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"Addressing 1,4-Dioxane Concerns in Personal Care: New Alcohol Ether Sulfates for the Future"

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1. Introduction

In the personal care industry, achieving a balance between product efficacy and environmental safety is paramount. Sodium Laureth Sulfate (SLES) is widely recognized for its effective cleansing properties and suitability for sensitive skin due to its milder and less irritating nature compared to Sodium Lauryl Sulfate (SLS). It is a popular choice for shampoos, body washes, and facial cleansers, known for its ability to form a rich, stable lather. However, the production of SLES is mired in environmental and health concerns, primarily due to the formation of 1,4-dioxane, a probable human carcinogen [1]. This byproduct has led regulatory bodies such as those in New York, California [2], and especially the European Union [3], to impose strict limits on 1,4-dioxane levels in consumer products, typically set below 1 ppm. The EU's regulatory framework, among the strictest globally, underscores a deep commitment to consumer safety and environmental protection, influencing cosmetic ingredient standards across the continent.

The primary formation of 1,4-dioxane occurs during the sulfation step of SLES production, particularly in surfactants with higher levels of ethoxylation. Under acidic sulfation conditions, a back-biting reaction between adjacent ethoxylate units can occur, leading to the formation of 1,4-dioxane as a by-product (**Figure 1**) [4]. To mitigate this, traditional post-sulfation treatments such as vacuum stripping or loop-type neutralization systems like the Neutrex process [5] are used to remove residual dioxane. However, these methods are costly, energy-intensive, and may not prevent dioxane from reforming over time. This creates ongoing regulatory risk as products remain on store shelves, where aging or formulation instability could push levels out of spec. As such, there is a clear need for upstream process innovations that minimize dioxane formation at the source.

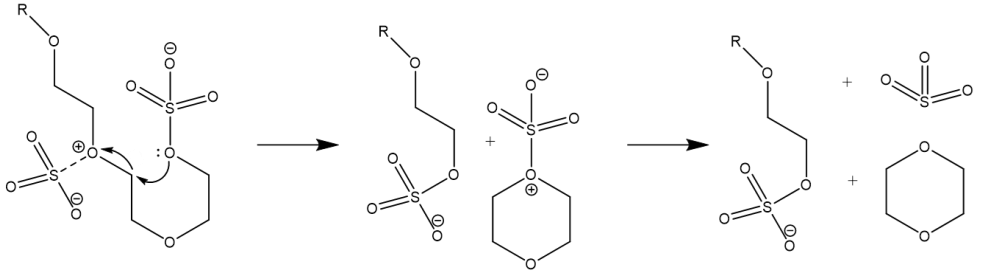


Figure 1. Proposed back-biting mechanism responsible for 1,4-dioxane formation during sulfation of higher EO adducts.

Due to these regulatory and technical constraints, formulators are increasingly reevaluating their dependence on traditional ether sulfates like SLES. In many cases, this has led to a return to older surfactants such as Alcohol Sulfates (AS) and Linear Alkylbenzene Sulfonate (LAS), or to newer alternatives like Alpha Olefin Sulfonates (AOS), Isethionates, Taurates, and fully nonionic systems. However, each of these alternatives presents limitations. AS and LAS tend to be harsher on skin, while the more exotic options come with higher cost or formulation complexity. In addition, switching surfactants often triggers extensive product rework, including re-registration under frameworks such as the EU's Cosmetic Products Regulation (EC) No 1223/2009 [3].

Recent industry efforts have aimed to reduce dioxane formation through novel chemical process design. Dow and Stepan, for example, have developed proprietary sulfation systems to mitigate by-product formation during manufacturing [6,7]. Other approaches include blending lower-ethoxylated SLES with SLS, or reengineering the surfactant structure altogether [8]. While some of these solutions have had success, many require downstream changes, increase formulation cost, or compromise performance.

Our work addresses this gap by taking a different approach—optimizing the structure of the ethoxylate itself, prior to sulfation. By engineering a low-dioxane (LD) ethoxylate that minimizes the precursors associated with dioxane formation, we demonstrate that it is possible to maintain performance, simplify processing, and achieve compliance without relying on downstream stripping. This strategy not only reduces cost and complexity but helps restore an essential surfactant class to the formulator's toolbox in an era of increasing regulatory pressure.

