

APPENDIX F. READ-ACROSS (INTERPOLATION) RULES FOR MINERALIZATION DATA

Appendix F.1. Introduction

The principle of “read-across” of data from one substance to a similar substance is already recognized in international risk assessment activities, including the OECD HPV Chemicals Programme. The new draft EU REACH Regulation proposal also provides, in Annex IX Section 1.5, for the Grouping of substances and a read-across approach:

“Substances whose physicochemical, toxicological or ecotoxicological properties are likely to be similar or follow a regular pattern as a result of structural similarity may be considered as a group, or “category” of substances. Application of the group concept requires that physicochemical properties, human health effects and environmental effects or environmental fate may be predicted from data for a reference substance within the group by interpolation to other substances in the group (read-across approach). This avoids the need to test every substance for every endpoint.

The similarities may be based upon:

- (1) A common functional group,
- (2) The common precursors and/or the likelihood of common breakdown products via physical and biological processes, which result in structurally similar chemicals, or
- (3) A constant pattern in the changing of the potency of the properties across the category.”

Surfactants are ideally suited to this approach since they are generally members of homologous series and usually satisfy all three of the above requirements. The hydrophobic part of the vast majority of surfactant products is a hydrocarbon chain or mixture of hydrocarbon chains; generally consisting of between 8 and 22 carbon atoms. Over all, the nature of the hydrophilic part of surfactants is more variable, but when restricted to a series of homologues it is either unchanged (e.g. many anionics) or systematically varying (e.g. many nonionics).

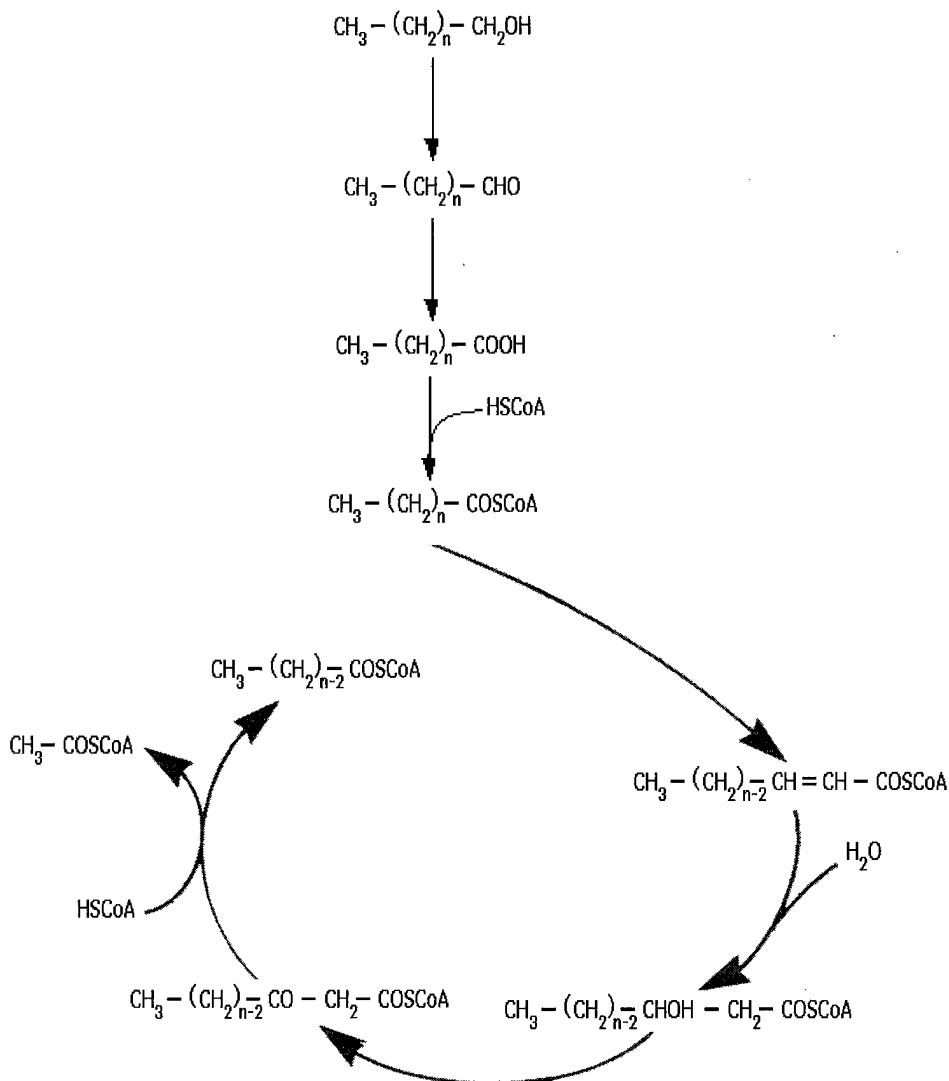
Appendix F.2. Structural considerations

- **Ionic surfactants**

- **Homologs**

Each of the ionic families or groups of surfactants has a common hydrophilic end-group which defines the functional type of the product, such as (ether)sulphate; sulphonate; carboxylates; (ether)phosphate; amine; betaine; quaternary ammonium salt; imidazoline. The only variable factor between homologues within each of these families is the length and branching of the hydrocarbon chain; which constitutes the hydrophobe.

