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# Decyl glucoside as a sustainable surfactant for cosmetic formulations: environmental stability under hardness, pH, and temperature variations

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Environmental variability (including fluctuations in water hardness, pH, and temperature) can markedly affect the performance and stability of surfactants in cosmetic formulations. This study systematically evaluates the environmental robustness of three representative surfactants—Sodium Lauryl Ether Sulfate (SLES, anionic), Cocamidopropyl Betaine (CAPB, amphoteric), and Decyl glucoside (non-ionic)—with a focus on the sustainable performance of decyl glucoside in diverse conditions. Physicochemical parameters including surface tension, critical micelle concentration (CMC), viscosity, and physical stability were analyzed across hardness levels (0–400 mg per L CaCO<sub>3</sub>), pH (5.5–9.0), and temperatures (4–40 °C). SLES exhibited pronounced sensitivity to hard water, showing increased surface tension (32.5 → 36.8 mN m<sup>-1</sup>) and elevated CMC (0.25 → 0.45 mM), resulting in precipitation and reduced viscosity. CAPB demonstrated moderate resilience (CMC 0.15–0.24 mM), while decyl glucoside maintained stable physicochemical behavior (CMC ≈ 1.0 mM) regardless of ionic or thermal stress. Statistical analyses (ANOVA, *p* < 0.01) confirmed significant environmental effects on ionic surfactants but not on decyl glucoside. Mechanistic interpretation based on ion–micelle interactions revealed that the non-ionic structure of decyl glucoside prevents cation binding and aggregation, ensuring consistent interfacial activity and viscosity. The results highlight decyl glucoside's superior environmental stability, biodegradability, and formulation compatibility, positioning it as an ideal candidate for next-generation eco-friendly cosmetics. This work advances the understanding of surfactant–environment interactions and supports sustainable formulation design aligned with green chemistry principles.

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## 1. Introduction

Surfactants are amphiphilic compounds composed of hydrophilic and hydrophobic moieties, widely employed in cosmetic, pharmaceutical, household, and industrial formulations for their capacity to reduce surface and interfacial tensions,

enhance wetting, solubilization, emulsification, and detergency.<sup>1–3</sup> In personal care products, especially facial cleansers, surfactants serve as primary active agents that dictate foaming, cleansing efficiency, rheology, and overall formulation aesthetics.<sup>4–6</sup> The selection of surfactants directly affects product performance and user satisfaction, yet their behavior is highly influenced by external environmental factors such as water hardness, temperature, and pH, which can vary significantly between geographical locations and usage conditions.<sup>7–9</sup> Water hardness is one of the most critical variables affecting surfactant systems. It is determined by the concentration of divalent cations, primarily calcium (Ca<sup>2+</sup>) and magnesium (Mg<sup>2+</sup>), which originate from natural mineral deposits and groundwater sources.<sup>10,11</sup> These ions interact with charged surfactant headgroups and can significantly alter their physicochemical behavior. For example, in anionic surfactants like Sodium Lauryl Ether Sulfate (SLES), the negatively charged sulfate headgroup forms complexes with Ca<sup>2+</sup> and Mg<sup>2+</sup>, leading to micelle aggregation, increased critical micelle concentration (CMC), and even precipitation.<sup>12–14</sup> Such effects compromise surface activity, viscosity, and product stability, often resulting

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in decreased cleansing efficiency or visible formulation breakdown.<sup>15,16</sup>

Amphoteric surfactants, such as Cocamidopropyl Betaine (CAPB), possess both positive and negative charges on their headgroups, allowing them to exhibit variable behavior depending on pH and ionic strength. CAPB generally demonstrates better tolerance to hard water compared to anionic surfactants, although it is not entirely immune to ionic interference.<sup>17–19</sup> Non-ionic surfactants, such as decyl glucoside, exhibit exceptional resistance to water hardness due to their uncharged headgroups. Their performance remains consistent even in high concentrations of divalent ions, making them ideal candidates for environmentally robust formulations.<sup>20,21</sup> Temperature also plays a fundamental role in surfactant behavior. It influences micellization, viscosity, and solubility through changes in hydrophobic interactions, molecular motion, and hydration layers. Typically, elevated temperatures decrease the CMC of ionic surfactants by promoting micelle formation, while lowering viscosity due to reduced intermolecular forces.<sup>22,23</sup> Conversely, low temperatures can increase micelle size and enhance viscosity, sometimes leading to gelation or instability in certain systems.<sup>24</sup> These temperature-induced changes are essential to consider during formulation development, especially for products intended for broad climate markets.

pH is another key parameter that affects surfactant performance, especially in systems containing ionizable functional groups. For anionic surfactants, deviations from neutral pH can lead to protonation or deprotonation of headgroups, altering charge density and interfacial behavior.<sup>25</sup> In amphoteric surfactants, pH influences the zwitterionic nature of the molecule, shifting the balance between cationic and anionic character. Such changes can affect solubility, micelle shape, and surface activity.<sup>26</sup> Non-ionic surfactants are generally stable across a broad pH range, although extreme conditions can lead to hydrolysis or degradation depending on the molecular structure.<sup>27</sup> Although numerous studies have investigated individual environmental effects on surfactants, there remains a lack of integrative research that simultaneously evaluates water hardness, pH, and temperature across multiple surfactant classes under standardized conditions. Most studies tend to focus on a single variable or surfactant type, limiting their applicability to real-world formulation challenges.<sup>28</sup> Furthermore, few studies provide a mechanistic, molecular-level interpretation of how divalent cations alter surfactant behavior, particularly with respect to micellization and interfacial activity.<sup>29,30</sup>

Recent studies further highlight the importance of electrolyte–surfactant interactions in governing micellization and interfacial behavior. Patra *et al.* demonstrated that the Krafft temperature, aggregation number, and thermodynamic parameters of sodium tetradecyl sulfate vary significantly with solvent composition and additives such as NaCl,  $\beta$ -cyclodextrin, and OTAB, underscoring the complexity of ionic effects on surfactant assembly.<sup>31</sup> Complementarily, Chakraborty and Ghosh provided a unified evaluation of mixed micelle theories, showing how mixed monolayers and aggregated phases deviate from ideality due to component interactions.<sup>32</sup> These findings reinforce the relevance of electrolyte-mediated structural transitions in interpreting surfactant stability under environmental stress.

In this context, quantitative evaluation of interfacial parameters such as the maximum surface excess ( $\Gamma_{\max}$ ) and minimum molecular area ( $A_{\min}$ ) can indeed be accomplished using the Gibbs adsorption isotherm when combined with precise surface tension measurements. Ghosh and Chakraborty demonstrated that  $\Gamma_{\max}$ ,  $A_{\min}$ ,  $\gamma_{\text{CMC}}$ , and adsorption thermodynamics can be reliably extracted for mixed anionic–nonionic systems, validating the applicability of Gibbs-based models to surfactant aggregation in saline environments.<sup>33</sup> Likewise, Banik *et al.* showed that zwitterionic gemini surfactants form complex mixed aggregates whose interfacial compositions and interaction parameters can be interpreted through theoretical frameworks such as Clint, Rubingh, Motomura, and SPB models.<sup>34</sup> These studies confirm that Gibbs adsorption-derived metrics are robust tools for characterizing mixed-surfactant interfaces, supporting their use in evaluating environmental stability.