2. Materials and Methods

Free Fatty Alcohol and Distribution of Ethoxymers. Free alcohol percent is determined using an Agilent 7890 Gas Chromatography with a Flame Ionization Detection (GCFID) and a DB-17 HT (50% Phenyl Methylsiloxane) column, 30m x 0.25mm, film thickness of 0.15 µm. Standard samples are prepared from the raw material (i.e. lauryl alcohol). Bis-Trimethyl Silyltrifluoroacetamide (BSTFA) is added to both the standard and the unknown samples and allowed to heat to produce via silylation. An internal standard of non-overlapping retention is additionally added to both standard and unknown samples to determine the final non-ethoxylated free alcohol content. The oligomer distribution is derived from the area percentage calculation.

Sulfation of ethoxylates: Alcohol ethoxylates were sulfated in a lab-scale glass tube reactor modeled after Ballestra-type configurations, with a length of 0.8 meters and ¼" internal diameter. SO_3 was used as the sulfonating agent, reacting with the ethoxylates at 40 C at a mole ratio of SO_3 to alcohol ethoxylate of 1.01. A 3% v/v nitrogen dilution was used to help control reaction kinetics and temperature uniformity. Post-sulfation, the product mixture was neutralized with NaOH solution at 30 C, resulting in final products with approximately 30% active matter. Importantly, these sulfated samples were not subjected to post-treatment deodorization or stripping. This allowed for direct evaluation of 1,4-dioxane formation under unaltered conditions and a clearer comparison of how structural differences in the ethoxylate impacted sulfation outcomes.

Quantification of 1,4-dioxane: To quantify 1,4-dioxane in ether sulfate samples, we utilized a Gas Chromatography-Mass Spectrometry (GCMS) setup with a headspace autosampler. The GCMS was operated with a split injection mode at a 10:1 ratio, using a carrier gas velocity of 46 cm/sec for Hydrogen. The starting oven temperature is 40°C, held for 4 minutes, and

then ramped up at 25°C per minute to a final temperature of 240°C. For mass spectrometry, the settings included a transfer line temperature of 280°C and a source temperature of 300°C, focusing on ions at m/z 57, 64, 88, and 96. The calibration curves were prepared with standard solutions of 1,4-dioxane ranging from 0.030 ppm to 5 ppm with addition of an internal standard of 1,4-dioxane-d8 at 1ppm to reduce matrix effects, achieving a correlation coefficient (R^2) of 0.9996, which ensured the precision of our measurements. The method's limit of quantification was determined to be 0.06 ppm, facilitating the detection of 1,4-dioxane at concentrations well below the established regulatory limits. Further validation of the methodology was performed and met limits of accuracy and precision, set by AOAC, across the full calibration range.

Foam Testing: Foam performance was evaluated using both Ross-Miles and dynamic foam methods. Ross-Miles testing was performed on 0.1 wt% surfactant solutions, with initial and 5-minute foam heights recorded at 25 °C. Dynamic foam behavior was measured using a Krüss DFA100 Foam Analyzer. All samples were tested at 25 °C, and foam height and decay were monitored over time to assess stability under continuous aeration.

Wetting and Viscosity Measurements: Draves wetting time was determined using 0.1 wt% surfactant solutions on cotton skeins, with time to full submersion recorded in seconds [9]. Detergent formulation viscosity was measured with a TA Instruments Discovery HR-2 rheometer (cone and plate geometry) at 25 °C and a shear rate of 100 s^{-1}. Shampoo viscosity was measured using a Brookfield viscometer with LV-3 spindle at 10 rpm after overnight rest at room temperature, reflecting end-use handling conditions.

Critical Micelle Concentration (CMC): CMC values were determined using a fully automated Krüss surface tension analyzer [10]. Surfactant dilution series were prepared, and the surface tension inflection point identified micelle formation. All tests were performed at 25 °C.

