Von: Uhlein, Mareike (Dr.)
Gesendet: Freitag, 7. Februar 2025 09:53
An: axel.vorwerk@bmuv.bund.de
Cc: Kattanek, Ralf <ralf.kattanek@vci.de>
Betreff: Stand der Revision der Detergenzien-Verordnung – Ergänzende Informationen

Sehr geehrter Herr Dr. Vorwerk,

am 6. August 2024 hatten wir Sie bereits per E-Mail zur laufenden Revision der Detergenzien-Verordnung auf EU-Ebene informiert. In der Zwischenzeit haben wir weitere Informationen von CESIO (europäischer Tensidverband) erhalten, die für die anstehenden Trilogverhandlungen von Bedeutung sind.

Hierzu finden Sie folgende Informationen im Anhang:

- Key concerns from CESIO
- Factsheet Surfactant vs. Detergents
- Biodegradability of Surfactants in Detergents
- CESIO TMS Guidance Document Surfactants
- Latest Statement from CESIO

Gerne stellen wir Ihnen diese Informationen zur Verfügung. Sollten Sie derartige Informationen nicht benötigen, so lassen Sie uns dies bitte wissen.
Wir stehen Ihnen selbstverständlich für Rückfragen oder weiterführende Diskussionen zur Verfügung.

Mit freundlichen Grüßen

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European Committee of Organic Surfactants and their intermediates

Subject: Reaction to Council General Approach for a Regulation on detergents and surfactants, asking for technical clarity on surfactants

Brussels, 21 June 2024. Following the Council's adoption of the General Approach for a regulation on detergents and surfactants on 14 June 2024, CESIO, a sector group of Cefic representing manufacturers and suppliers of surfactants in the EU, would like to highlight the urgent need for technical clarifications to ensure that the regulation of surfactants that are used in detergents remains fit for purpose and delivers the intended results.

Surfactants are raw material chemicals used in B2B transactions in the formulation of finished products, including but not limited to detergents. They are typically not intended for standalone consumer use and are used in many non-detergent products ranging from construction and cosmetics to printing inks and adhesives, to name a few. The references to "surfactants and surfactants in detergents" only add confusion and uncertainty as to the scope of this legislation. Our understanding is that this regulation refers to surfactants used in detergents.

Biodegradability and information requirements have already existed for surfactants used in detergents since entry into force of the existing Regulation EU 648/2004. In addition, surfactants are already well regulated within EU REACH and EU CLP. Consequently, additional information on "surfactants" requested by the proposal, should be limited to "surfactants used in detergents sold directly to consumers".

Moreover, the reference testing methods for market surveillance should be reviewed to reflect the latest science, and it is essential to reinstall paragraph 30 of the current detergent regulation EC 648/2004, which allows to waive additional biodegradability tests on surfactants when previous reliable and scientifically robust studies are available. This will help to avoid the unnecessary duplication of tests that otherwise would be conducted without any benefit (please see CESIO detailed position for more detailed comments on this topic and other technical comments).

Conclusion

CESIO remains deeply concerned that the current EU proposal for a regulation on detergents and surfactants adds uncertainty to the regulatory landscape for surfactants with no assessment of impact and unnecessarily duplicates already existing regulatory requirements for surfactants that are used in detergents. We therefore highlight the need to clarify the scope of any new measures and to provide further technical clarifications that will help to avoid regulatory uncertainty and any unnecessary duplication of measures. We remain committed to supporting the further evolution of the regulation in line with the latest scientific developments. We stress that the development of science-based legislation should support and not add burden to EU industries. We therefore call on the EU institutions to further develop fit for purpose legislation focused on the original aims of the revision.

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Revision of the EU Detergents Regulation: CESIO comments on current proposals

October 22, 2024

Background: surfactants used in detergents

- **Surfactants** used in detergents **already comply with a high level of standards**

- Whilst we welcome any targeted improvements and technical developments, especially where efficiencies can be found, we also highlight that the **Detergents Regulation was found to be generally fit for purpose** following the ex-post review in 2019

- CESIO participated in several consultations before publication of the Commission proposal, and at no point before publication of the new proposal in 2023 was there any extensive discussion about further extending requirements or the scope for surfactants, and **no impact assessment** on any such changes has been conducted

CESIO continuous engagement

With the Commission

Summer 2023: Responded to the 'Have Your Say' consultation

October 2023: Finalised position covering key issues

November 2023: Communicated concerns to the Commission during the Detergents Working Group meeting

With the EU Parliament

November 2023: Joint position with IFRA-CESIO-AISE on animal testing

December 2023: Updated position addressing key concerns

January 2024: Updated letter on surfactant-specific issues

February 2024: Published statement on EP vote, noting improvements but highlighting ongoing surfactant-specific concerns

With the EU Member States & Institutions

March - May 2024: Circulated positions and statements prior to Working Party meetings on Technical Harmonisation, requesting member support

June 2024: Statement following Council General Approach approval

May/June 2024: Reached out to the Commission, meeting scheduled for September 2024

Key concerns

1. Scope of regulation for surfactants
2. Biodegradability testing methods and validity of existing studies
3. New administrative burden
    a. Technical documentation
    b. Additional labelling for surfactants
    c. Design of the product passport

