997)
$C_{16/18}$-Monoalkyltrimethyl ammonium compound	Cationic	141	n.a	Fathead minnow *Pimephales promelas*	FW	Tolls et al. (1997)
(C16/18)2 Dimethyldialkyl ammonium compound	Cationic	32	0.034	Bluegill sunfish *Lepomis macrochirus*	FW	Lewis and Wee (1983)
(C16/18)2 Dimethyldialkyl ammonium compound	Cationic	13	0.039	Bluegill sunfish *Lepomis macrochirus*	FW	Lewis and Wee (1983)
(C18)2 Dimethyldialkyl ammonium compound	Cationic	38	n.a	Fathead minnow *Pimephales promelas*	FW	Veersteg and Shorter (1992)
(C18)2 Dimethyldialkyl ammonium compound	Cationic	104	n.a	Fathead minnow *Pimephales promelas*	FW	Veersteg and Shorter (1992)
(C18)2 Dimethyldialkyl ammonium compound	Cationic	3	n.a	Fathead minnow *Pimephales promelas*	FW	Veersteg and Shorter (1992)
Distearyl dimethyl ammonium chloride	Cationic	32	20	? *Proterorhinus marmaratus*		Topcuoglu and Birol (1981)
Nonylphenol (parent to Nonylphenol ethoxylates)	Non-Ionic	200	0.031	Fathead minnow *Pimephales promelas*	FW	Veersteg and Shorter (1992)
Nonylphenol (parent to Nonylphenol ethoxylates)	Non-Ionic	23		Common carp *Cyprinus carpio*	FW	Wakabyashi et al. (1981)
Alkyloxyethylene surfactant ($C_{12}EO_{16}$)	Non-Ionic	4.3	0.280	Common carp *Cyprinus carpio*	FW	Wakabyashi et al. (1987)
Alkyloxyethylene surfactant ($C_{12}EO_8$)	Non-Ionic	222	0.450	Common carp *Cyprinus carpio*	FW	Wakabyashi et al. (1987)
Alkyloxyethylene surfactant ($C_{12}EO_4$)	Non-Ionic	309	0.690	Common carp *Cyprinus carpio*	FW	Wakabyashi et al. (1987)

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Table 16. Contd

Surfactant name	Class of surfactant	Bioconcentration factor (BCF)	Aqueous exposure conc. (µmol l^{-1})	Organism	FW/M	Reference
$C_{14}EO_7$	Non-Ionic	684	4.100	Fathead minnow *Pimephales promelas*	FW	Tolls et al. (1997)
Nonylphenol (parent to Nonylphenol ethoxylates)	Non-Ionic	3430	0.022	Common carp *Cyprinus carpio*	FW	Wakabyashi et al. (1981)
Tetradecylheptaethoxylate	Non-Ionic	710	0.154	Bluegill sunfish *Lepomis macrochirus*	FW	Bishop and Maki (1980)
Tetradecylheptaethoxylate	Non-Ionic	710	0.014	Bluegill sunfish *Lepomis macrochirus*	FW	Bishop and Maki (1980)
$C_{14}EO_7$	Non-Ionic	721	0.41	Fathead minnow *Pimephales promelas*	FW	Tolls et al. (1997)
$C_{14}EO_7$	Non-Ionic	799	n.a.	Fathead minnow *Pimephales promelas*	FW	Tolls et al. (1997)
Nonylphenol (parent to Nonylphenol ethoxylates)	Non-Ionic	1250	0.028	Common carp *Cyprinus carpio*	FW	Wakabyashi et al. (1981)

FW = freshwater; M = marine

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Table 17. Existing log *P* data for surfactants

Surfactant name	Class of surfactant	log P (log K_{ow})	Organism/Method	Reference
C_{12}- Alkyl sulphate	Anionic	1.60	*Fish*	Tolls (1995)
C_{12}-Linear alkyl benzene sulphonate	Anionic	3.00	Log K_{ow} Calculation Program	Syracuse Research Corporation
C_{13}-Linear alkyl benzene sulphonate	Anionic	2.11	Rainbow trout *Onchorynchus mykiss*	Tolls (1995)
C_{13}-Linear alkyl benzene sulphonate	Anionic	2.52	-	Tolls (1995)
Linear alkyl benzene (LAB)	Parent To LAS	5.72-5.75	Calculated	Gledhill et al. (1991)
Linear alkyl benzene sulphonate	Anionic	-0.45	-	Tolls (1995)
Linear alkyl benzene sulphonate	Anionic	1.91	Rainbow trout *Onchorynchus mykiss*	Tolls (1995)
Linear alkyl benzene sulphonate	Anionic	1.96	QSAR	Tolls (1995)
$(C_{16/18})$2 Dimethyldialkyl ammonium compound	Cationic	2.69	-	Tolls (1995)
C_{16}-Monoalkyltrimethyl ammonium compound	Cationic	1.81	*Fish*	Tolls (1995)
Butyl diethyl phenol ethoxylate	Non-Ionic	4.70	Calculated	Schuurmann (1991)
Nonylphenol ethoxylate	Non-Ionic	5.10	*Calculated*	Schuurmann (1991)
Nonylphenol ethoxylate	Non-Ionic	1.00	*Calculated*	Schuurmann (1991)
Nonylphenol (parent to Nonylphenol ethoxylates)	Non-Ionic	4.20	-	Tolls (1995)
Nonylphenol (parent to Nonylphenol ethoxylates)	Non-Ionic	4.48	-	Tolls (1995)
Primary alcohol ethoxylate $(RO(EO)_nH)$, R= 10, n=6	Non-Ionic	4.19	Calculation	Roberts (1991)
Primary alcohol ethoxylate $(RO(EO)_nH)$, R= 10, n=6	Non-Ionic	4.98	Log K_{ow} Calculation Program	Syracuse Research Corporation
Primary alcohol ethoxylate $(RO(EO)_nH)$, R= 10, n=6	Non-Ionic	4.98	Log K_{ow} Calculation Program	Syracuse Research Corporation
Primary alcohol ethoxylate $(RO(EO)_nH)$, R= 10, n=6	Non-Ionic	4.98	Log K_{ow} Calculation Program	Syracuse Research Corporation
Primary alcohol ethoxylate $(RO(EO)_nH)$, R= 12, n=11	Non-Ionic	4.60	Log K_{ow} Calculation Program	Syracuse Research Corporation
Primary alcohol ethoxylate $(RO(EO)_nH)$, R= 12, n=11	Non-Ionic	4.77	Calculation	Roberts (1991)
Primary alcohol ethoxylate $(RO(EO)_nH)$, R= 12, n=3	Non-Ionic	5.73	Calculation	Roberts (1991)
Primary alcohol ethoxylate $(RO(EO)_nH)$, R= 12, n=3	Non-Ionic	7.25	Log K_{ow} Calculation Program	Syracuse Research Corporation
Primary alcohol ethoxylate $(RO(EO)_nH)$, R= 12, n=9	Non-Ionic	5.13	Calculation	Roberts (1991)
Primary alcohol ethoxylate $(RO(EO)_nH)$, R= 12, n=9	Non-Ionic	5.60	Log K_{ow} Calculation Program	Syracuse Research Corporation
Primary alcohol ethoxylate $(RO(EO)_nH)$, R= 13, n=9	Non-Ionic	5.13	Calculation	Roberts (1991)
Primary alcohol ethoxylate $(RO(EO)_nH)$, R= 13, n=9	Non-Ionic	5.63	Log K_{ow} Calculation Program	Syracuse Research Corporation
Primary alcohol ethoxylate $(RO(EO)_nH)$, R= 14, n=8	Non-Ionic	5.61	Calculation	Roberts (1991)