Detergency Testing: A base liquid laundry formulation was developed to evaluate performance using both the standard SLES (SLES-STD, 1 mole) and the low-dioxane SLES (SLES-LD, 1 mole), each incorporated at 30% actives. The composition included an anionic surfactant (10.1 wt% alkylbenzene sulfonate), a nonionic surfactant (4.9 wt% alcohol ethoxylate), a polymer (2.1 wt%)—a homopolymer of acrylic acid used to enhance formulation stability by reducing crystal growth and dispersing precipitates—a builder/chelating agent (0.2 wt% citric acid), a pH adjuster (2.7 wt% sodium hydroxide), a water softening agent (2.0 wt% sodium citrate), a hydrotrope (1.0 wt%), and deionized water to 100%. The detergent was evaluated under conditions designed to reflect typical household use. Washing was performed in a top-loading machine using a cold/cold cycle (21 °C) with 200 ppm hard water. Forty grams of detergent were dosed per cycle. Each run included three multi-stained swatches, which were dried at 80 °C and analyzed using a Mach 5+ system to calculate the average Stain Removal Index (SRI).

Shampoo testing: A base shampoo formulation was developed to evaluate performance using a 1-mole low-dioxane SLES (SLES-LD) against two standard SLES benchmarks: SLES-STD (1 mole) and SLES-STD (2 mole), each dosed at 30% actives. The composition included an amphoteric surfactant (5 wt%), a nonionic foam booster/thickener (2 wt%), sodium chloride (1 wt%), and deionized water to 100%. Citric acid was used to adjust the final pH to 5.5. The first four ingredients were added in sequence and mixed while heating to 75 °C. After cooling to room temperature, the remaining components were added. Viscosity measurements were conducted after the samples were allowed to sit overnight at room temperature.

3. Results

To better understand the structural source of dioxane formation, we analyzed the EO distribution of both lauryl ethoxylates prior to sulfation. As shown in **Figure 2**, the standard version (SND) contained a broader range of ethoxylate species, with ~20% falling in the 2+ EO category—known to be most susceptible to 1,4-dioxane formation via back-biting. In contrast, the low-dioxane (LD) version was treated to eliminate these higher EO adducts, resulting in a narrow distribution centered around EO0 and EO1. As shown in **Table 1**, the LD ethoxylate exhibited only 0.07 ppm of 1,4-dioxane in its unsulfated state, compared to 0.2 ppm in the standard, reinforcing the importance of controlling ethoxylation structure upstream to minimize by-product formation during sulfation.

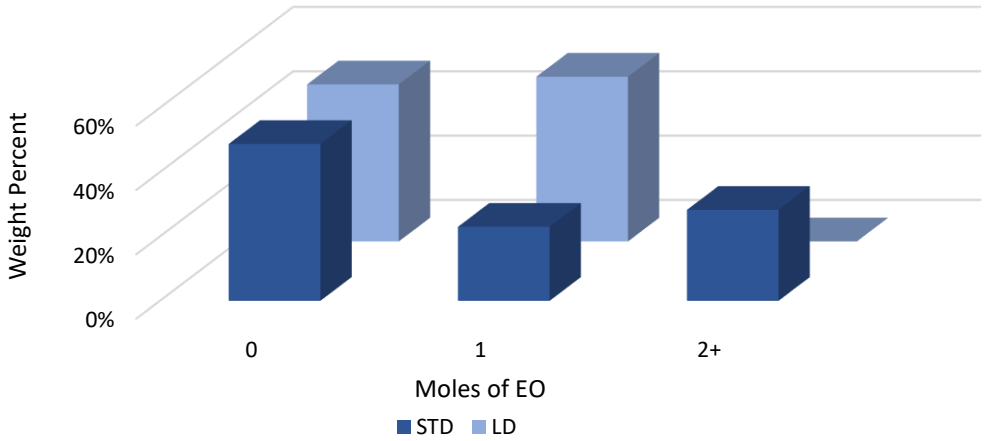


Figure 2. EO chain length distribution for standard (SND) and low-dioxane (LD) lauryl ethoxylates. The LD ethoxylate eliminates higher EO species (>EO2) most prone to back-biting, reducing 1,4-dioxane at the source.