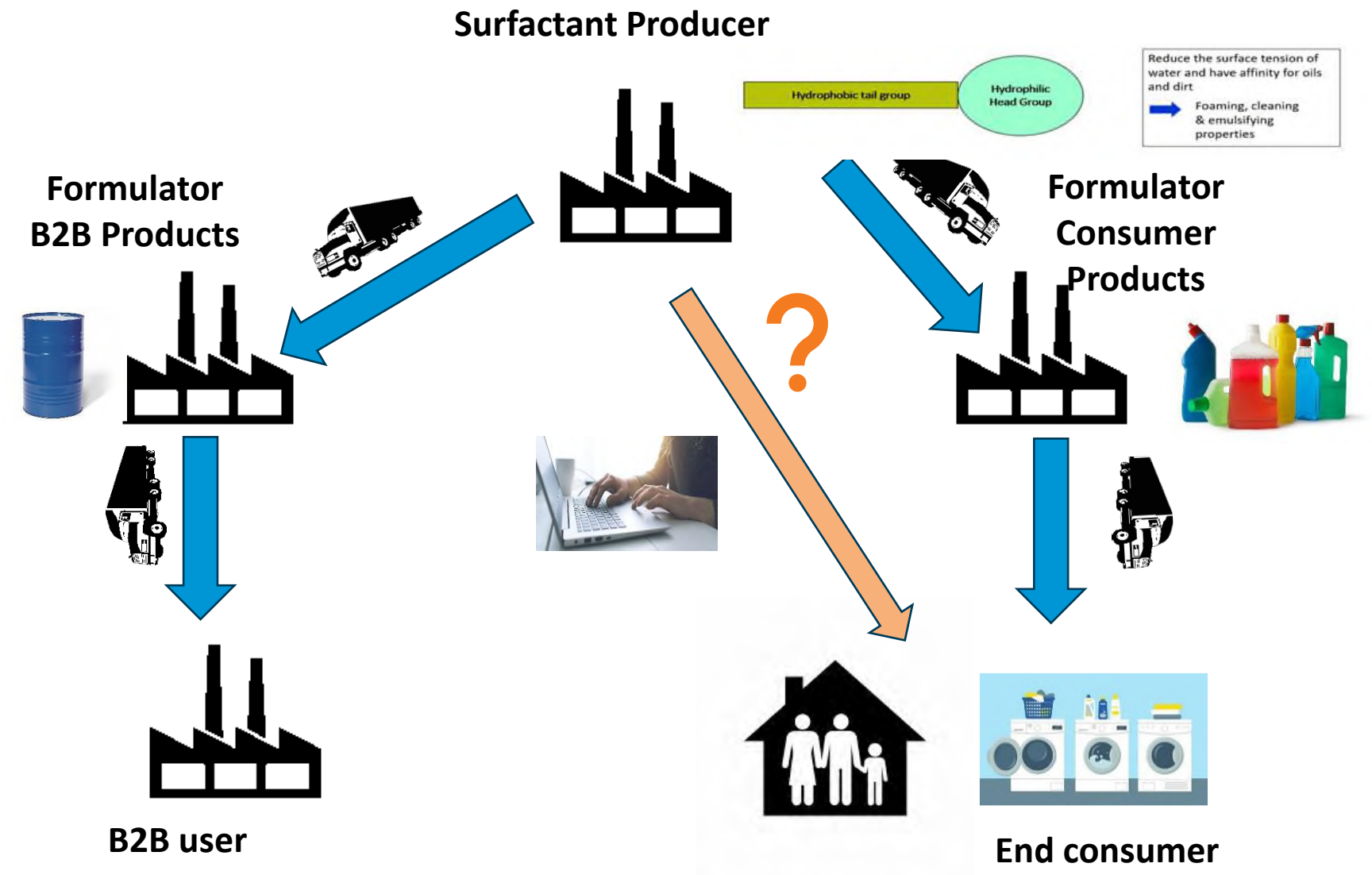
The revision of the Detergents Regulation tends to confuse the role of surfactants

- Surfactants are clearly defined as ingredients of detergents (Article 2 (11)) → the wording "surfactants and surfactants in detergents" confuses this definition and **should focus on "surfactants in detergents"**

- Surfactants are raw material chemicals used in B2B transactions that are typically not intended for standalone consumer use → **level of regulation should reflect raw material vs. end product use (label requirements, technical documentation, etc..)**

- Surfactants are already well regulated within EU REACH and EU CLP. Consequently, additional information on "surfactants" requested by **the proposal should be limited to "surfactants used in detergents sold directly to consumers"** → avoid unnecessary administrative burden

Are surfactants really B2C products?



Note on the proposed definition of surfactants

- The current definition proposed by the Commission and left unchanged by Parliament and Council leaves room for interpretation.

- We highlight the importance of an alignment of the phys-chem criteria within the definition with the definition in the EU Customs Tariff.

- CESIO has a specific working group (TMS) devoted to testing methods of surfactants.
  - We want to ensure that the right methods and procedures can be defined which are scientifically sound.
  - **CESIO TMS will now develop a guidance on testing methods for determining surfactants, which should be available in October of 2024.**

- CESIO remains available to answer any technical questions through our experts if needed.

Biodegradability requirements for surfactants miss latest science and are risk for inefficiencies

- Biodegradability and information requirements have already existed for surfactants used in detergents since entry into force of the existing Regulation EU 648/2004 → **Surfactants already comply with a high level of standards**

- Reference testing methods for market surveillance should be reviewed to reflect the latest science (Article 22, Annex I and VII): the choice of the method depends on the physical properties of the product → **no need for specific reference method**
  - 1. CO_2 headspace test is technically difficult to implement
  - 2. Methods described in Annex VII involve toxic solvents (e.g. chloroform)

- It is essential to reinstall Recital 30 of the current detergent regulation EC 648/2004, which allows to waive additional biodegradability tests on surfactants when previous reliable and scientifically robust studies are available → **avoid the unnecessary duplication of tests**

The revision of the Detergents Regulation introduces new administrative burden for surfactants

Recital 7

(7) Since surfactants are primarily sold in business-to-business transactions in order to be used in the manufacturing of detergents, they do not need to be subject to the same requirements as detergents. Therefore, minimum rules for surfactants should be laid down, namely rules on ultimate biodegradability, a minimum set of labelling information and the obligation of economic operators to draw up a technical documentation and to create a product passport.

