1,4-Dioxane Formation, Control, and Occurrence in Cleaning Products

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Quick Intro to ACI

• Founded in 1926, based in DC
• 140+ member companies
• Members include:
  • Manufacturers of household, I&I, healthcare cleaning products
  • Chemical producers (surfactants, fragrance, enzymes, etc.)
  • Finished packaging suppliers
  • Chemical distributors
A Snapshot of ACI Members
Surfactants

• Surfactants (surface active agents) are compounds that lower the surface tension (or interfacial tension) between two liquids, between a gas and a liquid, or between a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, and dispersants.

• Vital role in modern society – keeping consumers, our homes, workplaces, and public places, clean and sanitary.
  • Without surfactants many essential products would not exist: examples: laundry detergent, surface cleaners (kitchen, bathroom etc.), dish soaps, oven cleaners, body washes, shampoo etc.
There are two key classes of ethoxylated surfactants

- **Alcohol (Alkyl) Ethoxy Sulfate (ANIONIC SURFACTANT)**

  \[
  \text{C}_n\text{H}_{2n} (\text{C}_2\text{H}_4\text{O})_m\text{SO}_4\text{X} \\
  n = 12-18 \\
  m = 0-8 \\
  X = \text{sodium, ammonium or TEA}
  \]

  \[
  X = 10-13 \\
  (\text{total alkyl length} = \text{C}12-15) \\
  Y (\text{ethoxylates}) = 0-6
  \]

- **Alcohol (Alkyl) Ethoxylate (NONIONIC SURFACTANT)**

  \[
  \text{C}_n\text{AE}_m \\
  n = 8-18 \\
  m = 3-12 \\
  A = \text{alcohol} \\
  E = \text{ethylene oxide}
  \]

  \[
  X = 6-12 \\
  (\text{total alkyl length} = \text{C}12-18) \\
  Y (\text{ethoxylates}) = 0-18
  \]
Ethoxylolation and Sulfation
Ethoxylate

The process of reacting an alcohol with Ethylene Oxide to create an Ethoxylate/Alcohol Ethoxylate (non-ionic surfactant).

Where:
R = Carbon or Hydrogen (atom or molecule)
M⁺ = Molecular ion
EO = Ethylene Oxide
AE = Alcohol Ethoxylate

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SO₃ Sulfation of AE → AES

The process of reacting AE (nonionic surfactant) with Sulfur Trioxide to create an Alcohol (alkyl) Ethoxysulfate (anionic surfactant).

Where:
R = Carbon or Hydrogen (atom or molecule)
EO = Ethylene Oxide
AE = Alcohol Ethoxylate
AES = Alcohol Ethoxysulfate
SO₃ = Sulfur trioxide
Attributes Compared to Non-ethoxylayted Surfactants

Alkyl Ethoxysulfates
• Mass efficiency
• Better cleaning
• Better hardness tolerance
• Good for cold water
• Better for solubility/compaction
• Lower solvent requirement
• Good for grass cleaning
• Good for sebum cleaning
• Enzyme Stability
• Very high foaming

Alkyl Ethoxylates
• Mass efficiency
• Better hardness tolerance
• Better for solubility/compaction
• No solvent requirement in several formulations
• Good for grass cleaning
• Good for sebum cleaning
• Low foaming
• Mildness
• Enzyme stability
“Ethoxylated nonionic surfactant in laundry detergents is mostly biodegradable alcohol ethoxylates (AE), which can remove sebum efficiently at low temperature [3 – 6]. AE can maintain enzyme stability in the presence of anionic surfactant [7] and therefore has excellent compatibility with enzyme in laundry detergents. [8].”
Other references citing the attributes of ethoxylated surfactants
Environmental Attributes of Ethoxylated Surfactants

- Rapid and ultimate biodegradation
- 83.5-99.8% removal in WWTP
- No adverse impacts on the aquatic or sediment environments
Significance of Attributes of Ethoxylated (nonionic) and Sulfated (anionic) Ingredients

• Multiple performance benefits, formulation versatility
• Human and environmental safety profile
• Holistic sustainability benefits
Formation of 1,4-Dioxane
Why is 1,4-Dioxane found at low levels in AE and AES surfactants?

• 1,4-Dioxane is not intentionally added, or used as a raw material in production

• It is a trace level technically unavoidable byproduct (impurity) from the chemical reaction itself
Byproduct of Sulfation: 1,4-Dioxane

If $\frac{\text{mols } SO_3}{\text{mols feedstock}} > 1.04$ then rapid increase in 1,4-Dioxane (Foster, 1997)

Where:
$SO_3 = $ Sulfur Trioxide

$1,4$-Dioxane can be formed from ethoxymers with $\geq 1$ mole of EO when excess $SO_3$ is used.
Control/Remediation of 1,4-Dioxane in Cleaning Product Ingredients
Control of 1,4-Dioxane During Sulfation of AE → AES

- **Process and Equipment Factors**
  - $\text{SO}_3$: AE feed mole ratio
  - Reactor Loading
  - Residence time of AES acid prior to neutralization

- **Feedstock Composition Factors**
  - Average degree of ethoxylation
  - PEG and moisture content
  - EO adduct distribution
Remediation Mechanism – Stripping AES Paste
Occurrence of Ethoxylated/Sulfated Ingredients in Cleaning Products
Inventory of Cleaning Product Ingredients/Categories

• 57 ethoxylated ingredients in cleaning products
• All product categories contain ethoxylated ingredients
  • All Purpose Cleaners
  • Dish Care Products
  • Laundry Care Products
Measuring 1,4-Dioxane in Finished Products

- DTSC proposed EPA methods 8260 and 8270 use Flame Ionization Detection (FID) which is not considered very sensitive
  - Methods will measure to 2 ppm in liquid products without extraction, and down to 0.02 ppm with solid phase extractions, however, this approach may be problematic for cleaning products
  - Require time consuming steps and special equipment (steam distillation apparatus or purge and trap system)
  - More applicable for surface and drinking water and raw materials
- These limitations with current EPA analytical methods suggest there will be analytical challenges with more complex product matrices
- ACI and its members are partnering to advance and make available an aligned, robust and accurate quantitative method for 1,4-Dioxane in consumer products
Further Method Considerations

• Recent publications with personal care and cleaning products reference the use of 1,4 dioxane-d₈ as an internal standard:
  • Zhou, W. 2019 The Determination of 1,4-Dioxane in Cosmetic Products by Gas Chromatography with Tandem Mass Spectrometry. *Journal of Chromatography A* 460400 (FDA paper)
  • Shin, H.; Lim, H. 2011 Determination of 1,4-Dioxane in Water by Isotopic Dilution Headspace GC–MS. *Chromatographia*, 1233–1236

• Use of deuterated internal standard approach provides a simple, robust method that could be used by contract labs, avoiding the need for special equipment or high-end capability in a formulation setting for testing of finished products

• Additional considerations needed for manufacturing facilities

• Regardless of end-user, standard method development, validation, round robin testing for aligned industry approach requires attention
Environmental Monitoring Data

• 1,4-Dioxane is reported to be present in WWTP effluents at mean concentrations of ~1 ppb in the US (Simonich et al., 2013), and ~1 ppb in CA influents (DTSC AAT proposal, 2019)

• CA tap water levels are reported to range from <0.05 to 5.83 ppb (EWG National Tap Water Database)

• Probability is negligible that dioxane inputs from upstream WWTPs result in intake concentrations exceeding the USEPA drinking water advisory concentration of 0.35 μg/L, before any treatment of the water for drinking use (Simonich et al., 2013)
Thank you for your attention!

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