Table 1. 1,4-Dioxane levels in unsulfated lauryl-1 ethoxylates

Property	LAURYL-1 SND	LAURYL-1 LD
1,4-Dioxane post sulfation (ppm)	0.2	0.07

To evaluate the impact of ethoxylate structure on 1,4-dioxane formation during sulfation, two lauryl ether sulfates were prepared and analyzed: a standard 1-mole ethoxylate (LAURYL-1 SND) and a modified low-dioxane version (LAURYL-1 LD). Both were sulfated under identical lab-scale conditions using liquid SO_3 and neutralized with NaOH at controlled temperatures to yield ~30% active products. Neither sample was subjected to post-sulfation stripping or deodorization.GC-MS analysis revealed a substantial difference in 1,4-dioxane content between the two: as shown in **Table 2** the standard product contained 43 ppm, while the LD version measured below the quantification limit of 0.06 ppm, confirming that the modification to the ethoxylate structure effectively suppressed dioxane formation during the reaction.

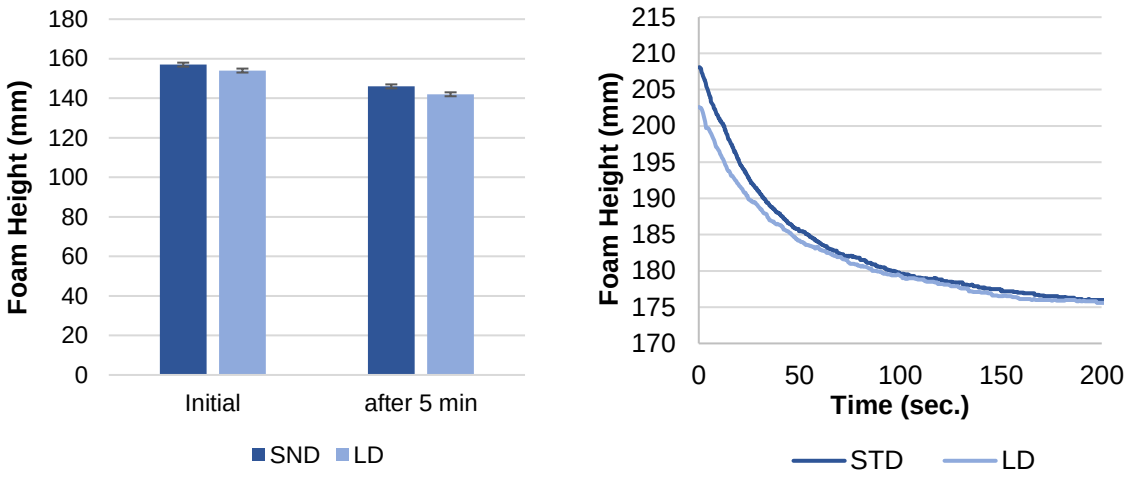
Despite this structural change, the LD sample exhibited equal or better performance across key physical parameters. At 0.1 wt%, the Draves wetting time was 3.5 seconds for LD, compared to 4.2 seconds for the standard. Viscosity measured at 100 s^{-1} was more than double in LD (91 cP vs. 38 cP), suggesting enhanced rheological behavior. Critical micelle concentration (CMC) was slightly higher in SLES-LD (0.09 g/L vs. 0.07 g/L), though the difference was

minimal and did not negatively impact surfactant performance.This was further supported by the foam behavior shown in **Figure 3**, where both Ross-Miles and dynamic foam analysis indicate similar initial height and long-term stability for SLES-STD and SLES-LD.

Table 2. Physical properties and 1,4-dioxane levels in sulfated SLES samples

Property	SLES - SND	SLES - LD
Active Content (%)	29.6	31.5
1,4-Dioxane post sulfation (ppm)	43.0	<0.06[1]
pH	9.8	10.6
Viscosity (cP, 100 s^{-1})	38	91
Draves Wetting (sec)	4.2	3.5
CMC (g/L)	0.07	0.09

[1]LoQ by GC-MS is 0.06 ppm



(**a**) (**b**)

Figure 3. Comparison of static (Ross-Miles) and dynamic foam performance between standard SLES (STD) and low-dioxane SLES (LD) at equivalent actives. The left panel (a) shows initial and 5-minute foam height (mm) using the Ross-Miles test, while the right panel (b) displays foam stability over time under dynamic conditions.