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Table 17. Contd

Surfactant name	Class of surfactant	Log P (log K_{ow})	Organism/Method	Reference
Primary alcohol ethoxylate ($RO(EO)_nH$), R= 14, n=8	Non-Ionic	5.68	Log K_{ow} Calculation Program	Syracuse Research Corporation
Primary alcohol ethoxylate ($RO(EO)_nH$), R= 16, n=14	Non-Ionic	5.74	Log K_{ow} Calculation Program	Syracuse Research Corporation
Primary alcohol ethoxylate ($RO(EO)_nH$), R= 16, n=14	Non-Ionic	6.63	Calculation	Roberts (1991)
Propyl dipropyl phenol ethoxylate	Non-Ionic	4.90	Calculation	Schuurmann (1991)
Propyl dipropyl phenol ethoxylate	Non-Ionic	4.30	Calculation	Schuurmann (1991)
Propyl dipropyl phenol ethoxylate	Non-Ionic	1.80	Calculation	Schuurmann (1991)
Propyl dipropyl phenol ethoxylate	Non-Ionic	0.80	Calculation	Schuurmann (1991)
$C_{14}EO_7$	Non-Ionic	2.47		Tolls (1995)
Coconut alcohol sulphate		1.96	Calculation	Roberts (1991)
Decanol ethoxylate	Non-Ionic	3.70	Calculation	Schuurmann (1991)
Tergitol		4.68	Calculation	Roberts (1991)

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Chapter

7

ALTERNATIVE ANALYTICAL APPROACHES

Introduction

This section of the review focuses on the evaluation of alternative QSAR approaches to determining a log P_{ow}/BCF for surfactants, using currently available analytical techniques that could be developed as alternatives to the OECD 107 and 117 tests. Reliability and costs are discussed and potential future innovations examined. Inevitably these methods will need to be correlated with data from live animal testing, and mathematical models (QSARs) developed and verified.

Database and literature searches were carried out using :-

- STN - Chemical Abstracts on-line
- BIDS ISI Data Service
- Analytical Chemistry
- SETAC
- HPCE - Capillary Electrophoresis Abstracts
- Journal of Chromatography
- Internet
- General Correspondence

The result of the searches indicated that there are currently two possible alternative approaches. A form of capillary electrophoresis called micro-emulsion electrokinetic chromatography (MEEKC), which would correlate well for the determination of log P_{ow} is one option. The other is more directly related to the BCF approach and is based on a semi-permeable membrane device (SPMD) . In principle this device mimics animal or single-cell function by allowing a partition to occur without formation of the emulsions that inevitably occur when handling surfactants.

Alternative Available Methods

Electrokinetic Chromatography

Micellar electrokinetic capillary chromatography (MECC)

MECC was initially developed (Strasters and Khaledi 1991) for the resolution of uncharged compounds that cannot be separated using simple free-solution capillary electrophoresis (CE). The separation conditions involve use of a high-pH electrolyte containing relatively high levels of surfactant such as sodium dodecyl sulphate (SDS). Above a specific surfactant concentration, i.e. the critical micelle concentration (CMC), the surfactant molecules begin to self-aggregate, forming micelles in which the hydrophilic head groups form an outer shell and the hydrophobic tail groups form a non-polar core into which solutes can partition. SDS micelles have a negative charge and migrate against the electro-osmotic force (EOF; see Fig. 4). However, the EOF is sufficiently strong to force the micelles to eventually pass through the detector. Sample species can partition into the interior of the micelle in a fashion similar to retention on a stationary phase in a HPLC. The differential partitioning between the buffered aqueous mobile phase and the micellar (pseudo) stationary phase is the sole basis for separation for neutral molecules .

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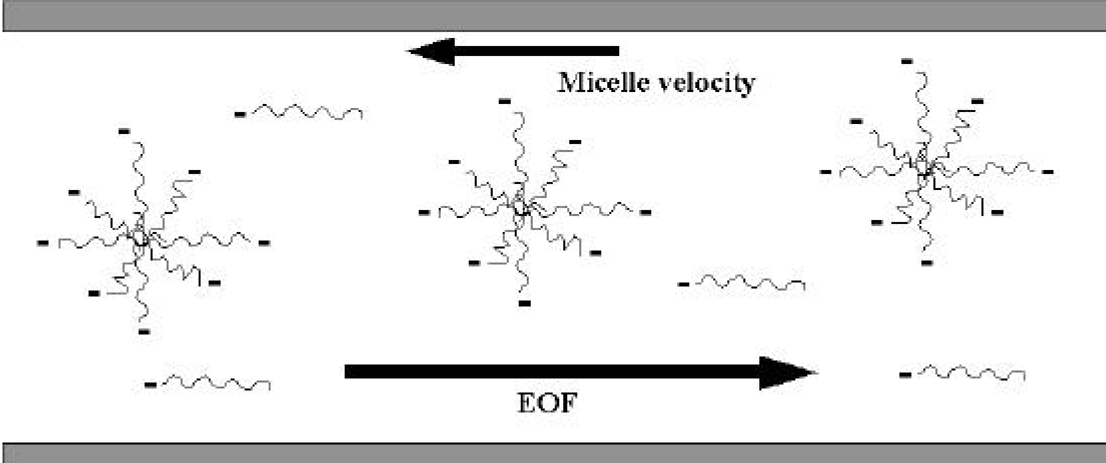

Fig. 4. Schematic of the principles of MECC

The retention time, t_r for a neutral species is always between t_o and t_{mc}:

$$tr = \left(\frac{1 + k'}{1 + \frac{to}{tmc} k'} \right) to \quad (6)$$

where t_o is the time required for an unretained substance to travel through the capillary (from injection point to detection window), t_{mc} is the time required for a micelle to traverse the capillary. Solutes being highly retained by the micelle will be eluted later (Fig. 6), while solutes that have only a limited interaction with the micelle will be eluted near to the EOF front (t_o). Extremely hydrophobic compounds may be totally included into the micelle and would be detected at t_{mc}. Sudan III is a hydrophobic dye that is totally included into the micelle (t_{mc}) and is widely used to mark the migration time of the micelle.

The capacity factor k' for a neutral species can be calculated in MECC using the equation:

$$k' = \frac{\frac{t_r}{t_o} - 1}{1 - \frac{t_r}{t_{mc}}} \quad (7)$$

A solute that elutes with the solvent front has a capacity factor of zero and a solute eluting with at the t_{mc} would be considered to have an infinite capacity factor. A solute spending equal time in the aqueous solute and in the micelle would have a capacity factor of 1 in the first instance as both of these factors affect solute capacity factors. The most common surfactant used for MECC is SDS (an anionic surfactant). Others include cetyltrimethylammonium bromide (cationic surfactant) and bile salts (an anionic surfactant). Mixtures of surfactants can be used, including neutral surfactants such as Tween and Brij. The selectivity of the MECC system is mainly controlled by the nature of the

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surfactant. Separations are invariably conducted at high pH where there is an appreciable EOF. Organic solvents and ion-pair reagents can also be added to the MECC buffer to adjust the capacity factors, just as in reverse-phase HPLC separations.

MECC is especially useful for the resolution of water-insoluble, neutral compounds such as steroids. There are a number of bile salts such as sodium cholate that can be used in MECC. The bile salts are chiral and can be used in chiral separations - alternatively chiral separations can be achieved through use of combinations of SDS micelles and cyclodextrins. The figure below shows separation of a range of insoluble neutral steroids by MECC using bile salt micelles.