But no differentiation foreseen between B2B surfactants and detergents in the requirements (Annex VI, V and VI):

- Technical documentation
- Labelling of contents
- Product passport

Technical documentation for conformity assessment

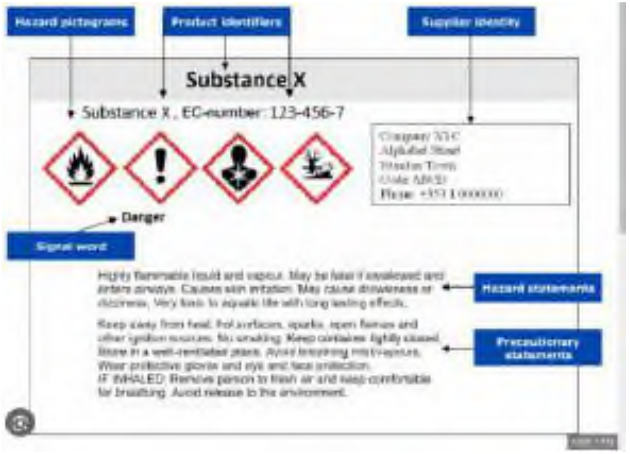
- All necessary information to ensure safety and protection of industrial and professional workers and the environment is already implemented in standard documentation laid down by appropriate parallel legislation (SDS, UFI number for poison centre notification).

- Compilation of information requested **is too much for an ingredient**:
  - General description and intended uses → already defined as being used in detergents
  - Test reports → can be made available for authorities directly upon request
  - List of methods → not clear what wanted in addition to what already in SDS
  - Ingredient data sheet → technical documentation & SDS already names ingredient
  - Analysis and risk assessment → not clear what wanted in addition to REACH

- Both technical documentation for detergents and surfactants shall include the **test reports** demonstrating the biodegradability of the surfactant → **ownership issue**
  - Surfactant manufacturers are usually owner of the studies
  - Those study reports would not be shared with all economic operators (e.g. detergent formulators) but directly with the competent authorities

No need for an additional label for surfactants

- Labelling of surfactants as B2B chemicals is **adequately covered by the CLP**
- Labelling of content defined by **Annex V (anionic vs. cationic, etc) is not needed for surfactants**
  - Surfactants are the ingredient, and
  - The nature of the surfactant is typically specified in technical documentation

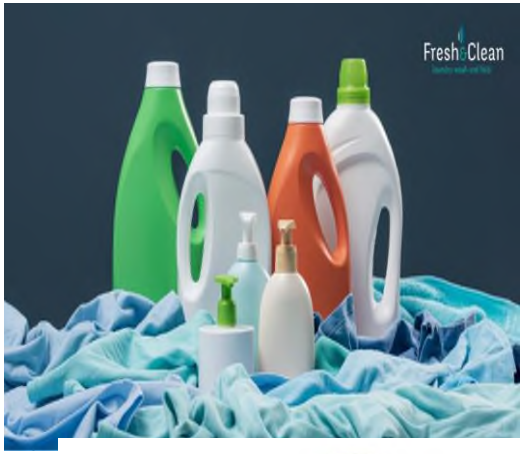


Product passport must be aligned with ESPR

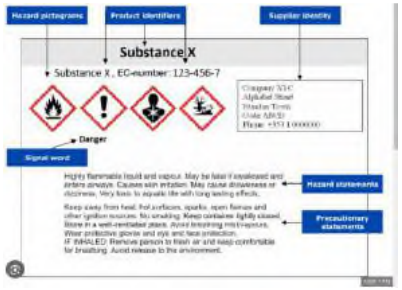
- Product passport for detergents and surfactants should not be the same
- We see the risk that one surfactant product may need to have several DPP´s
  - ESPR product categories for detergents but also cosmetics and textiles
  - ESPR product categories for chemicals or polymers
  - DPP as defined by the detergent regulation
- As surfactants can be used for different purposes other than detergents, requirements should be fixed by horizontal legislation (ESPR)

→ avoid duplication of legislation

Do surfactants need the same requirements as B2C products?



sold to detergent formulators to obtain detergents



sold to formulators to obtain different products

A sector group of Cefic

Conclusions

- Surfactants as B2B ingredients should be regulated differently than detergents, in line with draft Recital 7 – there is no need to set the same requirements.
- The scope “surfactants in detergents” needs to be clear throughout the entire text. The definition should be aligned with the phys-chem criteria in the EU Customs Tariff.
- Market surveillance doesn’t require a specific reference method. The methods should be updated to respect the latest science.
- It is essential to reinstall Recital 30 of the current detergent regulation EC 648/2004, which allows to waive additional biodegradability tests on surfactants when previous reliable and scientifically robust studies are available.
- Many additional obligations (technical documentation, product passport, label of contents) increase the complexity and costs for surfactants as B2B products without added value for consumer health & environment.

Thank you!

ANNEX V

LABELLING REQUIREMENTS

PART A – LABELLING OF CONTENTS

The information to be included on the labels of detergents and surfactants made available on the market

1. The weight percentage ranges 'less than 5 %', '5 % or over but less than 15 %', '15 % or over but less than 30 %', '30 % and more', shall be used to indicate the content of the constituents listed below where they are added in a concentration above 0,2 % by weight:

   (a) phosphates,

   (b) phosphonates,

   (c) anionic surfactants,

   (d) cationic surfactants,

   (e) amphoteric surfactants,

   (f) non-ionic surfactants,

   (g) oxygen-based bleaching agents,

   (h) chlorine-based bleaching agents,

   (i) EDTA and salts thereof,

   (j) NTA (nitrilotriacetic acid) and salts thereof,

   (k) phenols and halogenated phenols,

   (l) paradichlorobenzene,

   (m) aromatic hydrocarbons,

   (n) aliphatic hydrocarbons,

   (o) halogenated hydrocarbons,

   (p) soap,

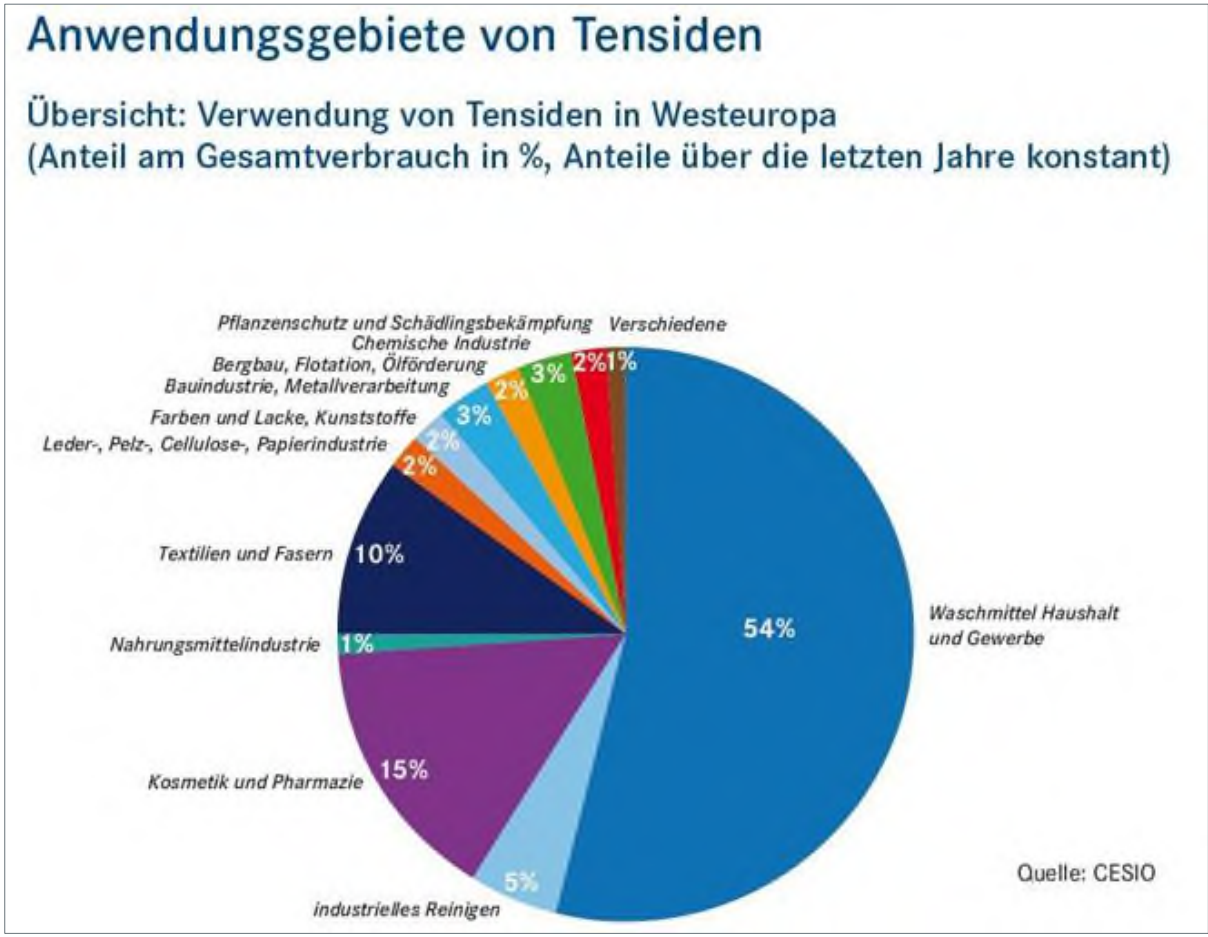
   (q) zeolites,

   (r) polycarboxylates.

Proposal for a regulation on detergents and surfactants ?

Surfactants:

- Are mainly sold as raw materials/ ingredients: B2B in detergents
- Contain one or few components well described in the Safety Data Sheets (SDS)



→ **Why regulate surfactants on the same level as detergents?**

FACTSHEET

November 2024

Biodegradability of surfactants in detergents

In the EU, strict requirements regulating the biodegradability of surfactants used in detergents were introduced over 20 years ago, with the entry into force of Regulation (EC) 648/2004. Consequently, surfactants available on the EU market today already comply with the ultimate biodegradability standard, as defined under Annex III of Regulation (EC) 648/2004. The proposed revision of Regulation (EC) 648/2004 retains this high standard.

Biodegradability testing methods

Various test methods listed in Annex III of Regulation (EC) 648/2004, which correspond to the OECD guidelines 301 A to F and 310, are commonly used. Since the appropriate method for ready biodegradability testing depends on the type of substance being tested, its physical properties, and characteristics such as solubility, volatility and sorption, it is appropriate and essential to retain the availability of these various methods in the proposed revision of Regulation (EC) 648/2004.

Recital 30 of Regulation (EC) 648/2004 allows for the waiver of additional biodegradability tests on surfactants when reliable and scientifically robust studies are available. This derogation has been removed from the proposed revision of Regulation (EC) 648/2004, which poses a massive risk of redundant testing without added value. Therefore, the derogation option provided by Recital 30 should be reinstalled in the proposed revision, allowing for the continued use of previous tests, CESIO.

Reference testing methods

The CO2 headspace test (EN ISO 14593 or OECD 310) is currently defined as the reference method for laboratory testing in both the existing regulation (see Annex III) and the proposed revision. This choice lacks scientific justification, as (a) the specific method was developed by OECD for volatile substances and (b) the diverse chemical properties of surfactants conceptually hinder the selection of a single preferential method suitable for all surfactant types. Ultimately, it would be more appropriate to consider the full range of methods for biodegradability testing listed in Annex III as potential references.

Regulation (EC) EC 648/2004 requires market surveillance authorities to use a reference testing method to reassess the biodegradability of surfactants in case of litigation or concern about validity of existing data. The proposed revision of Regulation (EC) 648/2004 maintains this approach. In addition to the CO2 headspace test as overall reference method for laboratory testing, additional reference methods for surveillance have been compiled in a separate annex.