To bridge this knowledge gap, the present study systematically examines the physicochemical behavior of three widely used surfactants (SLES (anionic), CAPB (amphoteric), and decyl glucoside (non-ionic)) across controlled variations of water hardness, temperature, and pH. Key formulation-relevant parameters such as surface tension, CMC, viscosity, and physical stability are evaluated to generate a comprehensive profile of each surfactant's environmental robustness. A conceptual model is also proposed to explain the interactions between surfactants and divalent cations at the molecular level, using principles of colloid and surface chemistry. This study offers practical insights for cosmetic scientists and formulation chemists seeking to develop high-performance, consumer-safe, and sustainable cleansing products that can withstand variable environmental conditions. In particular, the results reinforce the superiority of non-ionic surfactants like decyl glucoside in hard water scenarios, promoting their use in eco-friendly and globally compatible formulations. The findings also provide a scientific foundation for surfactant selection in accordance with regulatory trends emphasizing biodegradability, reduced aquatic toxicity, and green chemistry.

## 2. Materials and methods

This section outlines the materials, experimental procedures, and analytical methods employed to investigate the impact of water hardness, temperature, and pH on the physicochemical properties of surfactants commonly used in facial cleansing formulations. The study focuses on SLES, CAPB, and decyl glucoside, representing anionic, amphoteric, and non-ionic surfactant classes, respectively. A conceptual framework is introduced to elucidate the molecular mechanisms by which divalent cations ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) influence micellar structures, enhancing the novelty of this work.

### 2.1. Materials

**2.1.1. Surfactants.** Three cosmetic-grade surfactants were selected for this study. Sodium Lauryl Ether Sulfate (SLES, 70% active content) was obtained from Sigma-Aldrich (Merck, Germany). Cocamidopropyl Betaine (CAPB, 30% active content) was



Table 1 Surfactant properties<sup>a</sup>

Surfactant	Type	Approx. CMC (mM, deionized water)	Key properties
SLES	Anionic	0.1–0.3	High foaming, sensitive to divalent ions
CAPB	Amphoteric	0.08–0.2	Mild, moderately resistant to hard water
Decyl glucoside	Non-ionic	0.5–2.0	Biodegradable, eco-friendly, stable in hard water

<sup>a</sup> Decyl glucoside's biodegradable nature aligns with sustainability goals in cosmetic formulations, offering reduced environmental impact compared to SLES and CAPB. Its alkyl glucoside structure, derived from renewable sources like glucose and fatty alcohols, minimizes aquatic toxicity, making it a preferred choice for eco-conscious products.<sup>35</sup>

purchased from Croda International Plc., UK. Decyl glucoside (55% active content) was sourced from BASF SE, Germany. All surfactants were used as received without further purification to reflect common industrial formulation practices. Table 1 summarizes their properties, including approximate CMC in deionized water and key characteristics relevant to their performance in cleansing formulations.

The chemical structures of the three surfactants examined in this work (Sodium Lauryl Ether Sulfate (SLES), cocamidopropyl betaine (CAPB), and decyl glucoside) are presented in Fig. 1. SLES is an anionic ethoxylated sulfate surfactant (laureth sulfate), CAPB is an amphoteric surfactant characterized by its betaine zwitterionic headgroup, and decyl glucoside is a non-ionic alkyl polyglucoside derived from glucose and fatty alcohols. Depiction of these structures facilitates clarification of headgroup chemistry, which plays a central role in their environmental stability and interactions with hardness ions.

**2.1.2. Water solutions with varying hardness.** To mimic real-world water conditions, solutions were prepared with hardness levels of 0 mg L<sup>-1</sup> (deionized water), 50 mg L<sup>-1</sup> (soft water), 100 mg L<sup>-1</sup> (moderately hard water), 200 mg L<sup>-1</sup> (hard water), and 400 mg L<sup>-1</sup> (very hard water), expressed as calcium carbonate (CaCO<sub>3</sub>) equivalents. Hardness was achieved by dissolving calcium chloride dihydrate (CaCl<sub>2</sub>·2H<sub>2</sub>O, ≥99% purity) and magnesium chloride hexahydrate (MgCl<sub>2</sub>·6H<sub>2</sub>O, ≥99% purity) in deionized water (resistivity ≥18 MΩ cm) from a laboratory purification system. A Ca<sup>2+</sup>:Mg<sup>2+</sup> ratio of 2:1 (w/w) was maintained to reflect typical groundwater compositions. The

pH was standardized at 7.0 ± 0.1 using 0.1 M HCl or NaOH, except in experiments exploring pH effects.

**2.1.3. Other reagents.** Sodium chloride (NaCl, ≥99.5%) was used to maintain consistent ionic strength where necessary. All glassware was cleaned with a 2% (v/v) detergent solution, rinsed with deionized water, and dried at 60 °C to eliminate contamination risks, following standard laboratory protocols.

## 2.2. Methods

**2.2.1. Conceptual framework for divalent ion effects.** The study proposes a conceptual model to explain how divalent cations (Ca<sup>2+</sup> and Mg<sup>2+</sup>) affect surfactant micelles, enhancing the scientific novelty of the work. For anionic surfactants like SLES, divalent cations bind to the negatively charged sulfate headgroups, reducing electrostatic repulsion and promoting micellar aggregation or precipitation. This interaction lowers the effective surfactant concentration at the interface, increasing surface tension and CMC.<sup>36</sup> For amphoteric CAPB, the zwitterionic headgroup partially mitigates cation binding, resulting in moderate stability. Non-ionic decyl glucoside, lacking charged headgroups, is unaffected by ionic interactions, maintaining consistent micellar properties across hardness levels.

**2.2.2. Preparation of surfactant solutions.** Surfactant solutions were prepared at concentrations of 0.01% to 2% (w/v) in each water hardness level to span below and above the CMC. Each surfactant was dissolved in 100 mL of the respective hardness solution under gentle stirring at 25 °C for 30 minutes to ensure uniformity. Solutions were stored in airtight

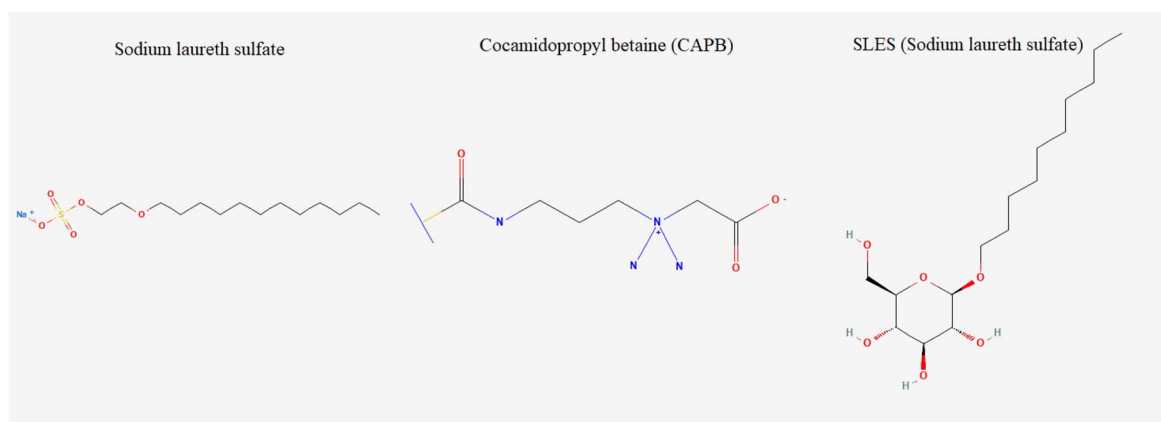


Fig. 1 Chemical structures of the surfactants used in this study: SLES, CAPB, and decyl glucoside.



