"New formulation design of cleansing products created using foaming science - Foam volume enhancement by controlling viscoelasticity at air-water interface - "

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1. Introduction

Skin cleansing serves not only to remove dirt and sebum but also to enhance sensory experiences, such as emotional response and a sense of well-being, with abundant foam playing a key role [1, 2]. Foam volume is determined by two primary factors: foamability and foam stability [3]. Foams are inherently thermodynamically unstable systems in which dynamic processes such as formation, coalescence, and collapse occur continuously. Therefore, it is difficult to separate and independently evaluate foamability and foam stability [4].

Foam drainage, defined as the expulsion of liquid from foam films, is a key factor in foam stability because the complete loss of water can result in foam collapse. The Gibbs-Marangoni effect plays an important role in influencing drainage, as it restores the air-water interface by equalizing surface tension gradients over time, which arise from fluctuations in the foam film. The equalization of surface tension occurs via two main mechanisms: the lateral diffusion of surfactants from areas of high to low surface tension and adsorption of surfactants in the foam film to the foam interface. These processes are related to dilatational viscoelasticity at the air-water interface. Restoration through lateral diffusion is associated with dilatational elasticity (*E'*), which helps maintain the thickness of the foam film. In contrast, restoration through adsorption, though inevitable due to its association with dilatational viscosity (*E"*), is generally considered insufficient to prevent film thinning (Figure 1) [5, 6].

Recently, research has been conducted on the relationship between dilatational interfacial viscoelasticity and foam stability; i.e. a pendant-drop-based and a rising-drop-based dilatational interfacial rheometer. Koolivand-Salooki et al. demonstrated that the combination of specific concentrations of cationic surfactants with anionic polymers increases dilatational elasticity (*E'*) and stabilizes the foam [7]. Studies investigating the hydrophobic group structures of surfactants and interactions between surfactants and non-ionic polymers have primarily reported that *E'* plays a critical role in foam stability [8, 9]. On the other hand, few studies confirm the influence of dilatational viscosity (*E"*) on foam stability. In the report by Aono et al. [8], it was shown that although *E"* contributes approximately 25% to *E'*, its influence on foam stability was not adequately considered.

The present study considers not only dilatational elasticity (*E'*) but also dilatational viscosity (*E"*) as important factors in the Gibbs–Marangoni effect, which influences foam stability.

It builds on the hypothesis that foam stability is enhanced when *E'* increases and *E"* decreases simultaneously. This study aimed to verify this hypothesis and assess its impact on the foam volume of actual cleaning products.