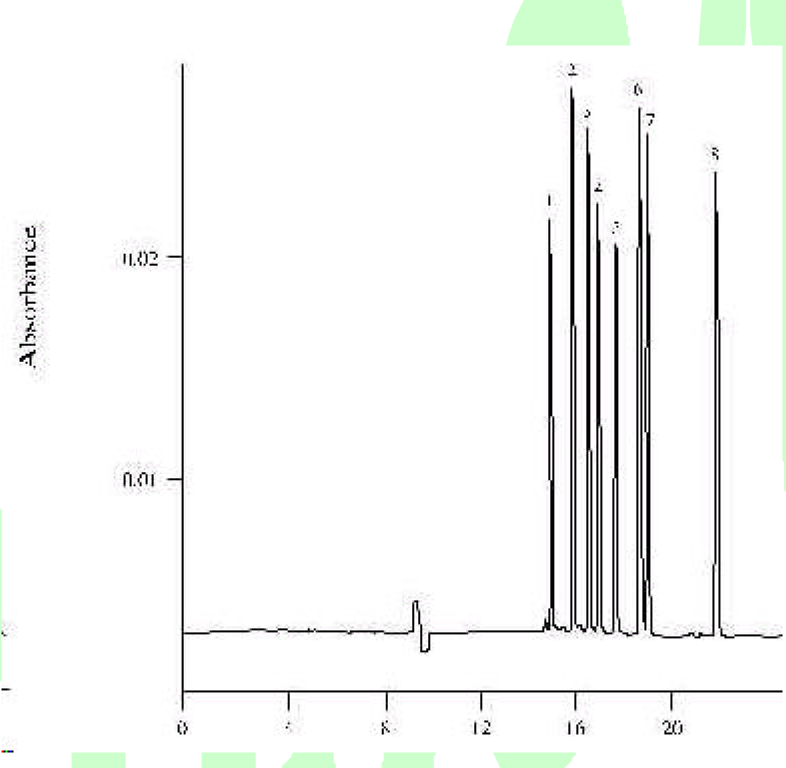

Fig. 5. Separation of corticosteroids by MECC. Buffer, 100 mM sodium cholate, 100 mM borate, pH 8.45. *1, triamcinolone; 2, hydrocortisone; 3, betamethasone; 4, hydrocortisone acetate; 5, dexamethasone acetate; 6, triamcinolone acetonide; 7, fluocinolone acetanide; 8, fluocinolone*

Since both HPLC and MECC are chromatography-based techniques the separation profiles are similar to reverse-phase HPLC. However, solute partitioning is different between MECC and HPLC, which results in different profiles. Additionally, if species are charged then they will be separated in MECC on the basis of the sum of both their electrophoretic mobility and partitioning. Therefore, MECC is useful for determination of drug-related impurities where mixtures of charged and uncharged components may be resolved. The other feature of MECC is that all components injected into the capillary, provided that they are sufficiently soluble in the electrolyte, will migrate between t_o and t_{mc}. This is unlike HPLC, where some components may be irreversibly adsorbed onto the stationary phase. MECC separations are performed on the same equipment as FSCE and employ capillaries of similar dimensions.

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Microemulsion electrokinetic capillary chromatography (MEEKC)

There is another form of electrokinetic chromatography that involves use of microemulsions composed of oil droplets suspended in buffers containing surfactants. This is known as **microemulsion electrokinetic capillary chromatography** (MEEKC). The most widely used MEEKC buffer involves a high-pH borate buffer containing SDS and octane. An alcohol such as butan-1-ol is often used to stabilise the emulsion. Separations in MEEKC are similar to MECC and for neutral solutes are based on the solubility and partitioning of the solutes. The figure below shows separation of a range of neutral solutes using a MEEKC method.

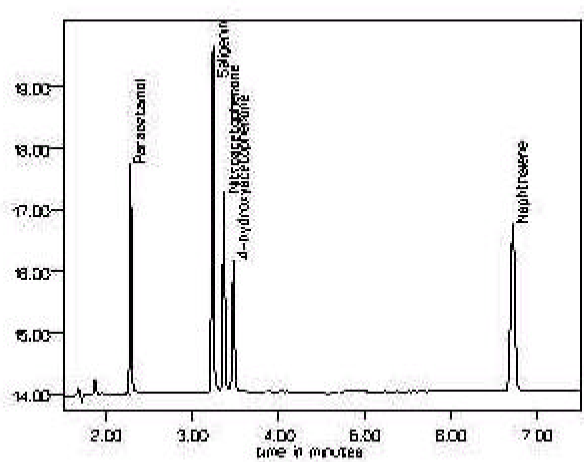

Fig. 6. Separation of neutral solutes using MEEKC

MEEKC has been used by Smith and Vinjamoori (1995) to determine K_{ow} values for a number of simple organic compounds, which gave a good correlation with HPLC-generated values. In addition, Salimi-Moosavi and Cassidy (1996) have further adapted the technique to separate long-chain surfactants, and have looked at improving the separation technique for general surfactant applications.

Micellar electrokinetic chromatography (MEKC)

Micellar electrokinetic chromatography (MEKC) is a mode of capillary electrophoresis (CE) in which the effective mobility of an analyte is a function of the extent of partitioning into a charged micelle (Vindervogel and Sandra 1992; Camilleri 1993; Weinberger 1993). Since the pioneering work by Terabe et al. (1984) a number of excellent papers have been published on the MEKC analysis of neutral (Foley 1990; Ghowski et al. 1990), cationic (Strasters and Khaledi 1991), and anionic (Khaledi et al. 1991) compounds by optimization of differences in their micellar binding equilibria.

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The method most frequently used to analyse neutral compounds is high-performance liquid chromatography (HPLC), especially the reversed-phase mode (Lough and Wainer 1996). The separation mechanisms of MEKC and RP-HPLC are often considered to be analogous (Weinberger 1993). Both techniques work by differential partitioning of the analytes into an alkyl phase. In MEKC, analytes partition into an alkyl surfactant micelle, while in HPLC analytes typically partition into an alkyl-chain stationary phase. MEKC and HPLC have their own particular benefits. MEKC has higher peak efficiency than HPLC and can often produce excellent analyte resolution. HPLC offers higher detection limits than MEKC, has preparative capabilities, and is generally more robust and reproducible.

In previous studies, correlations have been made between retention factors in MEKC and octanol-water partition coefficients K_{ow} (Ishihama et al. 1994), and also between retention factors in HPLC and K_{ow} values. These correlations have been used in quantitative structure-activity relationships (QSARs) for protein-drug interactions.

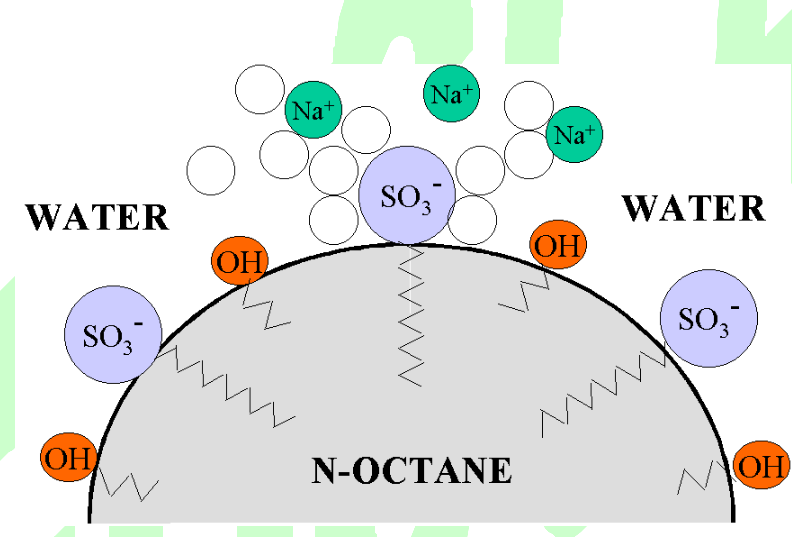

Fig. 7. Diagrammatic representation of anionic micelle structure

Reproducibility in Capillary Electrophoresis [courtesy Beckman Coulter]

Many factors are involved in reproducibility. Some of these, such as temperature control, voltage control, and sample injection precision, are inherent in the design of the instrument. Other factors, such as the quality of the reagents used and the manner in which the instrument is programmed and operated, are completely in the hands of the user. These two factors, the quality of the instrument and the quality of the operation, are both required in order to achieve reproducible results. To determine the typical reproducibility that can be achieved on the P/ACE System MDQ, we evaluated the separation of two very similar analytes in a commercially available test mixture (System Performance Test Mix "B," Beckman Coulter, Inc.). This test mix contains two organic acids: p-hydroxybenzoic acid (0.72 mmol/l) and p-hydroxyphenyl-acetic acid (0.66 mmol/l). The peak area %RSD for the entire set of 100 runs is 1.52% for Peak A and 1.67% for Peak B.