Table 2 Experimental conditions

Parameter	Levels
Surfactants	SLES, CAPB, decyl glucoside
Hardness (mg per L CaCO <sub>3</sub> )	0, 50, 100, 200, 400
Temperature (°C)	4, 25, 40
pH	5.5, 7.0, 9 interaction with divalent cations.0
Replicates	3

containers and used within 24 hours to prevent degradation or microbial growth, aligning with practices reported in similar studies.<sup>37</sup>

**2.2.3. Surface tension measurement.** Surface tension was measured using the pendant drop method with a Drop Shape Analyzer. A 10  $\mu\text{L}$  droplet was formed at a 1.8 mm stainless-steel needle tip in air at controlled temperatures (4 °C, 25 °C, or 40 °C) and pH levels (5.5, 7.0, or 9.0). The Young–Laplace equation was applied to calculate surface tension from droplet shapes captured by a high-resolution CCD camera. Measurements were conducted in triplicate after a 60-second equilibration period. The instrument was calibrated with deionized water (72.8 mN m<sup>-1</sup> at 25 °C). To address expanded conditions, surface tension was evaluated across all hardness levels (0–400 mg per L CaCO<sub>3</sub>), temperatures, and pH levels, with results compared to studies showing cation-induced surface tension increases for ionic surfactants.<sup>38</sup>

**2.2.4. Critical micelle concentration determination.** CMC was determined by plotting surface tension against the logarithm of surfactant concentration (0.001% to 2% w/v) across all hardness levels, temperatures, and pH conditions. The transition to micellar states was identified as the concentration where surface tension stabilized, with linear regression applied to pre- and post-CMC regions to calculate the intersection point. Triplicate measurements ensured precision, with results reported as means  $\pm$  standard deviation. Divalent cations increase CMC for ionic surfactants by reducing headgroup repulsion while non-ionic surfactants remain unaffected due to their neutral headgroups.

**2.2.5. Viscosity measurement.** Viscosity was measured at 1% (w/v) surfactant concentration using a viscometer with a small sample adapter at a shear rate of 100 s<sup>-1</sup>. Measurements were conducted at 4 °C, 25 °C, and 40 °C, and pH 5.5, 7.0, and 9.0, across all hardness levels. Viscosity measurements were performed at 4 °C, 25 °C, and 40 °C to represent cold-storage, ambient, and elevated-temperature stress conditions, respectively. The inclusion of 4 °C follows standard low-temperature stability testing practices for cosmetic surfactant systems, allowing evaluation of micellar structural changes and rheological behavior under cold environmental exposure. The viscometer was calibrated with a 100 cP standard fluid. Samples were equilibrated for 5 minutes, with viscosity recorded after 60 seconds of rotation in triplicate. This approach, consistent with viscosity studies of surfactant systems,<sup>39</sup> revealed that divalent

cations disrupt micellar networks in SLES, reducing viscosity, while CAPB and decyl glucoside exhibit greater resilience.

**2.2.6. Physical stability assessment.** Physical stability was evaluated over 14 days by monitoring color, precipitation, turbidity, viscosity, and phase separation at 25 °C and 50  $\pm$  5% relative humidity, with additional tests at 4 °C and 40 °C, and pH 5.5 and 9.0. Color changes were quantified using a spectrophotometer in the CIELAB color space ( $L^*$ ,  $a^*$ ,  $b^*$ ). Precipitation was assessed by centrifugation at 3000 rpm for 10 minutes, with sediment mass measured to  $\pm$ 0.1 mg. Turbidity was determined *via* absorbance at 600 nm. Phase separation was categorized as “none”, “minor”, or “pronounced” through visual inspection. These methods align with stability assessments in cosmetic formulations.<sup>40</sup> Decyl glucoside's stability supports its use in sustainable formulations, reducing environmental risks compared to ionic surfactants.<sup>35</sup>

**2.2.7. Experimental design.** The experimental design consolidated conditions to avoid redundancy, as summarized in Table 2. Each surfactant was tested across five hardness levels (0–400 mg per L CaCO<sub>3</sub>), three temperatures (4 °C, 25 °C, 40 °C), and three pH levels (5.5, 7.0, 9.0), with three replicates per condition, yielding 135 samples per measurement type (surface tension, CMC, viscosity, stability). Experiments were randomized to minimize systematic errors.

**2.2.8. Wetting time determination.** Wetting behavior was quantified using the Draves wetting test according to ASTM D2281. Surfactant solutions at 5% (w/v) were prepared in water hardness levels of 0, 100, and 400 mg per L CaCO<sub>3</sub> at pH 7.0 and 25 °C. A standardized 5 g cotton skein (previously washed, rinsed, and dried) was suspended in a 500 mL glass vessel containing the surfactant solution. The wetting time was defined as the sinking time of the skein from the moment of immersion until complete submersion. Each experiment was performed in triplicate, with careful control of air entrapment to ensure reproducibility. The wetting test provides direct insight into the dynamic surface-wetting efficiency of each surfactant and the impact of hardness-induced changes in interfacial activity.

**2.2.9. Foaming ability and foam stability (Ross–Miles method).** Foaming properties were evaluated using the Ross–Miles test following ASTM D1173–53. Surfactant solutions at 0.1% and 1% (w/v) were prepared in water hardness levels of 0, 100, and 400 mg per L CaCO<sub>3</sub>. The solutions were equilibrated at the target temperatures of 4 °C, 25 °C, and 40 °C.

A volume of 200 mL of solution was allowed to fall from a height of 90 cm through a vertical glass tube into a 500 mL graduated cylinder containing 50 mL of the same solution. Foam height was recorded immediately (initial foam height) and after 5 min (foam stability). All glassware was cleaned using a detergent-free protocol to avoid contamination of surface-active agents.

Foamability and stability provide essential information regarding film elasticity, surface rheology, and the extent of micelle adsorption at the air–water interface under varying ionic strengths.