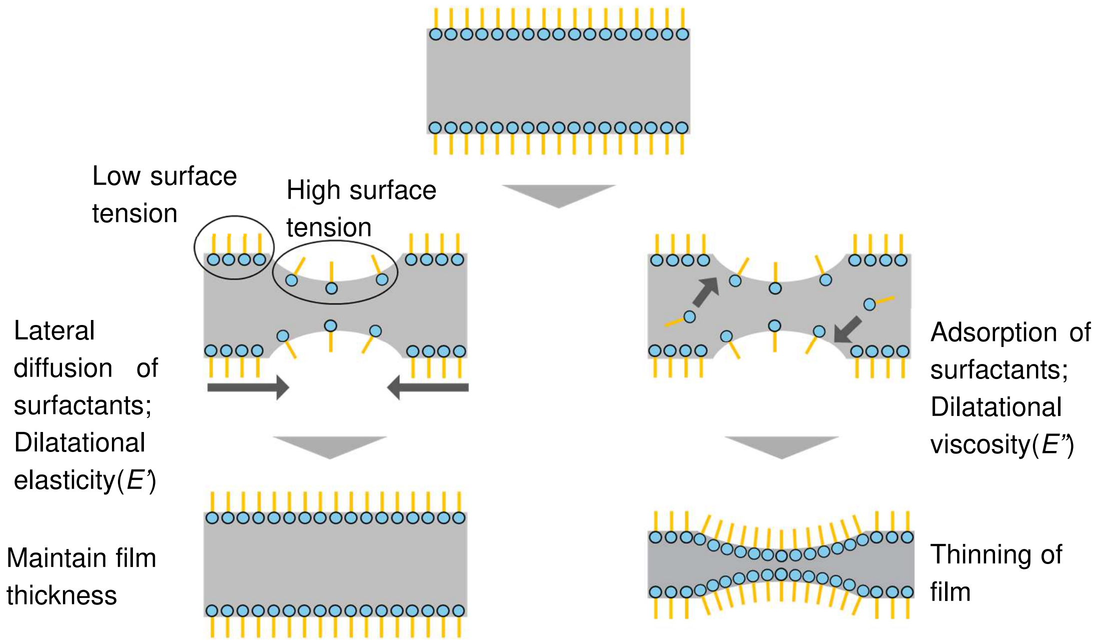


Figure 1. Restoration mechanism of the air-water interface against foam film fluctuation (Gibbs-Marangoni effect). Adapted and translated from a figure on p. 141 of Bunsan-kei no Reorojī: Kisoku, Hyōka, Seigyo, Oyō (Rheology of Dispersed Systems: Fundamentals, Evaluation, Control, and Applications) by S. Yada, 2021, NTS Publishing Co. Recreated by the author. [in Japanese]

2. Materials and Methods

Base wash formulations

A base wash formulation was prepared to contain 6% (w/w) potassium cocoyl glycinate (BASF), 2% (w/w) cocamidopropyl betaine (Clariant), 0.05% (w/w) disodium EDTA (EDTA-2Na) (Chelest), and 0.7% (w/w) phenoxyethanol (Clariant). The pH was adjusted to 7.4 using citric acid (Table 1).

As foam-boosting agents added to the base wash formulation, polyquaternium-7 (PQ-7) (Lubrizol), a cationic polymer, and inulin (Nippon Fine Chemical), a non-ionic polysaccharide that does not exhibit thickening effects, were selected. Both are commonly used foam boosters in cosmetic cleansers and were appropriately incorporated in each formulation, depending on the specific study conditions.

Table 1. Base wash formulation.

Ingredients	Quantity (% (w/w))
Purified water	Up to 100
Potassium cocoyl glycinate	6.00
Cocamidopropyl betain	2.00
EDTA-2Na	0.05
Phenoxyethanol	0.70
Citric acid	Adjusted to pH 7.4

Determination of dilational viscoelasticity at the air-water interface

The dilational viscoelasticity at the air-water interface was measured using a rising-drop dilatational interfacial rheometer [10]. Test samples were prepared by diluting each cleanser 1000-fold with purified water, which was then used for measurement. An overview of the equipment setup is shown in Figure 2. Measurements were performed at 25°C by sinusoidally oscillating 20% of the initial bubble volume at a frequency of 0.1 Hz, using a TECLIS Tracker (Civrieux-d'Azergues, France), after surface tension fluctuations stabilized.

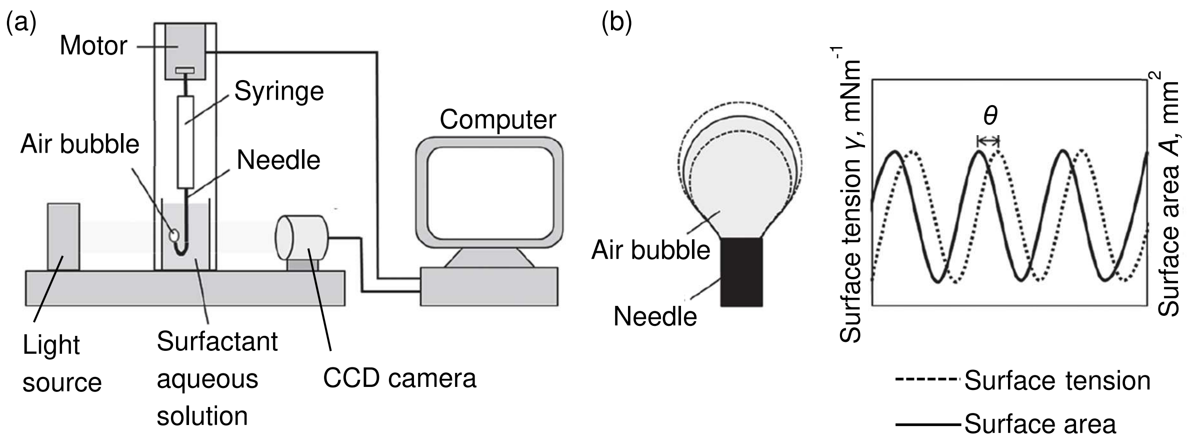


Figure 2. (a) Schematic diagram of the apparatus used in the rising-drop method, (b) Image of dilatational viscoelasticity measurement. Adapted and translated from a figure on p. 142 of Bunsan-kei no Reorojī: Kisoku, Hyōka, Seigyo, Oyō (Rheology of Dispersed Systems: Fundamentals, Evaluation, Control, and Applications) by S. Yada, 2021, NTS Publishing Co. Recreated by the author. [in Japanese]

Method of foam stability measurement

Various methods have been proposed for assessing foam stability. In this study, we employed a stirring method to measure the drainage volume from foam films. Each test cleanser was diluted five-fold with purified water and stirred for 10 s in a commercial mixer to generate sufficient foam. Twenty grams of the resulting foam was immediately weighed and poured into an angled funnel positioned over a 100 mL graduated cylinder. After pouring, the surface of the rod was sealed with plastic wrap to minimize evaporation. The volume of drainage that accumulated at the bottom of the graduated cylinder was measured at 25 °C at specific time intervals.

