**FAO: Consultancy / Contractor**
**RE: Literature Review Proposal EOSCA Fraction Released Working Group (FRWG)**

## *Background*

The European Oilfield Speciality Chemicals Association (EOSCA)[1] at the vanguard of developments acts as a focal point for interaction between the chemical supply industry and national regulatory groups.

A subject matter of particular relevance currently under discussion within EOSCA is the exposure and environmental risk of oilfield chemical residuals in produced water discharges assessed under the OSPAR risk-based approach (RBA).

One specific area where the accuracy of exposure assessments could be improved is with respect to the methodology and values used for the fraction released of an oilfield chemical within the Chemical Hazard Assessment and Risk Management (CHARM) model framework.[2] In particular surfactants (owing to their unique phase behaviour characteristics) are set standard/default release factor values of 0.0, 0.4, 0.7 or 1.0 depending upon the surfactant type and some literature data (field monitoring studies etc) suggests that these figures could be challenged and/or refined. This specific issue for surfactants was highlighted during a CHARM implementation network (CIN) meeting in 2017.

To address the issue on fraction released for oilfield chemicals, EOSCA set up a Fraction Released Working Group (FRWG) in July 2020. The FRWG Terms of Reference (ToR) and a presentation from the CIN 2017 meeting summarising the issue for surfactants are attached below for reference:

| FWRG Terms of Reference (ToR) | Surfactants Release Fraction - CIN 2017 |
|---|---|
| **Appendix 1** | **Appendix 2** |

## *Objectives & Scope of Work*

Particular focus of the FRWG currently is on examining the relevance and reliability of current default fractions release values for surfactants with the aim to investigate and develop more robust and accurate methods going forward. The level and type of information required to deviate from the current CHARM defaults for regulatory acceptance will also be addressed through dialogue with the relevant regulatory associations.

The FRWG concentrated initial efforts on identifying and reviewing relevant literature concerning partitioning of surfactants in oil/water systems and field data for measured residuals of surfactants in produced water effluent discharges. Approximately 12 papers have been subject to high-level review by a small sub-team of individuals from the FRWG with a further 12-13 paper identified and sourced but not yet subject to detailed review. An excel file has been used to capture high-level summary and relevance of the series of papers. Electronic copies of the publications have been uploaded and stored on a dedicated google drive space for easy access by all members of the FRWG.

[1] https://eosca.eu/
[2] https://eosca.eu/wp-content/uploads/2018/08/CHARM-User-Guide-Version-1-5.pdf

To advance literature review work EOSCA FRWG is seeking external consultancy support on the following topics and objectives:

1. To review the existing literature already identified by the group
2. To expand the literature review using targeted keyword searches and citations from the existing relevant publications
3. To compile a summary report outlining key and pertinent findings from the literature review. The report should also:
    a. Specifically outline the relevance and usefulness of the existing literature to address the fraction release issue for surfactants within the CHARM model framework
    b. Include recommendations for targeted approaches including possible experimental work that would underpin more accurate release fraction estimates for surfactants

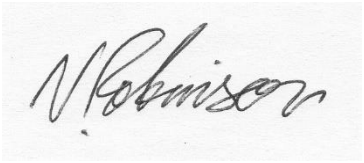
At a later stage, EOSCA FRWG would also be interested to pursue publication of the literature review summary report in a relevant peer-reviewed scientific journal (e.g. SPE journal)

This request for proposals (RfP) is for an initial cost and timeline estimate that will be refined pending additional discussions of interest, capability, and timing. Please note the deadline set by FRWG for bids on this RfP is 31st January 2022. The proposals will be reviewed by FRWG in February 2022 and the winning bid will be announced in March 2022.

In addition to the quote please provide an evidence-based summary of your expertise and knowledge of environmental fate, toxicity and behaviour of surfactants; CHARM; oilfield chemical environmental risk assessment; OSPAR Offshore Chemical Notification Scheme (OCNS); OSPAR risk-based approach (RBA).