**2.2.10. Emulsification capacity measurement ( $E_{24}$  index).** The emulsifying efficiency of surfactants was assessed using the



Table 3 Summary of experimental conditions for wetting, foaming, and emulsification assays

Parameter	Wetting test	Ross–Miles foaming	Emulsification ( $E_{24}$ )
Surfactant concentration	5% w/v	0.1% & 1% w/v	1% w/v
Hardness levels (mg per L CaCO <sub>3</sub> )	0, 100, 400	0, 100, 400	0, 100, 400
Temperatures (°C)	25	4, 25, 40	25
Measurements	Sinking time (s)	Initial foam height (mm), foam height at 5 min (mm)	Emulsion height after 24 h
Replicates	3	3	3
Standards used	ASTM D2281	ASTM D1173-53	Standard $E_{24}$ protocol

emulsification index after 24 h ( $E_{24}$ ). Surfactant solutions at 1% (w/v) were prepared across water hardness levels (0, 100, and 400 mg per L CaCO<sub>3</sub>). For each sample, 2 mL of surfactant solution was mixed with 2 mL of sunflower oil in a glass test tube and vortexed for 2 min at 2500 rpm.

The emulsion was allowed to stand undisturbed for 24 h at 25 °C. The height of the emulsion layer was measured, and  $E_{24}$  was calculated as:

$$E_{24}(\%) = \frac{\text{Emulsion layer height(mm)}}{\text{Total height(mm)}} \times 100 \quad (1)$$

This parameter reflects the ability of the surfactant to stabilize oil–water interfaces and form kinetically stable emulsions under ionic stress.

**2.2.11. Data reporting and controls.** All tests were conducted in triplicate ( $n = 3$ ), and results are expressed as mean  $\pm$  standard deviation. Water without surfactant served as a negative control for the Ross–Miles and emulsification tests. Calibration of volumetric and timing devices was performed prior to experiments. To ensure experimental integrity, all samples were equilibrated for 30 minutes prior to measurement, and all experiments were conducted under controlled laboratory conditions (25 °C and 50  $\pm$  5% relative humidity), with the pH maintained at 7.0 unless otherwise specified (Table 3).

### 2.3. Statistical analysis

Data were analyzed using one-way ANOVA to assess the effects of hardness, temperature, and pH on surface tension, CMC, viscosity, and stability parameters (color, sediment mass, turbidity, viscosity change, phase separation). Tukey's HSD test identified pairwise differences ( $p < 0.05$ ). Normality and variance homogeneity were confirmed using Shapiro–Wilk and Levene's tests.<sup>41–43</sup>

### 2.4. Safety and environmental considerations

Experiments adhered to strict safety protocols, with personal protective equipment (nitrile gloves, goggles, lab coats) worn during handling of chemicals. pH adjustments using HCl/NaOH were performed in a fume hood. Chemical waste, including surfactants and salts, was collected and disposed of *via* a licensed facility to prevent environmental harm. Decyl glucoside's biodegradability reduces its ecological footprint, aligning with sustainable cosmetic trends.<sup>44</sup> Calcium and magnesium salts were managed per regulations due to their minimal environmental impact.

## 3. Results and discussion

This section presents the findings from experiments evaluating the influence of water hardness, temperature, and pH on the physicochemical properties of three surfactants used in cosmetic formulations: Sodium Lauryl Ether Sulfate (SLES, anionic), Cocamidopropyl Betaine (CAPB, amphoteric), and decyl glucoside (non-ionic). The properties examined include surface tension, CMC, viscosity, and physical stability. Results are reported as means  $\pm$  standard deviation (SD) from triplicate measurements, with statistical significance assessed using one-way analysis of variance (ANOVA) and Tukey's Honestly Significant Difference (HSD) test ( $p < 0.05$ ). A conceptual framework elucidates how divalent cations (Ca<sup>2+</sup> and Mg<sup>2+</sup>) interact with surfactant micelles, enhancing the scientific novelty of the findings.

### 3.1. Surface tension

Surface tension was measured across surfactant concentrations (0.001% to 2% w/v), water hardness levels (0, 50, 100, 200, and 400 mg per L CaCO<sub>3</sub>), temperatures (4 °C, 25 °C, and 40 °C), and pH levels (5.5, 7.0, and 9.0) using the pendant drop method. Fig. 2 illustrates surface tension as a function of logarithm of surfactant concentration at 25 °C and pH 7.0 across hardness levels of 0, 100, and 400 mg per L CaCO<sub>3</sub>, providing a clear visualization of surfactant behavior.

For SLES, surface tension decreased markedly with increasing concentration until the CMC, stabilizing at a plateau. In deionized water (0 mg per L CaCO<sub>3</sub>), the plateau was 32.5  $\pm$  0.3 mN m<sup>-1</sup>, consistent with values reported for anionic surfactants.<sup>37</sup> At 400 mg L<sup>-1</sup> hardness, the plateau rose notably to 36.8  $\pm$  0.4 mN m<sup>-1</sup> ( $p < 0.01$ ), reflecting reduced surface activity. This elevation stems from divalent cations binding to SLES's anionic sulfate headgroup, forming surfactant-ion complexes that reduce the effective concentration at the air–water interface (Israelachvili, 2011). CAPB exhibited a similar trend, with surface tension plateauing at 30.2  $\pm$  0.2 mN m<sup>-1</sup> in deionized water and increasing to 34.1  $\pm$  0.3 mN m<sup>-1</sup> at 400 mg L<sup>-1</sup> ( $p < 0.01$ ). The zwitterionic nature of CAPB mitigates some cation interactions, but partial neutralization of its headgroup reduces surface activity, as noted in studies of amphoteric surfactants. Decyl glucoside, a non-ionic surfactant, showed minimal sensitivity to hardness, with surface tension values of 28.9  $\pm$  0.2 mN m<sup>-1</sup> at 0 mg L<sup>-1</sup> and 29.5  $\pm$  0.3 mN m<sup>-1</sup> at 400 mg L<sup>-1</sup> ( $p = 0.12$ ).

Temperature influenced surface tension distinctly. At 4 °C, values for all surfactants increased by 2–3% compared to 25 °C



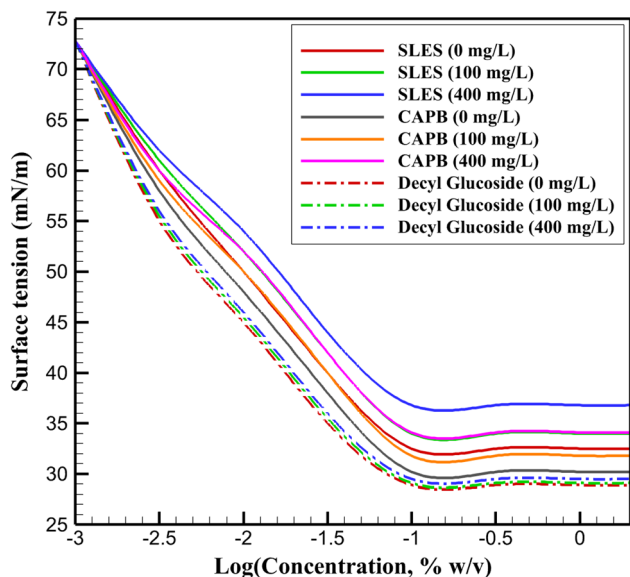


Fig. 2 Surface tension vs. log(concentration) at 25 °C, pH 7.0.