Sensory evaluation

Test cleansers were prepared by adding PQ-7 and inulin at a concentration of 0.2% (w/w), either individually or in combination. Four trained experts conducted evaluations. Two grams of each sample was diluted two-fold with purified water, and foam was generated by lathering the palm for 20 s. Foam volume was evaluated on a five-point scale, ranging from 1 (poor) to 5 (excellent), with a blank sample used as the midpoint (score = 3).

Evaluation of foamability

Foamability was determined using the cylinder-shaking method [11]. Briefly, 3.5 g of each formulation was diluted two-fold with purified water, mixed thoroughly, and transferred to a 100 mL graduated cylinder. The open end was sealed with a glass cap, and the cylinder was vigorously shaken ten times. The maximum foam volume was recorded 1 min after shaking.

3. Results

Effects of PQ-7 and inulin on dilatational elasticity and dilatational viscosity

PQ-7 and inulin were added to the base wash formulation at concentrations of 0%, 0.1%, 0.2%, and 0.4% (w/w), either individually or in combination. The measured values of dilatational interfacial viscoelasticity for each sample are presented in Table 2. The addition of PQ-7 tended to increase both dilatational elasticity (*E'*) and dilatational viscosity (*E"*), while the addition of inulin had minimal effect on *E'* and tended to decrease *E".*

Table 2. Results of dilatational interfacial viscoelasticity measurements of cleansers containing arbitrary amounts of PQ-7 and inulin

Form booster added		Dilatational viscoelasticity of cleanser	
PQ-7 % (w/w)	Inulin % (w/w)	Dilatational elasticity *E'* (mN・m^{-1})	Dilatational viscosity *E"* (mN・m^{-1})
0.00	0.00	9.3	9.0
0.20	0.00	11.6	10.2
0.00	0.20	9.2	8.1
0.20	0.20	10.3	8.5
0.10	0.00	19.1	12.3
0.40	0.00	11.6	9.2
0.00	0.10	10.3	7.8
0.20	0.10	16.3	7.3
0.20	0.40	19.2	7.3
0.00	0.40	13.3	9.6

Effects of PQ-7 and inulin on foam drainage volume

The drainage volume was measured for each sample diluted five-fold with purified water, using a cleanser containing PQ-7 and inulin at concentrations of 0%, 0.2%, and 0.4% (w/w), either individually or in combination. A time-course graph of drainage volume was plotted (Figure 3).

Variations in drainage volume were observed at each time point, depending on the concentrations of PQ-7 and inulin. The drainage volume of all samples increased over time, while the rate of drainage tended to decrease as time progressed.