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However, the necessity of this annex remains unclear in view of the already described methods for biodegradability testing. Furthermore, the proposed revision does not specify the conditions under which particular tests should be applied.

Moreover, the special methods for surveillance have notable drawbacks. The confirmatory test according to the standard EN ISO 11733 is a complicated, lengthy, and costly method making it unsuitable for routine surveillance. The titration methods for testing of anionic surfactants and non-ionic surfactants are nonspecific and involve the use of a toxic solvent (chloroform), reflecting practices from a time when today's state-of-the-art TOC (total organic carbon) determination approaches were nearly non-existent.

In conclusion, there is an urgent need to update and consolidate the set of reference methods to reflect the latest science. Streamlining towards the range of methods given in the annex for biodegradability testing (Annex III of Regulation (EC) 648/2004, Annex I in the proposed revision) appears both reasonable and efficient. In principle, each method therein can be useful and justified as a reference depending on the specific chemistry involved (see above). However, if market surveillance authorities require a prioritized approach, the CO2 evolution test (OECD 301 B) or the manometric respirometry test (OECD 301 F) may be recommended as widely used default approaches.

Availability of the test reports

The proposed revision of the regulation introduces a new requirement that manufacturers of surfactants and detergents shall draw up a technical documentation.

Among other requirements, test reports demonstrating the compliance with the biodegradability requirements shall be provided in the technical documentation without distinction between surfactants and detergents. The criteria on biodegradability only apply to surfactants and the surfactant manufacturers are owners of the studies. Given that the test reports are proprietary, confidential business information, they cannot be made available to all economic operators but could be provided directly to the authorities when asked. Only the test results and methods are shared with the economic operators. The proposed revision needs to be updated to reflect the respective information setup.

FACTSHEET

November 2024

Factsheet Surfactant vs Detergents

What is a surfactant?

A surfactant is a special type of chemical that can help mix substances that usually don't blend well, like oil and water. It has two parts: one that repels water (lipophilic) and one that attracts water (hydrophilic). This unique structure allows surfactants to reduce the surface tension of liquids, enabling them to spread better and wet surfaces more effectively, or to act as defoaming agents or emulsifiers.

Surfactants are versatile and can be produced from natural or synthetic materials. They play a crucial role in many industries, including cleaning products, cosmetics, pharmaceuticals, and numerous processing applications.

What are their uses?

In Detergents: Surfactants are key ingredients in various cleaning products, such as laundry detergents, dish soaps, and surface cleaners. They help remove dirt, grease, and stains by breaking down the surface tension between water and these substances, allowing them to mix and wash away easily. Whether doing laundry, or cleaning dishes, surfactants make these tasks more efficient.

In other industries: The properties of surfactants extend beyond cleaning products. They are also used in various other end products (e.g. cosmetics, pharmaceuticals, agriculture) and processing applications (e.g. textiles, pulp and paper). Their ability to mix and disperse ingredients is invaluable across many sectors. For further information on surfactant applications, please visit CESIO Applications.

What is the difference between a surfactant and a detergent?

While all detergents contain surfactants, they are not the same. Detergents are complex mixtures that include various ingredients designed to clean effectively. A single surfactant alone is usually not enough for effective cleaning. Detergent formulations often combine multiple types of surfactants and additional components, such as enzymes and agents that prevent colors from bleeding, to enhance cleaning performance.

In simple terms, surfactants are one component of detergents, i.e., of products tailored for household and professional cleaning tasks. Detergents target consumers (B2C), professionals, and industrial uses, while surfactants are used in industrial environments (B2B) to formulate detergents.

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How are surfactants regulated?

Surfactants are chemical ingredients found in a wide variety of products and are regulated under EU horizontal legislation for chemicals, such as EU REACH and CLP. Depending on how a surfactant is used, additional industry-specific regulations may also apply. For instance, when surfactants are used in detergents, EU detergents legislation specifically addresses their biodegradability. As a result, all surfactants used in detergents within the EU must meet strict standards for biodegradability.

Conclusions

- **Surfactants are not detergents:** They are essential ingredients within detergents.
- **Detergents are complex mixtures:** They usually contain multiple surfactants and additives for effective cleaning.
- **Different uses:** Surfactants are mainly used in industrial environments (B2B) to formulate detergents that are often consumer-focused (B2C). Surfactants are further up the supply chain than detergents.

How to decide whether a substance is a surfactant?

Joachim Venzmer/Evonik, Jürgen Tropsch/BASF, Christophe Moineau/SYENSQO, Katrin Wunderlich/Zschimmer & Schwarz

Introduction

Both the EU Detergents Regulation[1] (EU DetReg) and the EU Customs Tariff regulation[2] contain a surfactant definition, but the two regulations do not provide any guidance on how to apply the respective criteria. For this reason, the CESIO working group Test Methods of Surfactants, comprised of leading phys-chem experts in the field of surfactants, has prepared this guidance document on how to use those definitions in practice. It should be noted that the current definition of the EU DetReg, which is likely to be transposed into the updated EU Detergents Regulation, is difficult to apply in practice. Therefore, with this guidance we hope to create some common understanding on the testing methods and phys-chem criteria which can be applied to identify a surfactant within the confines of the current definitions.

1. Current Definitions

EU DetReg (2004):

> 'surfactant' means any organic substance and/or mixture used in detergents, which has surface-active properties and which consists of one or more hydrophilic and one or more hydrophobic groups of such a nature and size that it is capable:
>
> - of reducing the surface tension of water (to below 45 mN/m as specified later in the "Questions and agreed answers" document[3])
> - and of forming spreading or adsorption monolayers at the water-air interface,
> - and of forming emulsions and/or microemulsions and/or micelles,
> - and of adsorption at water-solid interfaces.