( $p < 0.01$ ), due to reduced molecular mobility and weaker hydrophobic interactions, consistent with thermodynamic principles (Schott, 1997). At 40 °C, surface tension decreased by 1–2% ( $p < 0.05$ ), reflecting enhanced molecular agitation and looser interfacial packing. pH effects were pronounced for SLES, with surface tension rising by 1–2  $\text{mN m}^{-1}$  at pH 5.5 and 3–4  $\text{mN m}^{-1}$  at pH 9.0 compared to pH 7.0 ( $p < 0.01$ ), likely due to protonation (pH 5.5) or altered ionic interactions (pH 9.0) affecting the sulfate headgroup. CAPB showed minor increases at pH 5.5 (1  $\text{mN m}^{-1}$ ,  $p < 0.05$ ) but was stable at pH 9.0 ( $p = 0.08$ ), reflecting its zwitterionic buffering capacity. Decyl glucoside remained unaffected across pH levels ( $p > 0.05$ ), underscoring its stability for sustainable formulations.

The surface tension behavior reveals the pivotal role of surfactant headgroup chemistry in navigating environmental challenges. SLES's sensitivity to water hardness underscores how divalent cations disrupt its anionic headgroup, reducing

interfacial efficiency and elevating surface tension. CAPB's zwitterionic structure offers partial resistance, yet it still faces ion-induced limitations at higher hardness levels. Decyl glucoside's non-ionic nature ensures consistent performance, making it a prime choice for eco-friendly formulations resilient to diverse conditions. Temperature and pH further shape these dynamics, with ionic surfactants showing heightened susceptibility due to altered molecular interactions, guiding the design of robust cosmetic formulations.

### 3.2. Critical micelle concentration

CMC was determined by identifying the intersection of pre- and post-CMC regions in surface tension *versus* logarithm of concentration plots. SLES exhibited a notable increase in CMC with hardness, from  $0.25 \pm 0.01 \text{ mM}$  at  $0 \text{ mg L}^{-1}$  to  $0.45 \pm 0.03 \text{ mM}$  at  $400 \text{ mg L}^{-1}$  ( $p < 0.01$ ). This shift results from  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  binding to the anionic headgroup, reducing electrostatic repulsion and promoting premature micelle formation. CAPB's CMC increased moderately from  $0.15 \pm 0.01 \text{ mM}$  to  $0.24 \pm 0.02 \text{ mM}$  ( $p < 0.05$ ), reflecting partial resistance due to its zwitterionic structure. Decyl glucoside's CMC was stable, ranging from  $1.00 \pm 0.05 \text{ mM}$  to  $1.06 \pm 0.07 \text{ mM}$  ( $p = 0.19$ ), owing to its non-ionic nature, which avoids ionic interactions, supporting its use in eco-friendly products.

Temperature affected CMC for ionic surfactants. At 4 °C, SLES and CAPB CMC values rose by 5–10% ( $p < 0.01$ ), due to reduced hydrophobic interactions, while decyl glucoside was unaffected ( $p = 0.22$ ). At 40 °C, SLES and CAPB CMC decreased by 3–5% ( $p < 0.05$ ), reflecting enhanced micelle formation, consistent with thermodynamic models. pH effects were significant for SLES, with CMC increasing by 8% at pH 5.5 ( $p < 0.01$ ) and 12% at pH 9.0 ( $p < 0.01$ ), likely due to protonation or altered charge interactions. CAPB and decyl glucoside showed negligible changes ( $p > 0.05$ ), reinforcing their stability across diverse conditions. Fig. 3 clearly demonstrates that increasing water hardness significantly elevates the CMC of ionic surfactants like SLES due to electrostatic screening by divalent cations, which promotes premature micellization. CAPB, with

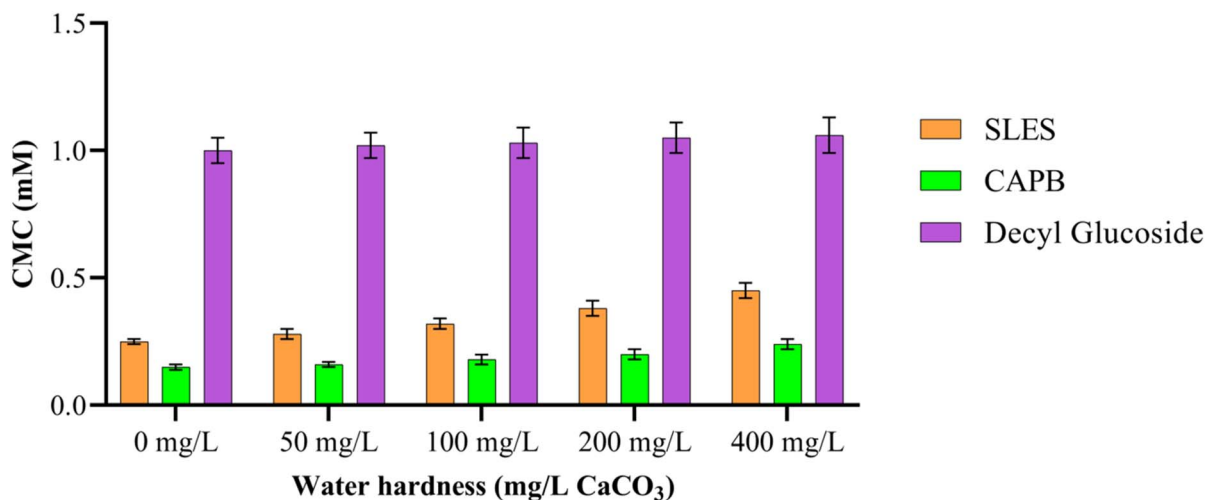


Fig. 3 CMC values (mM) of surfactants at different water hardness levels (25 °C, pH 7.0).

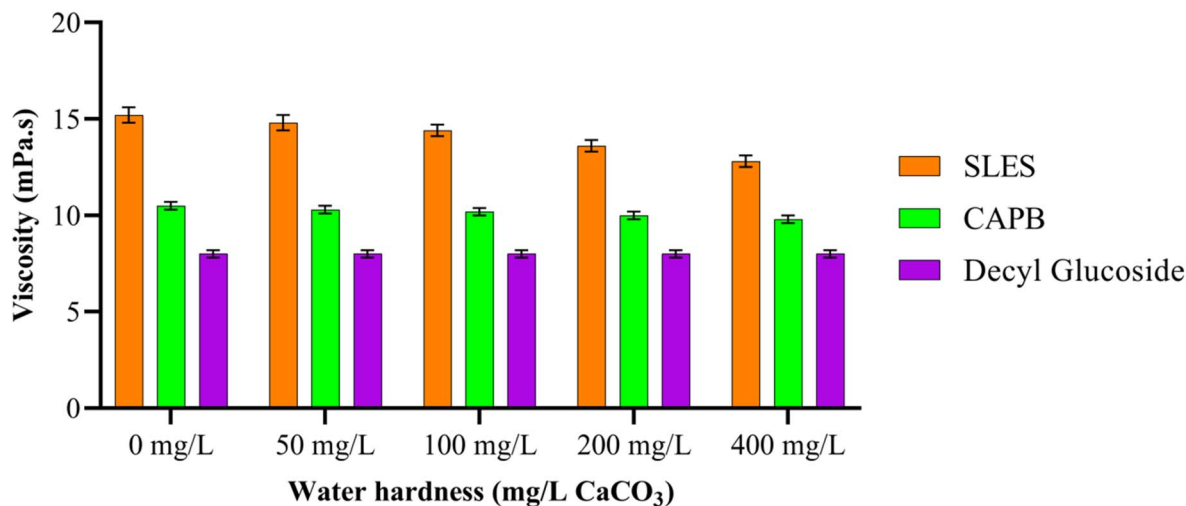


Fig. 4 Viscosity of 1% (w/v) surfactant solutions at 25 °C, pH 7.0.

