

Substances ionised in water

1. INTRODUCTION

The question whether substances ionised in water must be registered was raised by Germany by email from 21 November 2008 to ECHA, REHCORN and GRIP. On the basis of views expressed by ECHA, NL, UK, IR and SK, Germany prepared a paper for discussion at the 6th CA-meeting. At that meeting, it was decided that the issue would be further addressed by the Commission and ECHA for discussion at the next CA-meeting.

Question:

Must "potential new" salts which are formed by dissolving salts, acids and bases in water be registered?

2. BACKGROUND

A substance is by definition a chemical element and its compounds including impurities but excluding any solvent which may be separated without changing its composition.

That means that a salt which is dissolved in water remains the same salt after removal of the water (in accordance with the **substance definition**). However, by dissolving a mixture of two or more salts in water a solution is formed in which new salts (different combinations of cations and anions) may result if the water were to be removed.

In accordance with REACH Article 2(7)(b), substances covered by Annex V shall be exempted from Titles II, V and VI (registration, downstream users and evaluation), as registration is deemed inappropriate or unnecessary for these substances and their exemption from these titles does not prejudice the objectives of this Regulation. Annex V of the REACH Regulation, as recently amended (Commission Regulation (EC) No 987/2008 of 8 October 2008), contains an exemption for:

“3. Substances which result from a chemical reaction occurring upon end use of other substances, preparations or articles and which are not themselves manufactured, imported or placed on the market.”

The draft guidance on Annex V states with regard to point 3, that *"This entry also covers substances present as ionic mixtures in water-based solutions as a result of mixing salts, acids and bases without creating new covalent bonds. Registration would be inappropriate for these substances as the resulting ion pairs are not manufactured substances as such and isolated from the solution, but formed as part of the chemical equilibrium in the solution only. This applies if all acids, bases and salts mixed (i.e. introduced in the solution) have already been registered by an actor up the supply chain.. [etc]". "It must be emphasized that deliberate neutralisation of acids or bases to form the corresponding salts, including neutralisation during formulation, is usually a manufacturing process and is not covered by this entry."*

The exemption in Annex V originates from criteria for reporting substances for EINECS: *"Substances which result from a chemical reaction occurring upon end use of other substances, mixtures or articles (e.g. adhesives, paints, miscellaneous cleansers or housekeeping products, fuels, fuel additives, water softeners, photographic films, batteries, matches) and which are not themselves placed on the market should not be reported. Only substances which are components of adhesives, paints, cleansers, etc. can be reported."* (see Manual of Decisions for implementation of Directive 67/548/EEC, updated version July 2006, pg. 21)

Section 5.13 of the MoD (under Directive 67/548/EEC) addresses the release of a new substance in use and states that: *"The notification requirements for a new substance released in use but not marketed as such was discussed. It was agreed that substances released in use need not be notified"*. This discussion had arisen at the time concerning a washing powder, where the formulation put on the market contained only EINECS substances, but during the washing process a new (non EINECS) substance existed in the solution. It was decided that as the substance existed in the solution upon end use and was not put on the market, it did not require a notification.

Dissolving of a mixture of two or more different salts in water results in a solution of the salts in water. If this process takes place upon end use (e.g. the consumer using washing powder) then any substance existing in solution is exempted through Annex V.3 as it is an end use and the substance is not manufactured, imported or placed on the market. If this process takes place during formulation of a water solution (e.g. detergent) that is placed on the market, do the substances occurring in solution require registration?

Annex V of the REACH Regulation (as recently amended (Commission Regulation (EC) No 987/2008 of 8 October 2008), also contains an exemption for:

" 4. Substances which are not themselves manufactured, imported or placed on the market and which result from a chemical reaction that occurs when:

- (a) a stabiliser, colorant, flavouring agent, antioxidant, filler, solvent, carrier, surfactant, plasticiser, corrosion inhibitor, antifoamer or defoamer, dispersant, precipitation inhibitor, desiccant, binder, emulsifier, de-emulsifier, dewatering agent, agglomerating agent, adhesion promoter, flow modifier, pH neutraliser, sequesterant, coagulant, flocculant, fire retardant, lubricant, chelating agent, or quality control reagent functions as intended; or
- (b) a substance solely intended to provide a specific physicochemical characteristic functions as intended".