[1] Council. 2004. Regulation (EC) No 648/2004 of the European Parliament and of the Council of 31 March 2004 on detergents

[2] International Customs Tariff Regulation. Section VI – Chapter 34

[3] Questions and agreed answers concerning the correct implementation of Regulation (EC) No 648/2004 on detergents

Customs Tariff Regulation

"organic surface-active agents" are products which when mixed with water at a concentration of 0.5% at 20°C and left to stand for one hour at the same temperature:

- Give a transparent or translucent liquid or stable emulsion without separation of insoluble matter; and
- Reduce the surface tension of water to 45 mN/m or less.

2. Challenges of the current definitions

Apart from the fact that there are no details given how to perform the experiments necessary, the main difficulty in applying the existing definitions is that at least two of the five criteria of the current EU Detergents Regulation are not at all clear, and they are connected by "and", making interpretation all the more difficult. Materials which meet the first four criteria could very well fail to qualify as surfactants, since it is not clear how to use the last criterion (adsorption on solids) of the EU DetReg.

Reduction of surface tension to <45 mN/m (EU DetReg, Customs Tariff)

For most of the surfactants used in laundry and cleaning formulations, the surface tension is in the range of 25-35 mN/m, which means this requirement is met by a safety margin of 10-20 mN/m. This does not come as a surprise, since surface activity is a phys-chem property determined by the length and nature of the hydrophobic tail in relation to the size and nature of the hydrophilic headgroup. Therefore, experts having a sufficient amount of experience do not really need to measure surface tensions – one can pretty much predict surface tension by looking at the molecular architecture of the substance studied.

There are, however, a few cases which require some closer attention:

- Very hydrophilic surfactants (i.e. those having a large hydrophilic headgroup and a rather short alkyl tail) show reduced surface activity; hence, to be on the safe side, the surface tension should be measured. The use of classical equipment[4] (Wilhelmy plate[5], du Noüy ring[6]) to determine the surface tensions should not pose any problem.
- Large hydrophilic polymers with very few hydrophobic groups, which is the typical architecture of so-called associative thickeners, cannot bring a sufficient number of hydrophobic groups to the air/water interface to efficiently lower surface tension. Therefore, it is difficult to predict the 3D structure of the molecules and whether the surface tension criterium could be met. Since by using the classical equipment (Wilhelmy plate, du Noüy ring) the surface age is not controlled, such measurements are prone to artifacts.

[4] OECD (1995), Test No. 115: Surface Tension of Aqueous Solutions, OECD Guidelines for the Testing of Chemicals, Section 1, OECD Publishing, Paris

[5] Wilhelmy L. (1863). Ueber die Abhängigkeit der Capillaritäts-Constanten des Alkohols von Substanz und Gestalt des benetzten festen Körpers. Ann Physik 195:177-217

[6] du Noüy PL. (1919). A new apparatus for measuring surface tension. J Gen Physiol 1:521-524

Special care needs to be taken when measuring surface tension, since the classification as surfactant should be based upon the properties of the substance and not on deficiencies of unsuitable methods.

- In case of not sufficiently soluble substances, there are two challenges: On the one hand, a separation of some hydrophobic material at the air/water interface is quite likely, making a determination of surface tension difficult; especially using classical equipment (Wilhelmy plate, du Noüy ring) will lead to nothing but artifacts. On the other hand, the challenge concerning the surface tension criterion is not that surface activity of the material might be too low - the challenge is that surface activity could be quite high, but the methods originally developed for soluble surfactants cannot be applied. In these cases, the method of choice (but more or less only available in a limited number of specialized academic laboratories) would be a Langmuir film balance[7], which would need to be employed to determine the surface activity of lipids forming so-called insoluble monolayers (e.g. spread from a chloroform solution onto a water surface). Such purely academic studies should be outside the scope of this regulation and hence will not be discussed further.

While the Customs Tariff Regulation clearly specifies that the surface tension cut-off criterion of <45 mN/m should be met at a concentration of 0.5%, the EU DetReg does not add much precision, which leaves room for interpretation. Although the European Commission made clear in the "Questions and agreed answers" document that the surface tension cut-off criterion of <45 mN/m applicable under the EU DetReg is the exact same one as applicable under the Custom Tariff Regulation, it did not confirm the concentration of 0.5%. This introduces confusion, especially as the "legally existing" methods like the OECD 115 recommend a concentration of 0.1% to measure surface tension. Hence, either (i) the definition of the EU DetReg should be adapted to allow for a range of concentration (0.1-0.5%) to be consistent with the Custom Tariff Regulation and with the "legally existing" methods that have been long in place, or (ii) the definition shall be clearly aligned with the one of the Custom Tariff Regulation (concentration = 0.5%) and new preferred methods shall be recommended like the Pendant Drop Tensiometry method, that is applicable at any test concentration. The second option (ii) is the one supported by CESIO, as further explained in the sections below (cf. sections Preparation of the samples and Suggested experimental procedures).

Spreading or adsorption layer at the air/water interface (EU DetReg)

It is not clear what the idea behind this criterion is, since the consequence of such an adsorbed surfactant layer is a reduction in surface tension – but this is already the previous criterion on reducing surface tension. How should this adsorption layer be assessed experimentally, if not by measuring surface tension? There are reflectometry methods to study the internal structure of such adsorption layers at the air/water interface; however, they require highly specialized experts e.g. for X-ray reflectometry, available at some academic laboratories or at major research

[7] Gaines G.L. Insoluble Monolayers at Liquid-Gas Interfaces, Interscience Publishers, New York 1966

institutions (e.g. Neutron Reflectometry at ILL in Grenoble[8]). Therefore, since the reduction of surface tension is already a criterion, this "adsorption layer" criterion is probably not needed, as it only describes the structural origin of the surface tension reduction criterion. Otherwise, this criterion can be considered to be fulfilled without further ado, in case the surface tension criterion was met.