its zwitterionic headgroup, shows moderate CMC shifts, reflecting partial ionic tolerance. In contrast, decyl glucoside maintains a stable CMC across hardness levels, underscoring its non-ionic resilience. These findings highlight the critical role of headgroup chemistry in governing micelle formation under ionic stress.

The CMC trends reveal the profound influence of surfactant headgroup chemistry on micellar assembly under varying environmental conditions. SLES's heightened sensitivity to water hardness underscores how divalent cations disrupt its anionic headgroup, lowering repulsion and driving earlier micelle formation, which may compromise formulation efficiency. CAPB's zwitterionic nature mitigates these effects, offering a balance that enhances stability but not immunity to ionic challenges. Decyl glucoside's consistent CMC reflects its non-ionic resilience, ensuring reliable performance in diverse conditions, making it a cornerstone for sustainable cosmetic formulations. Temperature and pH further highlight the vulnerability of ionic surfactants, with molecular interactions shifting micellar thresholds, providing critical insights for tailoring surfactant systems to real-world applications.

### 3.3. Viscosity

Viscosity was measured at 1% (w/v) surfactant concentration across all hardness levels, temperatures, and pH conditions. Fig. 4 presents viscosity data at 25 °C and pH 7.0, expressed in mPa.s. SLES exhibited the highest viscosity, decreasing from  $15.2 \pm 0.4$  mPa s at  $0 \text{ mg L}^{-1}$  to  $12.8 \pm 0.3$  mPa s at  $400 \text{ mg L}^{-1}$  ( $p < 0.01$ ). This reduction results from divalent cations disrupting micellar networks, weakening intermolecular interactions, as observed in anionic surfactant systems. CAPB maintained relatively stable viscosity, from  $10.5 \pm 0.2$  mPa s to  $9.8 \pm 0.2$  mPa s ( $p = 0.04$ ), due to its zwitterionic structure mitigating ion effects. Decyl glucoside showed consistent viscosity at  $8.0 \pm 0.2$  mPa s across hardness levels ( $p = 0.15$ ), reflecting its non-ionic stability, ideal for sustainable formulations.

Temperature significantly altered viscosity. At 4 °C, SLES and CAPB viscosity increased by 10–15% ( $p < 0.01$ ), due to tighter

micellar packing, while decyl glucoside was stable ( $p = 0.20$ ). At 40 °C, SLES and CAPB viscosity decreased by 5–10% ( $p < 0.05$ ), reflecting looser micellar structures. pH 5.5 increased SLES viscosity by 7% ( $p < 0.01$ ), likely due to enhanced micellar interactions *via* protonation, while pH 9.0 reduced it by 5% ( $p < 0.05$ ). CAPB and decyl glucoside remained stable across pH levels ( $p > 0.05$ ). SLES's pronounced sensitivity to water hardness reveals how divalent cations destabilize its anionic micellar networks, reducing viscosity and potentially impacting formulation texture, depending on the presence of co-surfactants, polymers, or chelating agents. CAPB's zwitterionic nature provides moderate resilience, maintaining viscosity under ionic stress, though not entirely immune. Decyl glucoside's unwavering viscosity underscores its non-ionic stability, ensuring consistent performance across diverse conditions, making it a prime candidate for eco-friendly cosmetic systems.

### 3.4. Physical stability

Physical stability was assessed over 14 days, monitoring color ( $\Delta L^*$ ,  $\Delta a^*$ ,  $\Delta b^*$ ), precipitation, turbidity (absorbance at 600 nm), viscosity change, and phase separation across all conditions. Table 4 summarizes stability at 400 mg per L CaCO<sub>3</sub>, 25 °C, and pH 7.0 after 14 days. SLES showed pronounced instability in hard water, with significant precipitation ( $10.5 \pm 0.5$  mg) and minor phase separation, indicating surfactant-ion complex formation, consistent with anionic surfactant behavior. CAPB exhibited improved stability, with minimal precipitation ( $2.0 \pm 0.3$  mg) and no phase separation, reflecting its zwitterionic resistance to ion interactions. Decyl glucoside was highly stable, with negligible precipitation ( $0.5 \pm 0.2$  mg), low turbidity ( $0.05 \pm 0.01$ ), and no phase separation, supporting its use in eco-friendly products due to its biodegradability and low aquatic toxicity. Temperature and pH effects followed similar trends. At 4 °C, SLES precipitation increased to  $12.0 \pm 0.6$  mg ( $p < 0.05$ ), while CAPB and decyl glucoside remained stable. At 40 °C, SLES turbidity rose to  $0.30 \pm 0.03$  ( $p < 0.01$ ), indicating enhanced aggregation. At pH 5.5 and 9.0, SLES showed increased precipitation and turbidity ( $p < 0.01$ ), while CAPB and decyl glucoside



Table 4 Physical stability parameters at 400 mg per L CaCO<sub>3</sub>, 25 °C, pH 7.0 (Day 14)<sup>a</sup>

Surfactant	$\Delta L^*$	$\Delta a^*$	$\Delta b^*$	Sediment mass (mg)	Turbidity (abs. 600 nm)	Viscosity change (%)	Phase separation
SLES	2.5 ± 0.3	0.8 ± 0.1	1.2 ± 0.2	10.5 ± 0.5	0.25 ± 0.02	-8.0 ± 0.5	Minor
CAPB	0.5 ± 0.1	0.2 ± 0.1	0.3 ± 0.1	2.0 ± 0.3	0.10 ± 0.01	-2.5 ± 0.3	None
Decyl glucoside	0.2 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.5 ± 0.2	0.05 ± 0.01	-0.5 ± 0.2	None

<sup>a</sup> SLES's vulnerability to hard water reveals how divalent cations destabilize its anionic micelles, fostering aggregation and compromising formulation integrity. CAPB's zwitterionic character confers a balanced resilience, mitigating ionic disruptions while maintaining homogeneity. Decyl glucoside's exceptional robustness, driven by its non-ionic structure, ensures unwavering stability across diverse conditions, positioning it as a cornerstone for environmentally conscious formulations. Variations in temperature and pH amplify these disparities, with ionic surfactants succumbing to molecular perturbations, offering pivotal guidance for crafting durable cosmetic products.

maintained stability, reinforcing their suitability for diverse conditions.