Thanks in advance for your interest and response to this RfP. We remain at your disposal for further information or questions.

Yours sincerely,



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*Appendix 1*

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# Terms of Reference for EOSCA Fraction Released Working Group

Oct 2020

## Background

1. Risk assessments of chemicals are typically based on a quantitative comparison exposure and effect. Currently, there are significant regulatory pressures on the environmental effect assessment of oilfield chemicals to be more conservative (protective).For example, ECHA requiring higher assessment factors (AF) to be used for offshore oilfield chemical substances compared to those that have been used under the CHARM model[1] along with proposals to incorporate a mixture assessment factor (MAF) when deriving Predicted No Effect Concentrations (PNEC) to account for combination effects,[2,3]. To address the potential impact of these proposed regulatory changes on the effects assessment it is clear that increasing the accuracy of the exposure assessment is key.

2. One area that has already been highlighted where the accuracy of exposure assessments could be improved is with respect to the methodology and values used for the fraction released of an oilfield chemical within the CHARM model framework. In particular surfactants (owing to their unique phase behaviour characteristics) are set standard/default release factor values of 0.0, 0.4, 0.7 or 1.0 depending upon the surfactant type and some literature data (field monitoring studies etc) suggests that these figures could be challenged and/or refined.

3. Whilst originally there had been a call to set up a Fraction Released Working Group (FWRG) to respond to and steer the COWI/Aquateam Fraction Released project, this project did not ultimately receive funding and has not materialised. However, within EOSCA it was felt that this particular issue warranted further attention and discussion.

## Objectives and Scope of work

4. The FRWG will:

   a. Conduct virtual meetings to discuss and stimulate exchange of information and data relevant to more accurate exposure assessment of oilfield chemical discharges.

   b. Report back to the wider EOSCA membership at the Association's quarterly meetings.

5. Specific areas of work for the group will include:

   - Review the extent to which specific data concerning fractions released are submitted and the regulatory acceptance criteria for these.

[1] Sühring et al 2019. The past, present, and future of the regulation of offshore chemicals in the North Sea—a United Kingdom perspective, *ICES Journal of Marine Science*, Volume 77, Issue 3, May-June 2020, Pages 1157–1166, https://doi.org/10.1093/icesjms/fsz172
[2] https://www.chemischestoffengoedgeregeld.nl/sites/default/files/ECHA_Jack%20De%20Bruijn.pdf
[3] https://chemicalwatch.com/104658/eu-member-states-consider-reach-mixtures-assessment-factor

- Review available data to determine whether more accurate/refined release estimates can be made for some of the surfactant catgories, and/or whether the existing categories need to be sub-divided at all.
- Identify the key/critical surfactant chemistries which are driving environmental impact factors (EIF) through the produced water RBA programme
- Explore to what extent the fraction released issue is only relevant to surfactants, and if any other non surface-active oilfield chemistries are impacted.
- Discuss other new developments and alternative methodologies as appropriate.
- Determine and examine the need for a dedicated experimental studies (e.g. partitioning experiments) and the regulatory acceptance of such methods to justify a deviation from arbitrary default release fractions in CHARM

**Participants and mode of work**

6. The FRWG will be open to representatives from all Members and Associate Members. The group will work via correspondence and virtual meetings. The group agreed to be chaired by Jame Dawick (Innospec), with the participation of other Members and Associates.
7. The requirement for the continutation of the working group will be reviewed at least quarterly.