One idea behind using the term "spreading" in this criterion is probably to exclude more hydrophobic substances which are forming an oil lens at the air/water interface – but such cases could easily be covered (i.e. excluded) by using the remark "without separation of insoluble matter" as discussed below. Concerns mentioned in the European Commission's "Questions and agreed answers" document[9] that hydrophilic substances may reduce surface tension without forming an adsorption monolayer are unjustified; even at a concentration as high as 10%, acetic acid (which is mentioned there as an example) has a surface tension of 59.1 mN/m[10], which is closer to water (72.8 mN/m) than to the limit of 45 mN/m.

Formation of emulsions and/or microemulsions and/or micelles (EU DetReg)

The "micelle" requirement of this criterion excludes alcohols such as pentanol or hexanol, which might sufficiently reduce surface tension, but do not act as surfactants in terms of solubilization or formation of micelles. In case of clear aqueous solutions, the formation of micelles could be proven by using Dynamic Light Scattering; this, however, requires specific equipment as well as highly specialized experts. It would be much easier to just use a (green) laser pointer: in case the laser beam can be seen in the clear sample, there must be micelles – single low molecular weight molecules do not scatter light.[11]

However, the main idea behind this criterion is to cover not only hydrophilic surfactants giving clear micellar solutions in water, but also the more hydrophobic ones which are not water-soluble, but only water-dispersable. Therefore, amphiphilic materials which are not soluble in water, but able to act e.g. as w/o-emulsifiers are included in the surfactant definition. The inclusion of such hydrophobic substances poses several challenges.

The fundamental properties of **microemulsions**, i.e. thermodynamically stable, homogeneous mixtures of oil, water and surfactant, are extensively described in the literature[12], [13], [14]. Typical properties of microemulsions are a transparent or translucent appearance and a droplet size in the range of tens of nm. Typically,

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[8] Campbell R. A., Wacklin H. P., Sutton I., Cubitt R., and Fragneto G. (2011) "FIGARO: The new horizontal neutron reflectometer at the ILL," Eur. Phys. J. Plus, vol. 126, no. 11, pp. 1–22

[9] Questions and agreed answers concerning the correct implementation of Regulation (EC) No 648/2004 on detergents

[10] Yamada T., Ono N. (2015) A Study on Micromixing Utilizing Marangoni Effect Induced on Gas–Liquid Free Interfaces, J. Micro Nano-Manufacturing 3(2):021003

[11] K. Brandt, J. Venzmer: Micellar Formulations – Old Wine in New Skins? SOFW Journal 03/20, Vol 146, 2020, 34-37.

[12] J. H. Schulmann, W. Stoeckenuis, L. M. Prince, J. *Chem. Phys.* **63** (1959) 1677

[13] L. M. Prince, in: Microemulsions: Theory and Practice, Academic Press, Ney York 1977

[14] P. Winsor, in: Solvent Properties of Amphiphilic Compounds, Butterworth, London 1954

microemulsions require the existence of both oil and surfactant – so for a single substance, the formation of a microemulsion will hardly be possible. Only in case of multiconstituent substances, there could be an o/w-microemulsion consisting of micelles (formed by the more hydrophilic species) swollen by the more hydrophobic components of the substance.

An **emulsion** is "a heterogeneous system of two or more liquid phases, consisting of a continuous liquid phase and at least one other liquid phase dispersed into the first in the form of small droplets"[15]. According to this definition, an emulsion, at least temporarily, can be created from all, even completely incompatible, liquids – it is just a matter of shear force and time scale of observation, whether a homogeneous emulsion or (eventually complete) phase separation is observed. Therefore, without guidance on how to prepare the emulsion and without a stability criterion, this part of the surfactant definition is hardly useable. In fact, this part of the definition could be the basis of "reverse engineering": Depending on whether the substance tested should be a surfactant or not, the mixing conditions could be chosen in order to provide the expected result. Also, an inherently unstable emulsion poses challenges when it comes to the determination of surface tension: An oil film at the air/water interface will more or less dominate the results, depending on the method to measure surface tension.

Adsorption at solid/water interfaces (EU DetReg)

This last criterion of the EU Detergents Regulation is the most unclear for several reasons. Most importantly, the solid is not specified: It could have a variety of surface properties (hydrophobic or hydrophilic, cationic (e.g. mica) or anionic (e.g. silica)), and by choosing different materials (such as activated carbon, minerals, or PTFE powder) drastically different results will be obtained. In addition, the logic behind this criterion is not clear: In case the other four criteria were met, is one adsorbing solid sufficient for a material to qualify as surfactant, or is one non-adsorbing solid sufficient for a substance to disqualify as surfactant? Depending on how this criterion is being used, it does not allow to discriminate between a surfactant and a non-amphiphilic substance, e.g. almost everything adsorbs to activated carbon, but this does not mean that the molecules which are being adsorbed to activated carbon are surfactants. Also, because of Coulomb repulsion, it would be possible to show that cationic surfactants are not surfactants according to EU DetReg, since they do not adsorb to cationic solids (e.g. mica). The same holds true for anionic surfactants, which do not adsorb to anionic solids (e.g. silica). Therefore, this criterion could be deleted without any consequences; during the past two decades, it was (or in fact had to be) ignored anyway.

Transparent or translucent liquid or stable emulsion without separation of insoluble matter (Customs Tariff)

The addition "without separation of insoluble matter" is an important necessity, but difficult to assess experimentally. The idea is that an oily substance floating on top of water should not qualify as surfactant. The absence of such an oily layer is also crucial for the surface tension measurements using the only methods mentioned in OECD TG 115: Wilhelmy plate and du Noüy Ring. These classical methods are –

[15] EN ISO 862:1995

because of an undefined surface age – especially sensitive to artifacts caused by hydrophobic materials accumulating at the air/water interface.