### 3.5. Wetting, foaming, and emulsification results

This section presents the comparative wetting efficiency, foaming performance, and emulsification capacity of SLES, CAPB, and decyl glucoside under varying water hardness conditions. All measurements were conducted in triplicate, and results are reported as mean ± SD. These parameters provide additional insight into the interfacial behavior of the surfactants beyond surface tension, CMC, and viscosity, offering a more comprehensive assessment of their application-related performance.

**3.5.1. Wetting behavior.** Wetting time, determined using the Draves test at 5% (w/v) surfactant concentration, showed substantial differences among the three surfactants (Table 5). SLES demonstrated the fastest wetting, with a sinking time of 12.5 ± 0.4 s in deionized water, reflecting its strong ability to rapidly lower the dynamic surface tension. However, its wetting time increased markedly to 26.4 ± 0.8 s at 400 mg per L CaCO<sub>3</sub>, indicating significant impairment caused by interactions between divalent cations and its anionic headgroup.

CAPB displayed intermediate behavior, with wetting times moderately increasing with hardness (15.8 ± 0.5 s → 22.1 ± 0.7 s), reflecting partial shielding of ionic interactions due to its zwitterionic nature. Decyl glucoside exhibited the slowest but most stable wetting behavior, with minimal changes across hardness levels (21.0 ± 0.7 s → 22.3 ± 0.8 s), consistent with its non-ionic structure, which prevents interference from water hardness ions.

The results highlight the greater sensitivity of ionic surfactants to hardness-induced reduction in wetting efficiency, while non-ionic surfactants maintain near-constant interfacial performance.

Table 5 Wetting time (s) of surfactants at different water hardness levels (5% w/v, 25 °C)

Water hardness (mg per L CaCO <sub>3</sub> )	SLES	CAPB	Decyl glucoside
0	12.5 ± 0.4	15.8 ± 0.5	21.0 ± 0.7
100	18.2 ± 0.6	19.5 ± 0.6	21.8 ± 0.7
400	26.4 ± 0.8	22.1 ± 0.7	22.3 ± 0.8

**3.5.2. Foaming ability and foam stability.** Foaming behavior was assessed using the Ross–Miles method at 1% (w/v). Initial foam height and foam stability (height after 5 min) are shown in Table 6 and 7. SLES generated the highest initial foam (195 ± 5 mm at 0 mg L<sup>-1</sup> hardness), consistent with its strong surface activity. However, its foam height decreased significantly under hard water, dropping to 130 ± 5 mm at 400 mg L<sup>-1</sup>, indicating a detrimental effect of Ca<sup>2+</sup> and Mg<sup>2+</sup> on film elasticity and interfacial packing.

CAPB showed more moderate sensitivity, maintaining relatively stable foam heights even at high hardness (170 ± 4 mm → 145 ± 4 mm). Decyl glucoside produced lower foam overall (140 ± 3 mm), but its foam height decreased only slightly with hardness, demonstrating stable interfacial behavior.

Foam stability followed the same trend: SLES exhibited the greatest decline under hardness, while CAPB and especially decyl glucoside showed improved retention of foam structure over time.

Foaming results clearly reveal that SLES, although highly foamable in soft water, is severely affected by hardness, while CAPB retains a more balanced profile. Decyl glucoside, despite generating less foam, maintains exceptional stability and consistency—an important advantage for formulations requiring predictable performance in geographically diverse environments.

**3.5.3. Emulsification capacity ( $E_{24}$  index).** The emulsification index ( $E_{24}$ ) provides insight into the ability of surfactants to stabilize oil–water mixtures. Results for all surfactants at 1% (w/v) are shown in Table 8.

SLES exhibited the highest emulsification capacity in deionized water (68 ± 2%), but its performance declined sharply to 42 ± 3% at 400 mg L<sup>-1</sup> hardness, consistent with reduced interfacial stabilization caused by ion–headgroup interactions.

Table 6 Initial foam height (mm) at 1% (w/v) surfactant concentration (25 °C)

Water hardness (mg per L CaCO <sub>3</sub> )	SLES	CAPB	Decyl glucoside
0	195 ± 5	170 ± 4	140 ± 3
100	165 ± 4	160 ± 3	135 ± 3
400	130 ± 5	145 ± 4	130 ± 3



Table 7 Foam stability after 5 min (mm) at 1% (w/v) surfactant concentration (25 °C)

Water hardness (mg per L CaCO <sub>3</sub> )	SLES	CAPB	Decyl glucoside
0	168 ± 5	155 ± 4	120 ± 3
100	130 ± 5	145 ± 4	118 ± 3
400	95 ± 4	130 ± 3	115 ± 3

Table 8 Emulsification index  $E_{24}$  (%) of surfactants at different hardness levels (1% w/v, 25 °C)

Water hardness (mg per L CaCO <sub>3</sub> )	SLES	CAPB	Decyl glucoside
0	68 ± 2	60 ± 2	52 ± 2
100	55 ± 2	57 ± 2	51 ± 2
400	42 ± 3	50 ± 2	49 ± 2

CAPB demonstrated moderate emulsification efficiency and a more gradual decline ( $60 \pm 2\% \rightarrow 50 \pm 2\%$ ), suggesting partial resistance to ionic effects. Decyl glucoside showed the lowest but most stable emulsification capacity across hardness levels (52–49%), indicating that its non-ionic headgroup maintains consistent interfacial adsorption regardless of water composition.

**3.5.4. Summary of interfacial performance.** Overall, the wetting, foaming, and emulsification results collectively highlight the strong dependence of ionic surfactants on water hardness and the superior stability of non-ionic systems. SLES

exhibits excellent performance in soft water but experiences significant deterioration under hardness. CAPB demonstrates balanced behavior with moderate resilience. Decyl glucoside shows the most stable interfacial performance across all tests, reinforcing its suitability for environmentally robust and globally deployable cosmetic formulations.

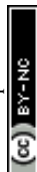
### 3.6. Statistical analysis

Statistical analysis was conducted to evaluate the effects of water hardness (0, 50, 100, 200, and 400 mg per L CaCO<sub>3</sub>), temperature (4 °C, 25 °C, and 40 °C), and pH (5.5, 7.0, and 9.0) on the physicochemical properties of SLES, CAPB, and decyl glucoside, including surface tension, CMC, viscosity, and physical stability parameters (color, sediment mass, turbidity, viscosity change, phase separation). One-way analysis of variance (ANOVA) was employed to assess the significance of these factors, with Tukey's Honestly Significant Difference (HSD) test used for post-hoc pairwise comparisons ( $p < 0.05$ ). Normality and homogeneity of variance were confirmed using Shapiro–Wilk and Levene's tests, respectively, ensuring robust statistical inference. Data were analyzed using statistical software, with results expressed as means ± standard deviation to capture experimental variability.