*Appendix 2*

# CHARM IMPLEMENTATION NETWORK (CIN) WORKSHOP

## Issue 3: Surfactants Release Fraction

Meeting of the CHARM Implementation Network (CIN)
IOGP Meeting, London 10-11th October

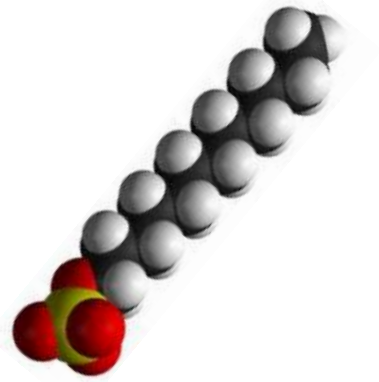
**James Dawick**
Environmental Scientist
Shell Health

# Agenda

- Background
- Overview of Surfactant Release Fractions ($f_r$)
- Technical Basis
- Approaches for Adjusting Current $f_r$ values
- Field Validation Studies
- Brainstorming and Discussion Points
- Actions/Forward Plan

# Background

- Many chemicals used in offshore E&P operations have surface active properties (antifoam; biocide; corrosion inhibitor; emulsion breakers)
- PEC calculation depends on chemical equilibrium partitioning of (organic) molecules between water and organic phases (in both topsides/sub-surface system and receiving environment)
- Surfactants not subject to simple chemical equilibrium partitioning processes and are more likely to form a layer at their interface → log $K_{ow}$ not relevant
- As a consequence, standard CHARM algorithms for calculating PEC cannot be used directly
- For surfactants, CHARM makes use of default release fraction ($f_r$) values to calculate concentrations in the PW phase, which introduce some additional uncertainties.
- Generally considered to give extreme overestimations of the actual amounts released to water; i.e. CHARM default values are considered overly conservative.



Production Chemicals

$$C_{pw} = \frac{C_t * F_t}{\left(10^{\log P_{ow}} * F_{o/c}\right) + F_{pw}}$$

Injection chemicals/Surfactants

$$C_{pw} = \frac{f_r * C_i * F_i}{F_{pw}}$$

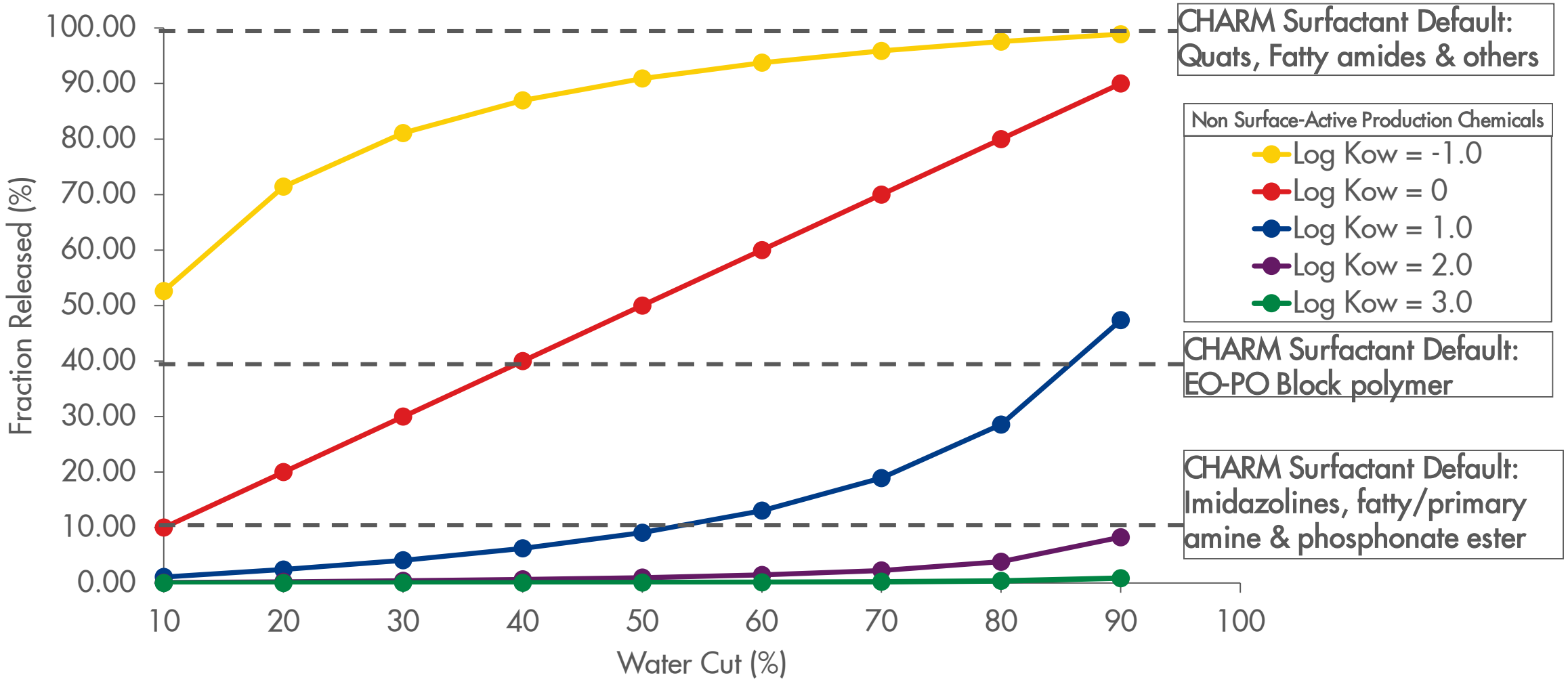
$f_r$ = 0.01 for injected chemicals
$f_r$ for surfactants depends on type