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Harry Whatley and Jeff Chapman
Beckman Coulter Inc.

Advantages of the electrokinetic technique

The application of HPLC for the determination of log P_{ow} on drilling fluids is far from satisfactory due to the limited resolution of complex mixtures and variable sensitivities towards major and minor components. While its main application is for single-component studies, there is a clear need for a method that can cope with mixtures and homologues of unknown molecular weight ranges. It seems to be generally acknowledged that reported values, particularly where weighted averages are used, overestimate the potential for bioaccumulation. Recent papers (reviewed by Altria 1999) indicate that MEEKC separation is directly proportional to hydrophobicity, i.e. log P_{ow}. The technique has been available since 1995 and there is a substantial body of supporting literature that would ease its transition to a standard method. It would appear that two instrument manufacturers supply systems at a cost of around £40,000, which is compatible with the HPLC systems currently used for current OECD 117 studies. However, some further development of methodology would be required for the application of this technique to surfactant analysis.

Semi-permeable Membrane Devices (SPMD)

A second analytical approach offering potential for development is the use of semi-permeable membrane devices [SPMDs], which would mimic the actual behaviour of surfactants between oil and water without causing the formation of emulsions. This can be seen as analogous to the shake flask method (OECD 107), which has been superseded by the more convenient HPLC method (OECD117). The following description of the function of SPMDs is taken from a project by Darius Sabaliunas and Anders Södergren at Lund University, Sweden, where significant research is being performed with these devices.

Application of Semi-permeable Membrane Devices in Environmental Analysis

Modern environmental analysis and monitoring methods have become increasingly expensive as a consequence of constantly rising environmental quality criteria, and the necessity to measure concentrations of pollutants at ultra-low levels. Nowadays, there is a clear need for rapid, effective and low-cost integrated methods that would allow not only direct monitoring of the fate and concentrations of chemical pollutants in the environment, but also an evaluation of the effects and risks these chemicals pose to the environment and human health.

Membrane-based passive samplers seem to be a promising tool for the time-integrated monitoring of hydrophobic pollutants in aquatic ecosystems. In these devices, the uptake of chemicals is based on the process of passive partitioning of a compound between water and a lipophilic solvent enclosed in a semi-permeable polymeric membrane. Thus, the passive samplers can be used as indicators of bioavailability of chemical pollutants. Furthermore, contrary to most living organisms, SPMDs can be exposed to harsh environmental conditions for long time periods and still remain operative.

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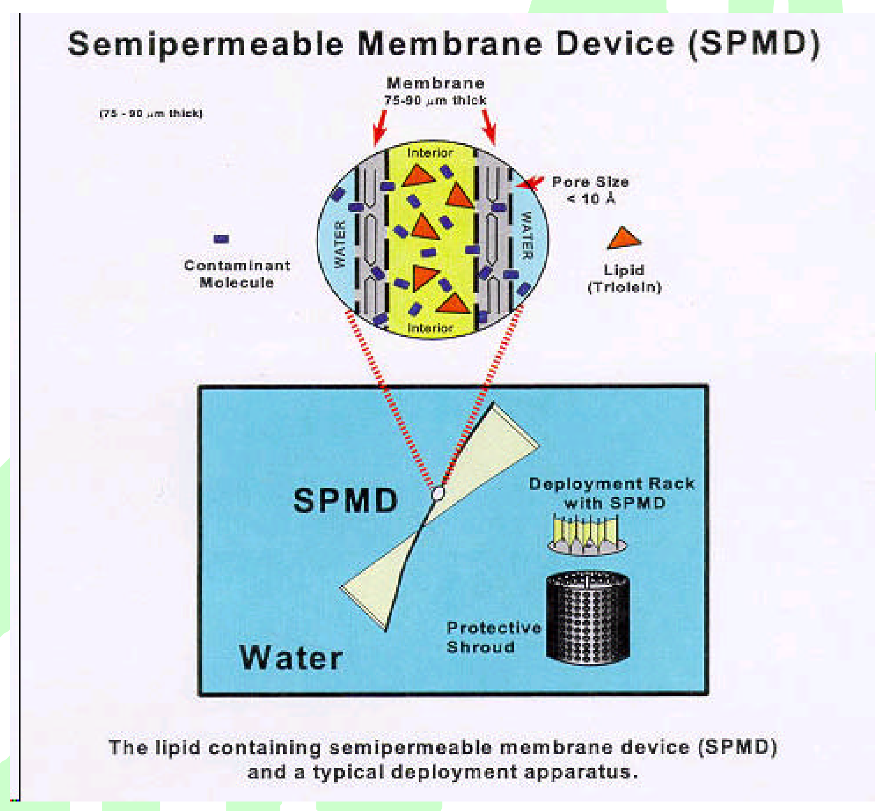
Laboratory analysis of the passive sampler is generally both faster and less expensive than many conventional water, sediment, or tissue analysis methods. Several designs of membrane samplers have been proposed. They include SPMDs; hexane-filled dialysis bags made of cellulose tubing, SPMDs consisting of a thin film of neutral lipid, enclosed in thin-walled, flat tubing made of low-density polyethylene or other non-porous polymer; cellulose dialysis membranes containing micellar receiving solvent; and polyethylene tubes filled with isooctane. Of these systems, SPMDs proved to be most effective in their capacity to accumulate lipophilic substances. Chemicals can be concentrated in SPMDs to levels comparable to or even higher than the values of their octanol/water partition coefficients or bioconcentration factors in aquatic organisms.

The following diagram illustrates how an SPMD works



The lipid containing semipermeable membrane device (SPMD) and a typical deployment apparatus.

Fig. 8. How an SPMD works

The SPMD itself consists of a flat plastic tube with lipid or fat sealed inside. As shown in Fig. 8, the membrane allows free (bioavailable) contaminants to pass through to the lipid while excluding water. The SPMD is placed on a rack, which is inserted within a protective "shroud," and is then ready for use in the water.