The metabolic pathways of most surfactants are well understood. A central cleavage of surfactants yields the hydrophobic chain in the form of alcohols, alkanals or alkanic acids, which are readily assimilated by β -oxidation. A second strategy for microorganisms to metabolize the alkyl chain is from the far-end through ω - β -oxidation. The β -oxidation cycle of such structures in the range C8 to C22 is well known, leading to complete mineralisation,



and is illustrated as an example in Figure 1.

Figure 1: Activation of fatty acids and the β -oxidation cycle.

The β -oxidation cycle also handles unsaturated alcohols, alkanals, and fatty acids. Isomerization of the double bonds occurs to ensure the correct positioning of the double bonds in the substrate for the β -oxidation sequence.

Read-across rule: For ionic surfactant families where the sole difference between individual homologues is simply the carbon chain length of the hydrophobe, if positive mineralisation data is available for two members then it can be assumed that all homologues lying between these two will be mineralisable.

– Counter ions

Ionic surfactants are, of necessity, associated with so-called “counter ions” to balance the ionic charge. These are generally Na⁺; K⁺ or NH₄⁺ in the case of anionic surfactants and Cl⁻ or MeOSO₃⁻ in the case of cationic surfactants. Ionic surfactants will be largely dissociated in aqueous solution; and in the use and disposal situations will typically be in the presence of many different counter-ions arising from other chemical substances which might be present. These counter-ions play no part in the biodegradation process.

Read-across rule: For ionic surfactants where positive mineralisation data is available for the surfactant neutralised with one counter-ion then it can be assumed that the same surfactant neutralised with other counter-ions will also be mineralisable.

- **Non-ionic surfactants**

Non-ionic surfactants of the alcohol ethoxylate family have an additional feature in that the poly(oxyethylene) hydrophile can be varied as well as the carbon chain length of the alkyl hydrophobe. This is also true for alkyl ether sulphates. The additional structural factor to consider in both cases is: EO number or molecular weight of the EO block.

The metabolic pathway of polyethers of the poly(oxyethylene) type has been elaborated by Kawai (1985) and mixed microbial cultures are known which are capable of mineralising polyethylene glycols of molecular weight up to 20000.

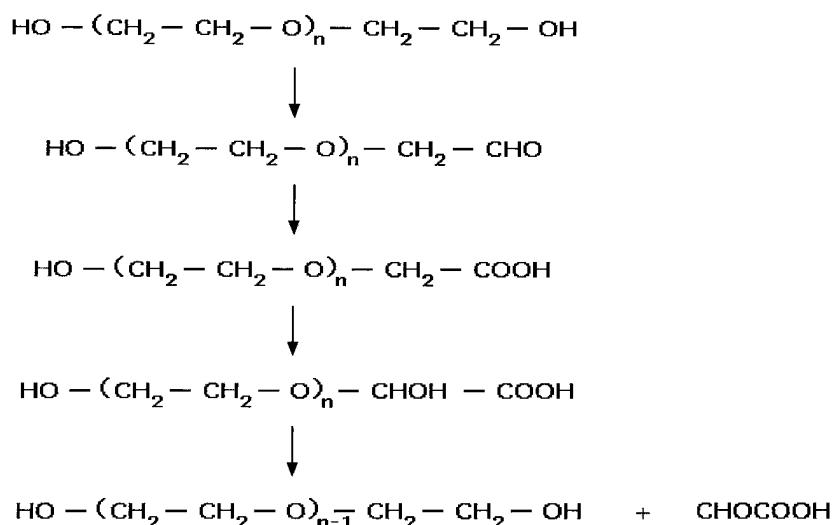


Figure 2: Oxidative mechanism for ether scission of polyglycols by microorganisms resulting in successive removal of ethylene glycol units.

Most non-ionic surfactants have alkyl chain hydrophobes containing between 8 and 18 carbon atoms and polyethylene glycol hydrophiles of molecular weight up to around 2000. Mechanistic studies show that the metabolic fragments (of primary biodegradation) of alcohol ethoxylates are fatty acids and polyethylene glycols; both of which are capable of complete mineralisation.

Read-across rule: For non-ionic surfactants of the alcohol ethoxylate type:

At a fixed degree of ethoxylation, or average EO number, where the sole difference between individual homologues is simply the carbon chain length of the hydrophobe, if positive

mineralisation results are available for substances of carbon chain lengths X and Y then all homologues with alkyl chain lengths between X and Y should be accepted as mineralisable.

With an alkyl chain hydrophobe of fixed composition, if positive mineralisation results are available for substances with average EO numbers of X and Y then all family members with EO numbers between X and Y should be accepted as mineralisable.