# Overview of Surfactant Release Fractions ($f_r$)

| Surfactant Type | Release Fraction ($f_r$) |
|---|---|
| Quaternary amines | 1.0 (100%) |
| EO-PO Block polymer demulsifier | 0.4 (40%) |
| Imidazolines | 0.1 (10%) |
| Fatty amines | 0.1 (10%) |
| Fatty amides | 1.0 (100%) |
| Primary amines (cationic type ≥C12) | 0.1 (10%) |
| Phosphonate esters (anionic type ≥C12) | 0.1 (10%) |
| Others | 1.0 (100%) |

**More Specific?**
Alcohol Ethoxylates (CI/BC/EB)
APG (CI)
Betaines (CI)
Alkyl Sulfates (AF)
Alkyl Sulfonates (EB/CI)
EOR surfactants (AOS/IOS)?

# Overview of Surfactant Release Fractions ($f_r$)



# Technical Basis

- No technical basis fully documented for current default surfactant $f_r$ values.
- Checked following sources:
  - CHARM User Guide Version 1.5 (2017)
  - EOSCA Bioaccumulation Surfactants report (2000)
  - CHARM III Technical background report (TNO-MEP – R 96/354)
  - CHARM III Main Report (TNO-MEP – R 96/355)
  - CHARM Workshop Report No 2: Calculation of Fraction Released (Oslo, June 13-14, 1994)
  - 1994 Report Summary and Conclusion Fraction Released (Aquateam report No 94-072)
- Surfactant $f_r$ values assumed based on expert judgment in combination with field validation studies (e.g. OLF, 1993 and Hudgins 1991)

| Surfactant Type | Release Fraction ($f_r$) | |
|---|---|---|
| Quaternary amines | 1.0 | |
| EO-PO Block polymer demulsifier | 0.4 | ? |
| Imidazolines | 0.1 | * |
| Fatty amines | 0.1 | * |
| Fatty amides | 1.0 | ? |
| Primary amines (cationic type ≥C12) | 0.1 | * |
| Phosphonate esters (anionic type ≥C12) | 0.1 | * |
| Others | 1.0 | ? |

*Zero discharge but 10% Safety Factor

| Chemical | Conc. theoretic at pipe outlet (µg/l) | Conc.measured in produced water (µg/l) | OWDF (from lab test) |
|---|---|---|---|
| Biocide | (a) 1,500 - 5,000 | 9-10 | 0.16 - 0.22 |
| Glutaraldehyde | (b) 3,000 - 12,000 | 21-22 | |
| | (c) 1,500 - 6,000 | <3-7 | |
| | (d) 20,200 | 5-21 | |
| Formaldehyde | (a) 400 - 1,500 | 35-37 | 1.19 - 1.67 |
| | (b) 700 - 3,000 | 950-980 | |
| | (c) 300 - 1,500 | 15-26 | |
| | (d) 6 - 7 | 18-30 | |
| Corrosion inhibitor | (a) 0.2 - 39 | 24-77 | 100 |
| Imidazoline | (b) < 20 | <20-31 | |
| Flocculant | | | |
| Polyamine | 900 - 4,500 | 87-1,070 | ~0 |