To evaluate long-term stability, a drift study was conducted under accelerated aging conditions. Samples were acidified to pH 4.5 and held at 80 °C for 100 hours to simulate harsh storage environments. As shown in **Figure 4**, the low-dioxane (SLES-LD) sample maintained 1,4-dioxane levels below the quantification limit (0.06 ppm) throughout the test period. In contrast, the standard SLES (STD) sample exhibited a measurable and steady increase in 1,4-dioxane, confirming the tendency for dioxane reformation over time in conventional systems. These results reinforce the value of structural control upstream, where tailoring the ethoxylate mitigates reformation risk and supports long-term product integrity and regulatory compliance.

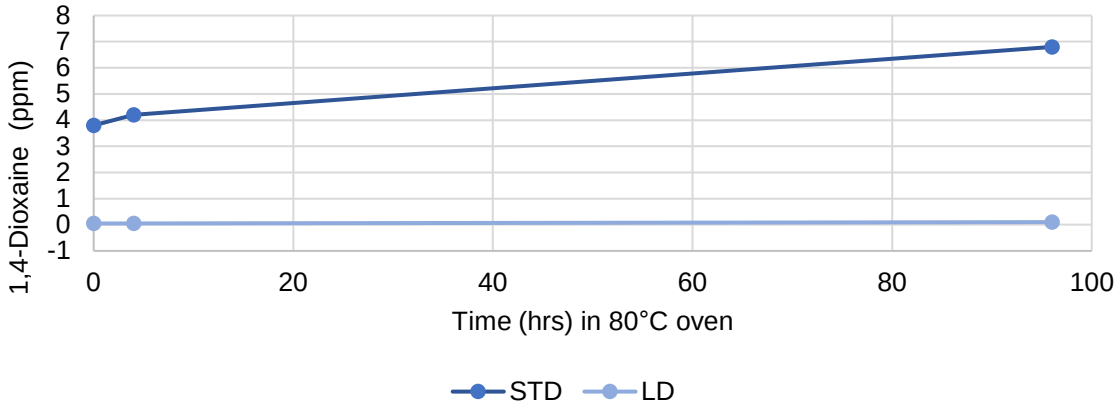


Figure 4. Drift study of 1,4-dioxane under accelerated aging at pH 4.5 and 80°C. LD remains below LoQ, while standard SND shows measurable reformation over time.

Application testing in a controlled laundry wash cycle further supported the functional equivalency of the two materials. Using a standard detergent base formulation with 20% active surfactant and 10% LD or SND, white cotton swatches were soiled and laundered under hard water conditions. Post-wash stain removal was analyzed using Mach 5+ image analysis software. The LD version achieved a soil removal index (SRI) of 340, slightly higher than the 327 SRI observed for the standard product. This indicates that cleaning performance is not only maintained but may be slightly improved with the LD version.

Shampoo formulations incorporating low-dioxane SLES (SLES-LD, 1 mole) were compared against two standard benchmarks: SLES-STD (1 mole) and SLES-STD (2 mole), each tested at 30% actives. As seen in **Table 3**, initial 1,4-dioxane levels in the SLES-LD formulation were below the quantification limit (<0.06 ppm), compared to 0.31 ppm for the SLES-STD (1 mole) and 1.25 ppm for the SLES-STD (2 mole). Following 144 hours of accelerated aging at 80 °C, the SLES-LD formulation exhibited a modest increase to 2.4 ppm, while the SLES-STD (2 mole) sample increased to 3.8 ppm. In contrast, the SLES-STD (1 mole) formulation remained below the detection limit after aging.

In addition to its regulatory advantages, the SLES-LD formulation maintained a final viscosity of 23,253 cP, closely matching the SLES-STD (1 mole) at 26,623 cP and significantly exceeding the SLES-STD (2 mole) at 11,390 cP. This viscosity stability is critical for maintaining user-perceived quality, such as product richness and ease of application, without requiring additional thickeners or viscosity boosters.

While **Figure 5** illustrates the dioxane drift behavior of the surfactants under comparable conditions, **Table 3** provides specific data for the finished shampoo formulations, reinforcing the broader trend of reduced 1,4-dioxane reformation with the LD technology.

Table 3. Stability and viscosity of shampoo formulations made with 1-mole and 2-mole SLES (STD) and low-dioxane SLES (LD).