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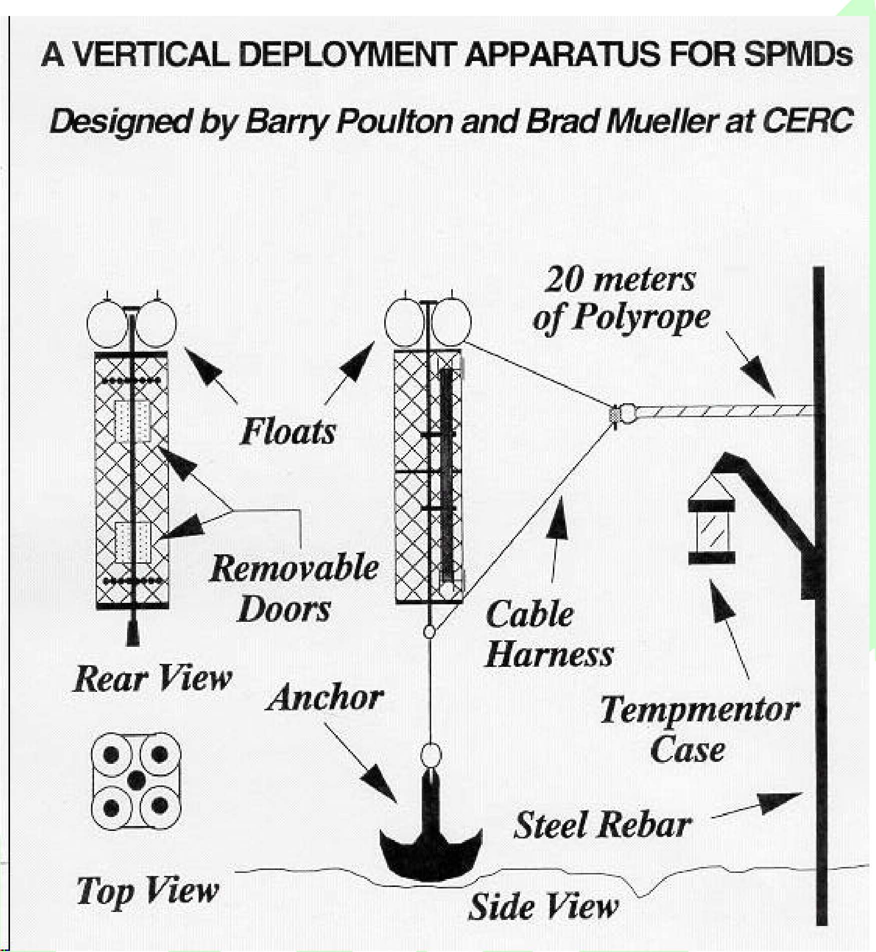
A SPMD can also be used vertically and horizontally as illustrated below:



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As can be seen from the above description the use of SPMDs would involve a fairly large-scale test and therefore the costs would be relatively higher than those performed using MEEKC, which would be of the same order as the OECD 117 tests.

In any event, to gain widespread acceptance, correlation and comparison with existing methods needs to be undertaken. The accumulated surfactants would need to be analysed and the extraction processes are complex.

Future Requirements

For any development project to be successful the exact requirements of the analytical method must be defined. Topics which need to be addressed are:

- method scope - range of compounds
- costs
- development of a standard method for surfactants
- data comparison with HPLC (OECD 117)
- data comparison with live animal testing
- timescales

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Capillary elektrophoresis

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EOSCA

Chapter

8

CONCLUSIONS and SUMMARY

Conclusions

This review of the available information on the bioaccumulation potential of surfactants, while extensive, is by no means exhaustive. The review has considered the following environmental issues of the use and discharge of surfactants in general: existing oilfield surfactant chemistry and classification; environmental risk assessment; toxicity of surfactants to aquatic organisms; environmental fate and behaviour of surfactants; mechanisms and routes of surfactant bioaccumulation and biomagnification; existing bioaccumulation data for surfactants; alternative analytical approaches to estimating BCF. While each of these topics has been presented and discussed more fully in the main body of the report, the following general conclusions can be drawn from the information that has been obtained and evaluated:

1. There is a need for an industry standard definition of a surfactant.

2. There is limited ecotoxicological data for surfactants in the marine environment. Existing (largely freshwater) data does not indicate a specific generic problem with aquatic toxicity.

3. There is a lack of relevant and reliable partitioning data for surfactants currently used and discharged in the North Sea.

4. There is a need for a greater understanding of the potential of surfactants to modify the availability and/or toxicity of other pollutants in the marine environment.

5. Bioconcentration factors (BCFs) for surfactants in the aqueous phase are generally below the level for concern. Many reported BCFs are probably overestimates.

6. BCFs derived from current QSARs based on log P_{ow} data for surfactants are not reliable. The majority of the surrogate partitioning parameters (OECD 117/107, QSARs) do not give reliable and robust quantitation for use in hazard and risk assessment of surfactant molecules.

7. Available data from biodegradation studies on surfactants in seawater do not indicate that persistence of surfactant molecules in the marine environment is likely to be a problem. Existing HOCNF data from studies of biodegradation of surfactants in seawater (OECD 306 and Marine BODIS) are not included in this review, but represent a valuable source of (quality-assured) data.

8. There is no evidence to support concerns with respect to biomagnification of surfactants.

9. There is no evidence to support concerns with respect to long-term retention of bioaccumulated surfactants.

10. Two surrogate techniques which may be usefully explored as alternative approaches to determining partition coefficients for surfactants are: MEEKC (MicroEmulsion ElectroKinetic Chromatography); and SPMDs (Semi-Permeable Membrane Devices).
    Direct assessment of surface tension may also be a worthwhile candidate for further investigation.

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SUMMARY

Environmental Issues

All major surfactant groups (anionic, cationic, nonionic and amphoteric) are currently used to some extent by the offshore oil industry. Nonionic surfactants are the most widely used, with perhaps the greatest concern focusing on the bioaccumulation potential of alkylphenol ethoxylates, for some of which there is tentative evidence of weak endocrine disruption activity. Interest in the bioaccumulation of surfactants has increased over recent years due to the large quantities of these materials manufactured and the relatively high proportion discharged to the environment. In environmental terms, surfactants possess properties that mean that their fate and behaviour in an aqueous environment will differ from that predicted for non-surface-active chemicals. In particular, they all have a combined lipophilic/hydrophilic structure which gives them a tendency to collect at aqueous/organic-phase boundaries, and they will form micelles in water when present above critical levels (CMC). Most surfactants are susceptible to biodegradation, metabolism and other breakdown reactions that may lead to metabolites with significantly different chemical properties.

The quantities of each class of surfactant used are difficult to estimate and no specific information has been provided in this review. As an approximation, anionic surfactants are the most important, representing 60-70% of surfactants currently in use. Non-ionic compounds constitute around 30% but their use is increasing, while cationic and amphoteric products make up the smallest proportion. Currently adopted approaches to hazard assessment and risk management of chemicals, including surfactants, used and discharged offshore in the North Sea are based on a harmonised scheme of testing and evaluation (Harmonised Offshore Chemical Notification Format, OSPAR HOCNF 1995; and CHARM). The octanol-water partition coefficient (log P_{ow}) has been defined as a central parameter in the risk assessment of offshore chemicals, being used to estimate predicted environmental concentration (PEC) through its use in partitioning calculations (CHARM), but the evidence is not convincing enough to support the view that it *is* a key parameter, especially for surfactants or complex mixtures. There are a lot of experimental data which indicate that it is often useless in this respect for oilfield chemicals, and that indeed there is no single partition coefficient for many chemicals (i.e., their partitioning behaviour depends on various factors such as salinity, pH and temperature). Log P_{ow} demonstrably does *not* determine environmental fate, although it is used for this purpose.

If log P_{ow} is not considered to be satisfactory for bioaccumulation prediction, then it is not only unsatisfactory for sediment partitioning estimation, but it is *a priori* unsatisfactory for estimating the amount released in produced water. Surfactants are important, and often significant (in terms of quantity) components of production chemicals, and using current approaches, log P_{ow} is clearly an unsatisfactory parameter as a basis for hazard and risk assessment of surfactants and/or highly hydrophobic chemicals. The current (mandatory) test methods adopted in the HOCNF (OECD 117 HPLC method or OECD 107 Shake Flask method) are inherently unsuitable for the determination of a log P_{ow} for surface-active chemicals, not least because of the tendency for surfactant molecules to accumulate at phase interfaces or form emulsions, thereby giving spurious and unreliable results. Despite these obvious limitations, regulatory authorities have based environmental hazard and risk assessment of surfactants on log P_{ow} data obtained from these tests (HOCNF). In reality the existing OECD 117 HPLC method is being misused by being applied to formulations of "unknown" content, and in particular the estimation of a weighted-average log P_{ow} for anything other than a group of homologues cannot be construed as scientifically valid. Intended changes to the present requirements of the HOCNF (Summary Record SEBA 2000) propose that log P_{ow} determinations for surfactants should be abandoned in favour of a sediment-water partitioning coefficient (K_{oc}), and

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that default values should be used for fraction released to water and for BCF. This should be regarded as only a temporary measure, until industry and regulatory authorities have explored other approaches or looked at ways of improving current methodology, particularly focusing on some of the large-volume surfactants currently in use.