# Approaches for Adjusting Current ($f_r$)

- Mass balance studies per CHARM user guide Table 10 (Risk Analysis):

*Table 10: Overview of parameters which can be replaced by actual data in Risk Analysis of production chemicals.*

| Parameter | Unit | Site specific data |
|---|---|---|
| water production | $m_3.d^{-1}$ | Actual on-installation measurements |
| oil production | $m_3.d^{-1}$ | Actual on-installation measurements |
| gas production | $m_3.d^{-1}$ | Actual on-installation measurements |
| condensate production | $m_3.d^{-1}$ | Actual on-installation measurements |
| dilution at reference distance | - | Dilution field study of the installation itself or an installation in the same region with comparable water production. It is also possible to use the results of a detailed chemical dispersion model. |
| surfactant fraction released | - | Mass balance study performed on the actual installation or another installation with comparable water and oil/condensate flows |
| injection chemical fraction released | - | Mass balance study performed on the actual installation or another installation with comparable water and oil/condensate flows |
| sediment organic carbon content | fraction | Data from on-site sediment samples. These data might be available from a baseline study carried out before installing the installation, but should preferably reflect the current situation. |

# Field Validation (Mass Balance) Study Data

| Surfactant Type | CHARM Release Fraction ($f_r$) | Fraction Released in Field Validation Studies ($f_r$) |
|---|---|---|
| Quaternary amines | 1.0 | 1.0[1]; 0.038[2]; 0.0025[4]; 0.06-0.39[5] |
| EO-PO Block polymer demulsifier | 0.4 | |
| Imidazolines | 0.1 | 0.01[3]; 0.027-0.028[4] (see next slide) |
| Fatty amines | 0.1 | |
| Fatty amides | 1.0 | |
| Primary amines (cationic type ≥C12) | 0.1 | |
| Phosphonate esters (anionic type ≥C12) | 0.1 | 0.002[1]; |
| Others | 1.0 | |

Different quats/field conditions/ analytical methods?

1) OLF 1993 (referenced in CHARM III Technical Background Report) – Assuming this is a Quat Cl….? [unable to source ref]
2) TNO: Fokema et al 1998 (TNO-MEP R 98/317)
3) Statoil: Saeten et al 1999
4) Grigson et al 2000 (BP Magnus platform PW)
5) CHARMVAL Project (Gagliardi and Grigson 2003)

# Field Validation Study Data (Imidazolines)

Bakke et al 2000 (SPE 61199):