Property of formulation	SLES - SND (1-mole)	SLES - SND (2-mole)	SLES – LD (1-mole)
1,4-Dioxane (Initial, ppm)	0.31	1.25	<0.06[1]
1,4-Dioxane (after 144 hr at 80°C, ppm)	2.4	3.8	<0.06[1]
Viscosity (cP)[2]	26,623	11,390	23,253

[1]LoQ by GC-MS is 0.06 ppm

[2]Viscosity measured using a Brookfield viscometer (LV-3 spindle, 10 rpm) after overnight rest at room temperature.

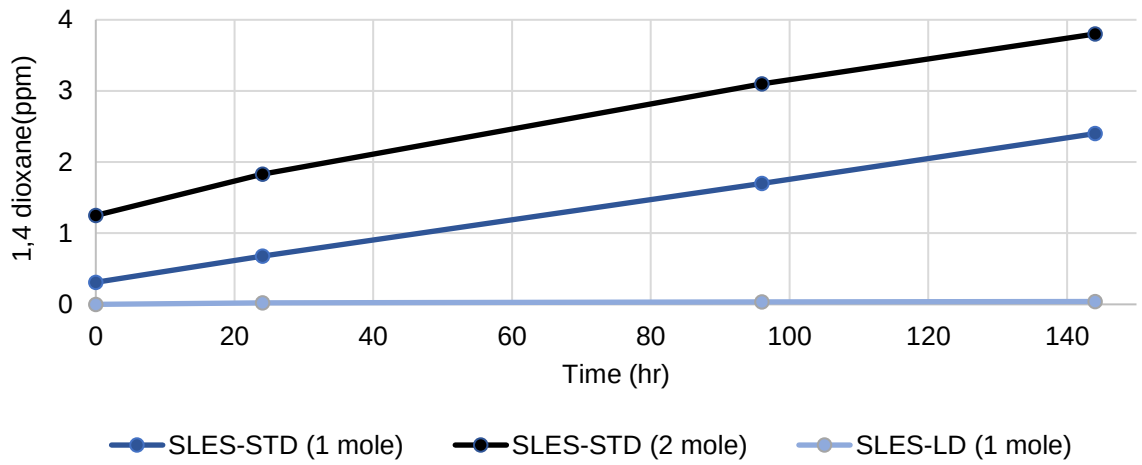


Figure 5. 1,4-Dioxane concentration during accelerated aging (80 °C) in shampoo formulations containing SLES-STD (1 mole), SLES-STD (2 mole), and SLES-LD (1 mole). The SLES-LD formulation showed minimal drift, remaining below 2 ppm throughout the 144-hour period.

4. Discussion

The formation of 1,4-dioxane during the sulfation of alcohol ethoxylates has become a growing concern in the personal care industry due to increasing regulatory scrutiny and tightening global limits. Traditionally, formulators have relied on downstream stripping or deodorization to reduce 1,4-dioxane levels. However, these methods are costly, energy-intensive, and do not prevent the potential for reformation over time.

This study demonstrates that by tailoring the ethoxylate structure prior to sulfation, it is possible to dramatically reduce or eliminate 1,4-dioxane formation at the source—without compromising the functional performance of the resulting ether sulfate.

The low-dioxane (LD) lauryl ether sulfate evaluated in this work was synthesized using a modified ethoxylation approach designed to minimize higher EO adducts, which are most prone to back-biting and cyclization during sulfation (**Figure 1**). When sulfated under identical lab-scale conditions with no post-stripping, the LD sample exhibited 1,4-dioxane levels below the quantification limit (<0.06 ppm), compared to 43 ppm in the standard sample. This clearly illustrates that 1,4-dioxane is not an unavoidable by-product of sulfation chemistry, but rather a controllable outcome that can be addressed through upstream ethoxylate design.

Despite this change in ethoxylate structure, the LD material met or exceeded standard benchmarks across key performance metrics. It delivered faster wetting, slightly higher critical micelle concentration (CMC), and improved viscosity—indicative of a more surface-active and efficient surfactant system. Foam height and stability were maintained, as shown by both Ross-Miles and dynamic foam results, confirming that the LD structure does not compromise the sensorial characteristics valued in personal care formulations. These performance benefits were achieved without changes to formulation design or processing parameters—an important consideration for ease of implementation at scale.

In application testing, the LD surfactant showed slightly improved detergency in controlled laundry studies and remained stable under acidic and elevated temperature conditions, where traditional SLES materials showed dioxane reformation over time. This supports the conclusion that structural optimization upstream yields a more robust solution than relying on downstream mitigation.