A factor that has been largely overlooked in the environmental assessment of surfactants, apart from the intrinsic toxicity of the surfactant, is that of the potential synergistic effects on migration, dispersion, bioavailability, etc. of otherwise low-toxicity chemical compounds in a formulation. The current HOCNF guidelines accept that surfactants may increase the bioavailability of other substances in preparations, and suggest that a bioconcentration test may be required in such cases. However, it is difficult to justify a "black box" regulatory approach that relies on a single and often arbitrary measurement. Any assessment of bioaccumulation potential should, realistically, take into account as much information as possible on the chemistry, metabolism, degradability and potential breakdown products of the chemical. With oilfield chemicals, this can be difficult, since they are often quite complex mixtures and their chemistry is often very poorly described.

Default fraction released values estimated from available log P_{ow} data and adopted in CHARM evaluations are viewed as extremely conservative, as exemplified by the often significant disagreement (up to an order of magnitude or more) between adopted values and those determined by field validation studies on various surfactants (see Table 2 in Chapter 2 of this report). Default fraction released values, i.e. chemical discharge factors, have been established in CHARM for some surfactant categories (Table 2). This list should be expanded to include all the relevant surfactant categories/classes included in this review. There are doubts that it is practical to relate such default values to the water-cut. Measured values are "real", but can only be related to the particular operation at the time of the measurement, since the process is unlikely ever to be in equilibrium. Factors determined this way may thus be a valid tool for documentation, but the results may be inappropriate for modelling over the lifetime of a field. Site-specific environmental risk assessment should preferably be based on experimentally determined discharge factors obtained from mass-balance studies (e.g. Sæten et al. 1999; Bakke et al. 2000). If the circumstances upon which the site-specific discharge factors have been determined are studied in detail, it could be judged whether the same figures could be applied under other conditions (expert judgement).

How reliable is existing data?

Physico-chemical properties of a substance, such as solubility, P_{ow} and sorption properties, are parameters that can be used early in an evaluation process to assess its likely fate and to determine the environmental compartments into which it will partition. An octanol-water partition coefficient can be used to predict bioconcentration factor (BCF), and in many cases molecular structure has been used to estimate P_{ow}, using so-called 'fragment contribution' methods. These fragment methods do not, however, take into account the branching positions on the molecule, and may therefore not give a true representation of bioaccumulation potential. For some molecules there are significant differences between the results obtained using different calculation methods, and as the complexity of the surfactant molecule increases the reliability of the methods decreases. The development of QSARs to predict partition coefficients has been a useful approach to reducing the need for extensive live animal or surrogate testing, but such approaches require extensive validation before they can be adopted and used with any degree of confidence. The available data indicate that the use of QSARs to estimate log P_{ow} for some classes of surfactant are not reliable. Not least, the development of QSARs depends on valid data on which to develop the relationship. For surfactants, the reliability of existing P_{ow} data is questionable. The OECD 117 HPLC method, for example, adopts a QSAR approach to the estimation of a log P_{ow} for a substance, but for surfactants there are insufficient established log P_{ow} values for specific surfactant molecules to enable a valid calibration of the system.

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Experimentally derived log P_{ow} values were found for a small number of surfactants (Tolls et al. 1995). However, the formation of emulsions must be regarded as a serious problem when determining octanol-water partition coefficients for surfactants, and for ionic surfactants the use of current techniques will most likely yield distribution ratios rather than partition coefficients. For this reason, P_{ow} cannot be regarded as characterizing the partitioning of ionic surfactants, and current data obtained using OECD 107 or 117 tests cannot be viewed as valid. The majority of surfactant log P_{ow} data have been derived by calculation, many using equations based on the fragment contribution methods of Leo and Hansch (1979). Calculation methods are based on the theoretical fragmentation of the molecule into suitable substructures for which reliable log P_{ow} values are known. The log P_{ow} is obtained by summing these fragment values and applying correction factors for bonding, branching etc. However, the validity of calculated values must be questioned since the reliability of the various calculation methods decreases as the complexity of the molecule increases, and interpretations may often be subjective.

The existing BCF data set for surfactants is relatively small, with the majority of data relating to anionic surfactants, particularly LAS. Some data is available for cationic and nonionic surfactants, but no data were found for amphoteric surfactants. The usefulness of the data is limited by the lack of a unified approach to experimental determination of a BCF. Measurement of a BCF for a surfactant is an alternative to estimation of P_{ow}, but this approach can also be problematic, as described in Chapter 5 of this report. There is often significant variability in BCFs determined for the same surfactant with different species, and also for the same surfactant tested on the same species (e.g. Tolls et al. 1994). In addition, the vast majority of studies have been carried out on freshwater species. As indicated by Tolls et. al. (1995), much of the available data can only be used tentatively since it has been derived from experiments using radiolabelled compounds. Very few such studies can differentiate between parent compounds and metabolites or other breakdown products. Because of this limitation, many reported BCFs are probably significant overestimates. In general, BCFs for surfactants are reported as being comparatively low, and are generally below the conventional criteria for concern (i.e. log P_{ow} value of 3 - 4).

Is log P_{ow} / BCF relevant to surfactants?

In principle, partition coefficients are not relevant to surfactants since they do not partition between immiscible solvents such as octanol and water, but will tend to accumulate at the phase interface or form emulsions at high concentrations. The question should really be 'how relevant are existing (or potentially new) techniques to assessing the passage of surfactants across a biological membrane?', or 'how likely is it that a surfactant molecule will cross a biological membrane?'. In view of the surface-active properties of this class of chemicals, this consideration naturally leads on to the question of whether discharge of surfactants poses a risk as a result of *direct toxicity* in the marine environment, or whether *biotransformation, bioaccumulation and/or biomagnification* of surfactants constitute a greater risk.

In the longer term, the exposure of organisms to surfactants in the marine environment will be dependent on the fate and behaviour of this class of chemicals when discharged. In general terms, surfactants may be removed from the marine environment by mechanisms such as volatilisation, abiotic degradation, adsorption to particles, microbial degradation or uptake by marine organisms, factors that are applicable for any type of chemical. Volatilisation is not likely to be a significant factor because of the relatively high aqueous solubility and low/negligible vapour pressures of most surfactants. Surfactants are likely to adsorb to sediments, although sorption of surfactants on marine sediments has received little attention. Generally speaking, sorption behaviour of surfactants on marine sediments is consistent with observed characteristics in freshwater sediments, although other factors such as salinity, organic carbon content, temperature and pH may be important.