ANOVA revealed pronounced effects of water hardness, temperature, and pH on SLES and CAPB across most measured properties ( $p < 0.01$ ), reflecting their susceptibility to environmental perturbations. For SLES, an anionic surfactant, divalent cations may influence micellar organization, as indirectly suggested by changes in CMC, viscosity, and precipitation behavior. CAPB, with its zwitterionic nature, exhibited

Table 9 Summary of statistical analysis results for surfactant properties

Surfactant	Property	Water hardness effect	Temperature effect	pH effect
SLES	Surface tension	0.002	0.003	0.004
	CMC	0.001	0.002	0.003
	Viscosity	0.005	0.004	0.006
	Physical stability (color)	0.007	0.032	0.008
	Physical stability (sediment mass)	0.006	0.041	0.007
	Physical stability (turbidity)	0.004	0.005	0.009
	Physical stability (viscosity change)	0.003	0.038	0.005
	Physical stability (phase separation)	0.002	0.045	0.004
	CAPB	Surface tension	0.008	0.007
CMC		0.031	0.006	0.12
Viscosity		0.04	0.009	0.11
Physical stability (color)		0.009	0.15	0.13
Physical stability (sediment mass)		0.007	0.14	0.125
Physical stability (turbidity)		0.008	0.16	0.135
Physical stability (viscosity change)		0.006	0.145	0.115
Physical stability (phase separation)		0.2	0.17	0.18
Decyl glucoside		Surface tension	0.12	0.008
	CMC	0.19	0.22	0.15
	Viscosity	0.15	0.04	0.13
	Physical stability (color)	0.18	0.2	0.16
	Physical stability (sediment mass)	0.17	0.19	0.175
	Physical stability (turbidity)	0.165	0.185	0.17
	Physical stability (viscosity change)	0.155	0.195	0.165
	Physical stability (phase separation)	0.21	0.205	0.19



moderate sensitivity, as its balanced charge mitigated but did not eliminate ion-induced effects. Decyl glucoside, a non-ionic surfactant, demonstrated remarkable stability, with negligible effects across all conditions ( $p > 0.05$ ), except for slight temperature-related viscosity variations ( $p = 0.04$ ), underscoring its robustness due to the absence of charged headgroups. Tukey's HSD test pinpointed specific differences, confirming SLES's heightened vulnerability, followed by CAPB, while decyl glucoside's consistent performance supports its use in eco-friendly formulations resilient to diverse conditions. These statistical insights highlight the pivotal role of surfactant chemistry in modulating responses to environmental factors, guiding the optimization of cosmetic formulations for stability and sustainability under real-world conditions.

Table 9 summarizes the statistical significance ( $p$ -values) of the effects of water hardness (0, 50, 100, 200, 400 mg per L  $\text{CaCO}_3$ ), temperature (4 °C, 25 °C, 40 °C), and pH (5.5, 7.0, 9.0) on the physicochemical properties of SLES, CAPB, and decyl glucoside, as determined by one-way ANOVA with Tukey's HSD post-hoc tests ( $p < 0.05$  significance threshold). This table offers a quantitative snapshot of the statistical responsiveness of each surfactant to environmental stressors. Notably, SLES exhibited highly significant sensitivity ( $p < 0.01$ ) across nearly all parameters, emphasizing its vulnerability in real-world conditions. CAPB showed selective responsiveness, particularly in surface tension and CMC, suggesting conditional adaptability. In contrast, decyl glucoside's  $p$ -values consistently exceeded 0.1, reinforcing its inertness toward ionic and thermal fluctuations. This contrast illustrates how molecular charge architecture governs macroscopic formulation behavior. The table thus acts as a predictive tool for surfactant robustness, guiding selection for formulations destined for variable or extreme environments.

### 3.7. Indirect mechanistic interpretation of micellization behavior

The distinct micellization responses observed among SLES, CAPB, and decyl glucoside under varying environmental conditions can be mechanistically interpreted through electrostatic and thermodynamic principles. For SLES, an anionic surfactant, the introduction of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  reduces headgroup repulsion *via* ion bridging, thereby lowering the free energy barrier for micelle formation and increasing the CMC. This is consistent with classical DLVO theory, where reduced electrostatic repulsion favors aggregation, yet the resulting micelles are less stable and more prone to precipitation due to overcompensation of surface charge. CAPB exhibits partial ionic resilience attributed to its zwitterionic headgroup, which balances positive and negative charges internally. However, in high hardness environments, external divalent ions may still screen electrostatic interactions or distort the hydration shell, leading to moderate CMC increases. The amphiphilic character of CAPB allows some structural flexibility, but not full immunity.

In contrast, decyl glucoside, being non-ionic, lacks electrostatic interactions with water hardness ions, rendering its micellization behavior governed predominantly by hydrophobic

effects and hydrogen bonding. This leads to negligible CMC shifts across conditions. The stability of its micellar structures arises from enthalpy–entropy compensation mechanisms and strong solvation of the sugar headgroup, which remains unaffected by ionic species. These observations highlight the central role of headgroup charge and hydration dynamics in dictating micellization energetics. Understanding these mechanistic differences is essential for tailoring surfactant systems optimized for specific environmental and performance criteria, particularly in the development of robust, sustainable formulations.

## 4. Conclusion

This study systematically evaluated the physicochemical behavior of three representative cosmetic surfactants (SLES, CAPB, and decyl glucoside) under varying conditions of water hardness, temperature, and pH, focusing on critical formulation parameters such as surface tension, CMC, viscosity, and physical stability. The findings clearly demonstrate that ionic surfactants like SLES are highly susceptible to environmental perturbations, particularly divalent cation interference, which disrupts micellar integrity and reduces formulation robustness. CAPB exhibited moderate environmental resilience due to its zwitterionic nature but remained partially influenced by ionic stress. In contrast, decyl glucoside consistently maintained its physicochemical properties across all test conditions, reflecting its non-ionic architecture and minimal interaction with external ionic species. Mechanistic interpretation further revealed that the observed trends are rooted in the electrostatic and thermodynamic profiles of the surfactant headgroups. This highlights the importance of molecular design in predicting formulation behavior under real-world conditions. Decyl glucoside's superior environmental robustness and biodegradability position it as a leading candidate for sustainable and globally adaptable cosmetic formulations. Although biodegradability and formulation compatibility were not experimentally assessed in this work, decyl glucoside is widely reported in the literature as readily biodegradable and compatible with a broad range of cosmetic ingredients. It should be noted that commercial cosmetic formulations commonly incorporate chelating agents (*e.g.*, EDTA or citrates) to mitigate water hardness effects and preserve formulation stability. The present study intentionally focuses on single-surfactant systems to isolate intrinsic surfactant–environment interactions, rather than replicating fully optimized commercial formulations. Also no direct micelle-level structural characterization (*e.g.*, DLS, SAXS, or cryo-TEM) was performed in this study. Therefore, any discussion of micellar structural changes is based on indirect experimental evidence and established theoretical frameworks reported in the literature. Overall, these results provide formulation scientists with actionable insights for surfactant selection, emphasizing the necessity of integrating environmental stress testing into the early stages of product development. The study contributes to the advancement of eco-friendly and performance-consistent cleansing systems aligned with both consumer safety and regulatory trends in green chemistry.



## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

All data supporting the findings of this study are available from the corresponding author upon reasonable request.

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