The shampoo results, in particular, reinforce the effectiveness of SLES-LD in meeting both regulatory and performance demands. Despite being a 1-mole ethoxylate, the SLES-LD shampoo matched the viscosity of the 1-mole SLES-STD and outperformed the 2-mole SLES-STD—commonly used to enhance mildness and viscosity—in both viscosity and dioxane stability. After 144 hours at 80 °C, the LD sample showed only modest dioxane drift, while the 2-mole SLES increased significantly. This highlights a persistent challenge in formulation: the tendency for 1,4-dioxane to form or drift upward during shelf life. By minimizing formation at the molecular level, the LD material enables formulators to simplify their systems and avoid costly downstream processing—all while maintaining the performance characteristics consumers expect (**Table 3**, **Figure 5**).

Overall, these findings emphasize the importance of ethoxylate architecture in reducing downstream by-products like 1,4-dioxane. Rather than eliminating access to ether sulfates—widely appreciated for their versatility, cleansing power, and foam quality—this approach offers formulators a way to retain that utility. By removing the need for post-treatment, reducing regulatory risk, and preserving formulation aesthetics and stability, this technology presents a practical and scalable solution to one of the most urgent formulation challenges facing the personal care industry today.

5. Conclusion

This study demonstrates that by tailoring the ethoxylate structure prior to sulfation, it is possible to significantly reduce—or even eliminate—the formation of 1,4-dioxane without relying on downstream stripping processes. The resulting low-dioxane SLES (SLES-LD) delivers performance equivalent to, or better than, conventional SLES (SLES-STD) across key application parameters.

In shampoo systems, SLES-LD maintained high viscosity and formulation stability, even when compared to a 2-mole SLES benchmark—commonly selected for its mildness and thickening properties. Importantly, the LD shampoo sample exhibited minimal dioxane drift under accelerated aging, remaining below 1 ppm after 144 hours at 80 °C, while other formulations exceeded regulatory thresholds. In laundry applications, SLES-LD also performed favorably, achieving comparable or superior results in foam, wetting, and detergency.

These findings validate the viability of this upstream design strategy as a scalable solution. By addressing 1,4-dioxane formation at the molecular level, formulators can meet increasingly stringent global regulations without sacrificing performance, stability, or consumer experience—restoring an essential surfactant tool to the personal care formulator's toolbox.

6. References

[1] International Agency for Research on Cancer (IARC). IARC Monographs on the Identification of Carcinogenic Hazards to Humans, Volume 119: 1,4-Dioxane. 2019.

[2] New York State Department of Environmental Conservation. 1,4-Dioxane in Consumer Products. 6 NYCRR Part 492. 2022. Available at: https://www.dec.ny.gov/chemical/119600.html

[3] European Commission. Regulation (EC) No 1223/2009 of the European Parliament and of the Council on Cosmetic Products. Official Journal of the European Union. 2009.

[4] Hayes, D.G., et al. Precise measurement of 1,4-dioxane concentration in cleaning products: A review of the current state-of-the-art. Journal of Surfactants and Detergents. 2022. DOI:10.1002/jsde.12633

[5] Dow Global Technologies LLC. US Patent US20200322881A1: Sulfation Process Optimization for Reduced 1,4-Dioxane Generation. 2020.

[6] Stepan Company. US Patent US10731196B2: Process for Preparing Alkoxylated Alcohol Sulfates with Low 1,4-Dioxane Content. 2020.

[7] Ballestra. Neutrex Loop Type Double Neutralization. Available at: https://ballestra.com/detergents-surfactants/surfactants/neutralization-and-dioxane-removal. Accessed 14 Feb 2025.

[8] Rivera Cruz, L. J., et al. Cleaning Compositions Comprising Sodium Laureth Sulfate and Less than 1 ppm 1,4-Dioxane. WO2023122098A1. 23 Dec 2021.

[9] American Association of Textile Chemists and Colorists (AATCC). Test Method 17-2007: Draves Wetting Test. AATCC Technical Manual. 2007.

[10] Krüss GmbH. Critical Micelle Concentration (CMC) Measurement – Application Note. Krüss Scientific Instruments. 2021.