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The studies and data reviewed in this report indicate that the majority of surfactants are susceptible to biodegradation, both aerobic and anaerobic. Compared to freshwater studies, there is a limited data set of biodegradation values for surfactants in the marine environment. The majority of studies on the environmental fate and behaviour of surfactants in the marine environment have been carried out on LAS and other anionic surfactants (see Table 12 in Chapter 4 of this report). The general conclusion must be that surfactants are not likely to be persistent in the marine environment, although there is an observed trend of slower rates of biodegradation in marine compared to freshwater environments. For this reason a safety factor is applied in CHARM when only freshwater data are available. Therefore, while sediment sorption processes are undoubtedly of significance in reducing water column exposure concentrations of surfactants in aqueous environments, the most important process controlling the environmental fate of surfactants in the marine environment is undoubtedly biodegradation. Sorption will result in a redistribution of surfactants from water to sediments, while biodegradation results in a net loss of chemical from environmental compartments. However, with regard to environmental exposures, the primary consideration when reviewing biodegradation characteristics of surfactants, or any chemical for that matter, is that it is not the extent of biodegradation over an arbitrary time period that is important, but rather the rate of biodegradation compared to residence time in an environmental compartment that will ultimately determine exposure. Environmental exposure will vary, depending on solution strength, application method and rate, the degree of dilution and dispersion, and meteorological conditions. Subsequent biodegradation of surfactants will affect exposure concentration and duration, although the toxicity of surfactant metabolites is an issue on which no studies were found. Lewis (1991) notes that although comprehensive data on effect and exposure exists for LAS, comparable information is not available for other surfactants, especially in the marine environment. Consequently, existing risk assessments should be considered to be of limited validity since they are based on extrapolated data and may be inapplicable to all marine species and all surfactant classes without extensive validation

Current scientific understanding of the toxic effects of surfactants is based mainly on laboratory experiments for a few freshwater species. As a result, extrapolation of existing laboratory data to the marine environment is difficult. As a general observation, most surfactants appear to be less toxic in the environment than would be inferred from laboratory tests (Lewis 1990). Chapter 3 of this report discusses current awareness of surfactant toxicity to aquatic organisms, and highlights apparent trends in toxicity in relation to different surfactant classes. However, the range of species tested and the number of different surfactants involved is nevertheless limited, and broad generalisations should be viewed with caution. A taxonomic cross-comparison of the surfactant toxicity data in this review (Tables 4-10) highlights the difficulties in identifying trends in surfactant toxicity. For acute toxicity studies with anionic surfactants (see Table 4), the algae and fish species tested appear to be most sensitive, with the molluscs showing an intermediate sensitivity and crustaceans being the least sensitive. However, larval stages of crustacean species appear to show significantly higher sensitivity to this class of surfactant than adults.

Surfactants generally seem to impact on higher aquatic organisms via their respiratory structures. In invertebrates such as crustaceans these may be simple external gills or areas of specialised cells on the body surface. In higher organisms such as fish the respiratory structures (gills) consist of epithelial membranes that may be extensively folded to provide large surface areas for gaseous exchanges. Destabilisation of these epithelial membranes, as may occur when exposed to surfactants, results in changes in membrane permeability, cellular lysis, and impairment of cellular respiration. In lower organisms, in which exchange of respiratory gases is via mechanisms of simple diffusion across membrane surfaces, surfactant toxicity appears to result from an initial disruption of normal membrane function followed by physical disruption of the cellular membrane. As might be expected, charged surfactants (anionic and cationic) appear to have a greater denaturing effect than neutral surfactants. Cationic surfactants also appear to be the most toxic to both freshwater and marine species of algae, invertebrates and fish.

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Although only a limited range of surfactants has been investigated for aquatic toxicity, a few studies have illustrated a difference in toxicity between surfactant classes. Lewis (1990) noted that the toxicity of different surfactants on the same algal test species might vary over four orders of magnitude. Charged surfactants (anionic and cationic) have been reported to have a greater denaturing effect than neutral chemicals, and cationic surfactants are generally considered to be most toxic to both freshwater and marine algae, invertebrates and fish (Ukeles 1965; Lewis 1991). It is possible that existing HOCNF data includes reference to toxicity of various oilfield surfactants to marine organisms, and if made available, these could usefully supplement the comparatively limited marine data available in the public domain. However, the current emphasis on toxicity testing of complete preparations will mean that few such studies will be relevant.

Surfactant toxicity has also been found to vary between homologues within a given surfactant type and may also depend on chemical structure (see Chapter 3). Increasing the length of the alkyl chain can modify toxicity of LAS, and toxicity of nonionic ethoxylated surfactants depends on the length of the ethoxylate chain (Lewis 1991 and references therein). In some cases, toxicity may be predicted from the ethylene oxide molar ratio, with a ratio of 15 or less being associated with the most toxic surfactants and ratios of 30-50 being consistent with observations of low toxicity (Scott Hall et al. 1989). This observation applied both for a given series of homologues and across various surfactant types.

In reviewing the potential of surfactants to bioaccumulate (see Chapter 5), a general association of increasing alkyl chain length (i.e., increasing hydrophobicity) with an increase in BCF was noted (Tolls et al. 1997, 2000) for LAS compounds and isomers, and alcohol ethoxylate components. Conversely, increasing the length of the hydrophilic section of a surfactant molecule (i.e., decreasing overall hydrophobicity) results in a reduction in BCF (reviewed in Staples et al. 1998). Tolls et al. (2000) also found increased uptake rates and BCFs for alcohol ethoxylate surfactants when hydrophobicity was increased. Other studies supporting these observations are also cited in Chapter 5. These apparent steric influences on surfactant toxicity and BCF appear to be consistent, and may offer a means of predicting likely toxic effects of surfactants on marine organisms through a consideration of steric factors. A more thorough evaluation of existing data may be useful, particularly if combined with further investigative studies, to establish and validate some general principles describing the relationship between surfactant chemistry (molecular/steric factors) and toxicity/BCF. If modifications to the molecular structure of surfactants can result in predictable influences on bioaccumulation and toxicity to aqueous organisms, then environmental effects of new formulations could be predicted at an early stage in product development.

A tendency for surfactant molecules to be retained on epithelial surfaces, rather than to cross cellular/epithelial membranes (uptake) and hence bioaccumulate, may be a possible explanation for the longer-chain/lower-toxicity observations. Surfactant molecules residing (bound) on an epithelial membrane surface may be expected to disrupt membrane integrity (permeability/fluidity), and interact with mucus (a charged, fibrous glycoprotein-carbohydrate matrix). Studies of the effects of sodium lauryl sulphate (SLS) and LAS at concentrations of 100 mg l^{1} showed that the integrity of the upper layers of the epithelium of fish gills was severely disrupted, resulting in severe water imbalance. However, the test concentrations used are several orders of magnitude greater than would be expected in the environment. At low concentrations (e.g. 6 ìg l^{-1} of SLS) some effects are reversible, indicating temporary binding to specific sites (Stagg et al. 1981). The number of binding sites on epithelial or cellular membranes is usually limited, resulting, for example, in transmembrane transport mechanisms that display saturation kinetics. If a critical number of (surfactant) molecules must occupy the available binding (transport) sites in order for lethal poisoning to occur, then surfactants that can more easily cross the membrane and bioaccumulate (as indicated by a higher BCF) are less likely to exhibit acute toxic effects. Likely toxic mechanisms are discussed more fully in Chapter 3. In general, BCFs for surfactants are reported as being comparatively low, and are

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generally below the conventional level for concern (i.e. log P_{ow} value of 3 - 4). Although considerable evidence of surfactant bioaccumulation has been collected and published (see Table 16 in Chapter 6 of this report), lower lethal toxicity associated with an increased BCF would argue in favour of the contention that it is not surfactant bioaccumulation *per se* which is of concern, but direct toxicity.

Biotransformation and biomagnification are processes that may occur once a chemical has entered an organism (bioaccumulated). Evidence for biotransformation of surfactants in aquatic organisms is scant, and limited to radiolabel studies. For the few surfactants investigated (e.g., $C_{14}EO_8$: Tolls ands Sjim 1999; C_{12}-LAS and C_{13}-LAS: Tolls et al. 1997), biotransformation was deduced to be the dominant factor in the elimination of these surfactants from the test organisms.

In order for biomagnification of a chemical to take place the compound must be stable in the environment for significant periods of time. Compounds which (bio)degrade relatively rapidly or which are readily metabolised (biotransformed) will not be biomagnified within the food chain. While the bioaccumulation of a chemical can still present a problem where exposure levels and uptake rates are sufficiently high in relation to depuration and metabolism rates, a high bioaccumulation potential does not automatically imply the potential for biomagnification. Indeed, for some chemicals, which are readily taken up by organisms near the bottom of the food chain, a capacity for metabolism is more likely in successively higher trophic levels. In some cases, calculated BCF values for surfactants in higher aquatic organisms (fish) were found to be 30-3000 times lower than values for algae (Ahel et al. 1993). The available information indicates that most commonly used surfactants do not have the properties required to exhibit biomagnification, i.e., they have a tendency to be rapidly degraded and metabolised and are not highly hydrophobic.