Annex V point 4(b) covers the particular case where, in order to provide a specific physicochemical characteristic, water is added to a mixture of ionic substances (salts, acids and bases). The ionic pairs in equilibrium in the aqueous solution are then the result of the water functioning as intended and would consequently not be considered to be themselves manufactured, imported or placed on the market.

In order for this exemption to be applicable, the following conditions must be fulfilled:

1. All starting substances (salts, acids and bases) of the aqueous solution must be (pre)registered;
2. None of the salts in the aqueous solution is isolated from the solution; and
3. The salts remain in their ionic form in the solution.

These three conditions equally apply to imported solutions. In particular, this requires that all starting substances of the imported solution must be known and (pre)registered in the EU; otherwise the exemption does not apply.

The latter two conditions must also be fulfilled by any customer down the supply chain. If a customer removes any salt from the solution his/her role as downstream user is ending here and he/she becomes a manufacturer which must register the isolated substances.

For solutions of salts in water no registration is required of ionic pairs as long as the combinations of ions co-exist with their different equilibria in the solution and no salts are isolated. In this context, it might be useful to clarify that

(1) whenever ionic pairs exist only as a part of the chemical equilibrium in the aqueous solution, they are not themselves considered to be manufactured, imported or placed on the market and thus do not require registration.

(2) whenever a salt is isolated from the solution, it is manufactured and needs to be registered.

(3) deliberate neutralisation of acids or bases to form the corresponding salts, including neutralisation during formulation, is usually a manufacturing process and is not covered by this exemption.

It should be noted that although the registration of substances ionised in water as described above is deemed inappropriate and is therefore exempted, **the potential risks associated with the substances ionised in water must be taken into account in the chemical safety assessment of the starting materials (i.e. salts, acids or bases introduced in the aqueous solution), where applicable.**

3. CONCLUSION

Substances present in their ionic form in water-based solutions as a result of mixing salts, acids and bases do not require registration as long as they are not themselves manufactured and remain in their ionic form in the solution. A prerequisite to this exemption to apply is that all acids, bases and salts mixed (i.e. introduced in the solution) must have already been (pre)registered by an actor up the supply chain (or exempted from registration by another exemption, if applicable). However, deliberate neutralisation reaction between acids and bases to form the corresponding salts is considered to be a manufacturing process and is not covered by the exemption. Also the isolation of a salt from the solution is considered manufacturing and therefore not covered by the exemption.

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Annex

The example in this Annex is for illustration purposes in the context of this document only.

EXAMPLE Detergent formulation (all-purpose cleaner)

In some cases, there are water solutions that are manufactured by mixing many different kinds of substances (e.g. salts, acids, bases) in water. One example of this can be a detergent used as all-purpose cleaner. A formulation of such a product can contain the following substances (First list):

- Sodium lauryl ether sulphate
- (Linear) alkylbenzene sulphonic acid
- Oleic acid
- Nitrilotriacetic acid (NTA)
- Phosphoric acid
- Citric acid
- Sodium hydroxide
- Potassium hydroxide
- Non-ionic surfactant, preservative, dyes, fragrance: do not participate to acid/base equilibria

In this case, some salts, acids and basis are mixed in different proportions in order to achieve a product with a certain surfactant properties. As a consequence of the dissolution of the different substances, the different cations and anions find an equilibrium state forming pairs of ions. In the example shown above, it is theoretically possible to identify 12 anions and 2 cations. In this case, more than 40 substances may theoretically coexist in solution. Some of them may be the same as the precursor substances. A non-exhaustive list of potential substances in solution (based on acid-base reactions/equilibria achieved via the protolytic reactions with water) that could be formed in addition of the above-mentioned ingredients (and identified only if water is removed) is shown below (Second list):

- Sodium alkylbenzene sulphonate
- Potassium alkylbenzene sulphonate
- Trisodium citrate
- Disodium citrate
- Monosodium citrate
- Tripotassium citrate
- Dipotassium citrate
- Monopotassium citrate
- Monosodium, monopotassium citrate
- Sodium oleate
- Potassium oleate
- Sodium phosphates

- Potassium phosphates
- Potassium lauryl ether sulphate
- Potassium salt of NTA

Adding one more base (e.g. ammonia) to the formulation would lead to an even greater number of potential ion pairs in solution.

As long as the salts in solution remain in their ionic form in the solution and are not isolated from it, it is only necessary to register the precursors (first list) but not the potential substances that may be formed in a solution (second list).