Preparation of the samples

A concentration has not been defined in the EU DetReg; in order to be consistent and not to create confusion, the 0.5% from the Customs Tariff regulation should be used, just like the corresponding surface tension limit of 45 mN/m. For "typical" surfactants, i.e. hydrophilic and micelle-forming, the preparation of an aqueous solution is straight forward – no special care needs to be taken. But there are more difficult candidates, which could be rather hydrophobic (or contain more hydrophobic components) and/or are solid. In those cases, it is indispensable to both define a mixing procedure and a stability criterion, since "separation of insoluble matter" should lead to an exclusion as surfactant, also because such a separation makes a determination of surface tension pretty much impossible. Intensive, high shear mixing could force a substance incompatible with water to form an emulsion; this is, however, nothing the substance would do "voluntarily" – and therefore should rather be avoided; low-shear mixing using a magnetic stir bar would be recommended. Another question is how to deal with solids: Should they be molten before mixing in case they are sufficiently stable? Or should the dispersion be made above the melting point to facilitate the dispersion process? However, in both cases, ensuring the chemical stability of the substance is important. Otherwise, an unsuitable mixing process would be an excellent option to rule out that a solid surfactant is – legally-speaking - a surfactant. In this context, (anionic) surfactants having a Krafft point above room temperature also pose a challenge, since "separation of insoluble matter" means in this case "separation of crystals".

Some substances are hard to disperse in water; therefore, their delivery form might contain a considerable amount of a water-miscible solvent (e.g. glycols). This is intentionally added just for ease of handling by the formulators. Such substances shall also be tested in a neat form; this follows the rationale that the classification of a substance should be a property of the substance itself rather than its delivery form.

Some nonionic surfactants have a cloud point <20°C, typically measured at 1% in water; hence, they are insoluble in water at room temperature. If possible, the solution should be prepared at temperatures below cloud point.

The evaluation (visual observation, surface tension measurement) of the samples should be done at room temperature; for practical reasons, this could be 20 to 22 °C.

Some substances are insoluble at certain pH values, e.g. soaps at pH<8. This applies also to other ionic surfactants containing ionic groups of weak acids or bases. Therefore, the pH value of the aqueous mixture is relevant for both the determination of solubility and the measurement of surface tension. Since surface tension can depend on pH, there are several options to choose the "correct" pH: This could be either the pH of the substance as placed on the market, or the pH at which the substance is used in a typical application, or the pH of the substance after use. If pH adjusters are used, they must be chosen from the list described in the Ecotox test standards (e.g. OECD 201 or OECD 301).

3. Suggested experimental procedures

Preparation of aqueous samples

A 0.5 wt% aqueous solution is prepared by adding 0.45 g of the test substance to 89.55 g of demineralised water in a 100 mL beaker or glass jar (h = 10 cm; ∅ = 4 cm) with screw top. The mixture is thereafter stirred for one hour at room temperature (approximately 20 – 25 °C) using a magnetic stirrer (l = 29 mm; ∅ = 7 mm) between 500 and 1000 rpm. Solid substances should be molten first in order to facilitate preparation of a representative sample. At the end of the dissolution process, the evaluation time of one hour starts.

Evaluation of aqueous samples

a) **Clear micellar solution**: In this case, the formation of micelles needs to be proven, either by Dynamic Light Scattering or by using a (green) laser pointer.
b) **Microemulsion and** c) **Emulsion:** Concerning the separation stability of the mixture, it is reasonable to evaluate the optical appearance after one hour (just before measuring the surface tension); special care needs to be taken to look for separation either on top (creaming) or at the bottom (sedimentation).

   Recommended procedure for evaluating the stability of emulsions:
   An aliquot of the prepared sample is transferred to a cuvette and the turbidity (preferred: turbidity ratio at two widely separated wavelengths) is measured at the beginning of the test period and after standing for 1 h by using e.g. a nephelometer. If the change in turbidity units (preferred: turbidity ratio at two widely separated wavelengths) is >25%, the sample is regarded as not forming a stable emulsion. Otherwise, the stability criterion is fulfilled.

Surface tension measurement

Only if the stability criterion (micelle, microemulsion, or emulsion, and no separation of insoluble matter) is fulfilled, surface tension is to be measured. The classic methods (Wilhelmy plate and du Noüy ring) to determine surface tension are described in OECD 115. However, the state-of-the-art in both academic and industrial laboratories for more than 20 years is Drop Shape Analysis (a.k.a. Pendant Drop Tensiometry). This is much preferred, especially for turbid samples, since every measurement starts with a fresh surface, making this method more reliable and less prone for artifacts. A norm (DIN 53013) on the use of the Pendant Drop method to determine surface tension of surfactant solutions is currently being developed; as of today, there is only a norm from the area of paints and varnishes (EN ISO 19403-3[16]).

Experimental report

The evaluation report for each sample should include the following points:

- Used materials, concentrations, conditions, pH value, pH adjustment to reach solubility if appropriate
- Optical appearance directly after mixing

[16] EN ISO 19403-3. 2020. Paints and varnishes - Wettability - Part 3 : Determination of the surface tension of liquids using the pendant drop method

- In case of clear solution check for micelles using laser pointer
- Optical appearance (separation?) after storage for one hour at 20 °C
- Turbidity ratio measurements (1 hr vs. fresh) for an emulsion in case no oily layer is visible on top
- Surface tension, ideally determined via the Pendant Drop method; in case of turbid samples picture of magnified drop (used for the surface tension measurement) to substantiate the validity of the result.

4. Final Remarks

This document shows that it is not really possible according to the current EU DetReg to give a legally binding answer whether a substance is a surfactant or not. As discussed above, an omission of the criteria “spreading or adsorption layer at the air/water interface” and “adsorption to solids” and the addition of the remark “without separation of insoluble matter” would solve these issues; additionally, such an update of the surfactant definition in EU DetReg would also harmonize the regulations in Europe (EU DetReg and EU Customs Tariff). This is the reason CESIO has already proposed an amendment of the surfactant definition.