In conclusion, no evidence has been found to support concern with respect to the biomagnification of surfactants, although it is noted that most of the research effort has been devoted to a relatively small number of surfactant types. Bioconcentration factors in the aqueous phase are generally below the level of concern, and (for some nonionic surfactants at least) can be quantitatively related to the length of the hydrophobic and hydrophilic components. There is also evidence that overall molecular size may place constraints on biological uptake. The studies examined in this report raise no concerns with respect to long-term retention of accumulated surfactant material in tissue, and indeed they present considerable evidence that many surfactants are metabolised. The fate of metabolites has not been thoroughly studied, however, and there is consequently a degree of uncertainty as to the fate and longer-term effects of some hydrophobic components (such as some alkylphenols) following partial metabolism.

Alternative analytical approaches

In respect of the potential developments in analytical techniques this review addresses the following questions:

- Are the new methods likely to offer a better alternative to the existing ones?
- How practical and relevant are these new techniques to surfactants?
- Are surrogates to live animal testing reliable?
- Are the new methods suitable for standard tests?

Surfactant behaviour cannot be related to partitioning between two disparate liquid phases because of their inherent tendency to collect at phase interfaces or to form emulsions (micelles), placing the existing methods of estimating BCF in doubt. The lack of a widely-applicable, robust and simple method to assess bioaccumulation potential and sediment/water partitioning of surfactants has

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hindered the establishment of a rational and hence meaningful evaluation of the environmental hazards and risks that surfactants may pose. Surrogates to live animal testing are always preferable, and it is likely that the recently introduced MEEKC technique (see Chapter 7 of this report) will provide a more valid result in the form of a pseudo-log P_{ow}. The technique has been used to investigate octanol-water partitioning of a wide range of organic compounds giving a good correlation with HPLC-generated values for simple organic molecules (Smith and Vinjamoori 1995). Salimi-Moosavi and Cassidy (1996) used the technique to separate long-chain surfactants and have further investigated the potential of the technique for surfactant applications. The newly developed techniques of MEEKC use the properties of surfactants to great effect in the analytical process. Currently in reverse-phase HPLC there is a tendency for irreversible adsorption of some compounds. This is not the case with MEEKC. It is a fact that products are often presented for testing as a mixture of substances, for which no useful (in analytical terms) information on the formulation is provided. There is therefore little possibility to apply a "correct" analytical technique. The MEEKC approach seems to offer a broader scope for a wider range of compounds even if a series of different conditions needs to be used on a formulation.

The indications from the literature are that the MEEKC technique would be very suitable as a standard method. It also seems feasible that the equipment could be used to determine log P_{ow}s of ordinary compounds, and there are references citing the use of diode array detection. While capillary electrophoresis is not as widely used as HPLC, there are at least two commercial models available at comparable cost to a HPLC system. Test costs are therefore likely to be similar to those for current log P_{ow} analysis.

The suitability of SPMDs as an alternative surrogate technique to live animal testing for estimation of BCFs for surfactants needs to be more closely investigated. Although a good relationship between BCFs for PAHs obtained using SPMDs and live animal tests on blue mussels, *Mytilus edulis*, (Røe et al. 1998), the intrinsic properties of surfactants may pose problems when interpreting data from the use of such devices. The justification for using SPMD is based on uptake and BCF for lipophilic chemicals, and the whole question centres on whether lipophilic descriptors are valid for surfactants – this seems illogical. The use of an SPMD requires analysis of the solvent inside the device – if surfactants sit on or in the semi-permeable membrane, there might possibly be very little material present in the solvent phase inside. BCF tests are considered to be prohibitively expensive, but the main cost element is the chemical analysis, not the 'biological' component. If it is necessary to analyse both the water and the content of the SPMD, then the cost of the work will not be very different from the cost of a BCF, and the primary advantage would be that a SPMD might equilibrate faster than an experimental animal. In BCF tests, actual uptake and depuration rates are measured, and the resulting estimate takes account both of passive depuration and metabolic transformation. SPMDs will model only passive processes.

A weakness of the OECD 117 method is that it does not always provide a reliable indication of the *quantity* of each component present – in fact, in some instances the peaks detected represent only trace components or solvents and active ingredients are not registered at all. Surfactants submitted for testing may often be complex mixtures, rather than pure compounds, and the analytical costs associated with alternative surrogate techniques may be multiplied accordingly. When adopting alternative approaches, it might be better to focus initially on a selected range of widely used 'generic' individual surfactant compounds, and use the resulting data as a form of range-finding exercise. In any case, the 'success' of the studies will depend critically on the precision of the chemical assays that are developed – even using the SPMD it will be necessary to analyse for individual compounds both in the internal solvent and in the exposure medium. The SPMD method seems to simply represent a technical improvement of the OECD 107 shake-flask method, but would still be subject to the same constraints when applied to surfactants, although the formation of emulsions would be avoided. For all its shortcomings, a practical advantage of the OECD 117 method is that it is possible to 'analyse' mixtures, without the need for compound-specific analytical

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methods (and without in most instances knowing which compounds are represented by the chromatography peaks).

Current developments in SPMD technology involve fairly large-scale test systems that would impose unacceptably high costs on current testing requirements, and in many cases practical restraints on a general widespread adoption of the method. There is obviously a need for 'laboratory scale' systems providing low-cost integrated methods suitable for use at realistic environmental concentrations. Small SPMDs suitable for laboratory use are under development, but their suitability for use with surfactants or other highly hydrophobic chemicals is currently unknown. However, in any program designed to develop an alternative surrogate technique for estimating surfactant BCFs, a sufficiently large number of chemicals will need to be examined in order to derive an independent QSAR. In view of the likely cost restraints, it is almost inevitable that there will be greater reliance on existing data. A thorough review of the literature with a view to defining exactly what (in terms or reliability and precision) could be achieved from existing data is therefore desirable. This review provides a sound basis on which to further develop this approach. Such an assessment can then be compared with estimates of what could be achieved from an acceptable (in terms of time and cost) experimental programme, and an assessment made as to whether such a programme would actually offer real, quantifiable benefit in terms of the quality of the QSAR. Pragmatically, there is no advantage in having a more thoroughly validated data set if it does not result in a tangible improvement in precision and reliability.

The main stumbling block to further development of the QSAR approach to BCF estimation is the substantial effort and cost that would be associated with establishing experimental BCF values with which to compare surrogate measures. A unified (harmonised) approach to BCF testing in live animals is currently lacking, reflected by the uncertainty of the reliability of existing BCF values. The time and cost of developing appropriate extraction and analytical methods for a suitably large number of surfactants would be high; before starting, it would be essential to set targets for recovery and precision, so that it would be possible to judge when sufficient work had been done to deliver a reliable and useable method. There would be no point in correlating an experimental measure with a surrogate measure if the confidence limits on the former were as high as ±100%. Setting such performance parameters should be an integral part of any project.

While EOSCA as an industry organisation could not itself fund a project of this nature, this review could be used as the basis for a proposal to apply for EU Framework Programme 5 funding. Some of the key elements already present for a successful application are:

- End-user involvement and problem ownership (EOSCA)
- Protection of the environment
- Sustainable growth
- Large pan-European industry
- Creation of a ‘standard’ test method
- Clearly defined problem with identified solutions
- No obvious alternative for funding

Another alternative would be a collaborative R&D program with EOSCA as one of the members, and possibly including input from Spanish and Italian research groups to increase the pan-European aspects. Information dissemination and acceptance is a very important element and could be co-ordinated through EOSCA.

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