**TABLE 2 – COMPARISON OF REPORTED FRACTION RELEASED DATA FOR IMIDAZOLINES**

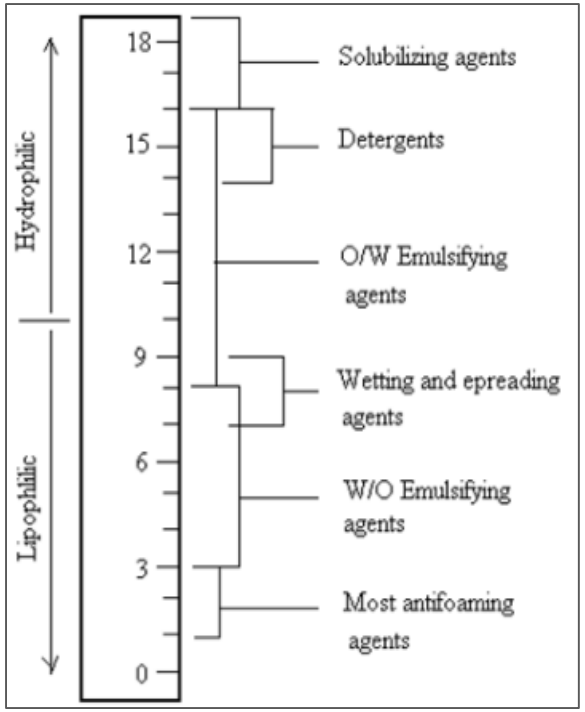
| Test/data | Fraction released (%) | Water-cut (%) | Test conditions |
|---|---|---|---|
| Aquateam # 1 | n.d. | 25-58 | Produced water analysis from Ekofisk B/K and Tor. Specific method impossible to establish. Nitrogen method not suitable for produced water. |
| Aquateam # 2 | <0.8*<br><3.2* | 20<br>80 | Lab tests. Dosage = 50 ppm (product). Water phase analysed using nitrogen method. |
| Chemical supplier | 15-35 | 2-50 | Lab tests, variable dosages (product). Nitrogen-in-water analysis. |
| OLF mass balance project[11,12] | 0.4-4<br>0.3 | 50<br>33 | Lab tests. GC/MS analysis (Phase I)<br>Field tests. GC/MS analysis (Phase II) |
| Statoil[7,13] | ~1<br>~ 2 | 20<br>~ 50-70 | Lab tests, bench-scale separation rig. $^{14}C$ radio-active labelling of chemical and GC/MS analysis. |
| | 1-2<br>~ 4.5 | 30-35<br>80 | Field tests. $^{14}C$ radio-active labelling of chemical and GC/MS analysis. |
| General literature values[6,15] | 1-20 | Not given | Imidazoline based corrosion inhibitors in general |
| Phillips | 20 | All | Estimated discharge factor for corrosion inhibitor no.1 |
| Mass balance model | 10 | All | CHARM default value[4] |

* The Aquateam tests were performed in duplicate, giving the same results for both parallels.
n.d. = not determined due to analytical problems.
GC/MS = gas chromatography/mass spectra

**Conclusion:** CHARM default surfactant fr value of 10% (0.1) for imidazolines is generally (overly) conservative but within range of field/lab data

# Brainstorming and Discussion Points

- Influence of following parameters on the partitioning/$f_r$ values for surfactants:
  - Composition/Type/Phys-chem properties of surfactant
    - Is the current generic groupings sufficient?
    - Could explain different field $f_r$ values obtained for Quats (different chemistries)……?
    - Vast range of different chemistries for non-ionic EO-PO block copolymers (and AE's) with both water soluble and oil soluble substances → is it sensible to have a single release fraction value for these?
      - Use HLB (Hydrophile-Lipophile Balance) data to group non-ionic surfactants into water soluble (i.e. high HLB) and oil soluble (i.e. low HLB) classes?
  - Adsorption in the process system (binding to metal surfaces, oil droplets, suspended solids)
  - Adsorption on reservoir rock (for injected surfactants)
  - (An)aerobic biodegradation in the process system and/or reservoir



# Brainstorming and Discussion Points

- How to address 'other' classes of surfactant (current default $f_r$ = 1.0)? Perhaps only a few "other" classes of surfactant are actually important from an oilfield chemical context….?
- Information on surfactants from hydraulic fracturing data and REACH GES/SpERCS (is it relevant)?
- Norwegian operator approach to derive surfactant concentrations in PW for DREAM/EIF modelling?
- Overview of issues from operators with high EIF numbers for surfactants using DREAM for RBA?

# Actions/Forward Plan


- Potential projects (tiered approach):

1. Detailed lit review of existing field validation/mass balance studies?

2. Additional experimental mass balance studies on PW field samples?
   - Acknowledge that experimentally determined $f_r$ values are real but can only be related to the time of measurement since the process is dynamic. However, if WoE suggests the current defaults are overly conservative then……?
   - Chemical analysis may be problematic (matrix effects, interference, sensitivity, specificity, adsorption of surfactants on glassware/instrumentation, supplier IP issues……)

# Questions and Answers