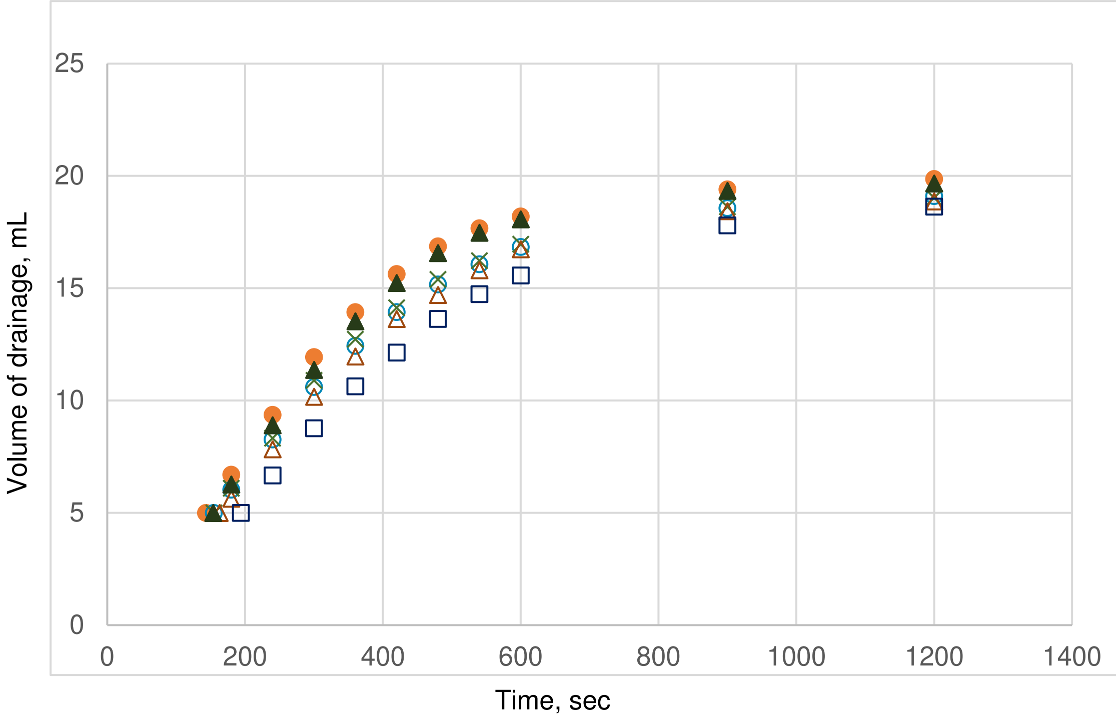


Figure 3. Time-dependent manner of drainage volume generated from foam. Symb□ls: ●, blank; ▲, + Inulin 0.2 % (w/w); ◯, + PQ-7 0.2 % (w/w); ×, + PQ-7 0.2 % (w/w) and Inulin 0.1 % (w/w); △, + PQ-7 0.2 % (w/w) and Inulin 0.2 % (w/w); □, + PQ-7 0.2 % (w/w); and Inulin 0.4 % (w/w).

Foam volume evaluations in the sensory test and cylinder shake test

The results of the foam volume evaluation of the cleansers containing 0.2% (w/w) PQ-7 and/or inulin are shown in Figure 4. Both the sensory evaluation (Figure 4 (a)) and the cylinder shake method (Figure 4 (b)) demonstrated a significant foam-enhancing effect from the individual incorporation of either PQ-7 or inulin, compared to the blank. In addition, when a combination of 0.2% (w/w) PQ-7 and 0.2% (w/w) inulin was added to the blank formulation, a significantly greater foam-enhancing effect was observed compared to the individual additions.

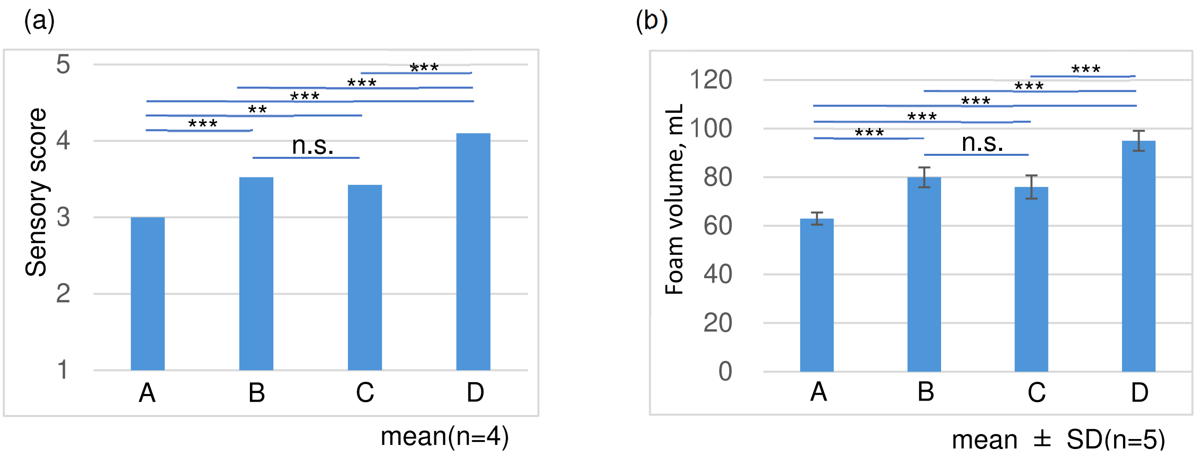


Figure 4. Evaluations of foam volume. (a) Sensory evaluations, (b) Cylinder shake method.
A: Blank, B: + PQ-7 0.2% (w/w), C: + Inulin 0.2% (w/w), D: Combination of PQ-7 (0.2% (w/w)) and Inulin (0.2% (w/w)), **p<0.01, ***p<0.001, n.s.: not significant (Tukey-Kramer test).

4. Discussion

To verify this hypothesis, the correlation between the measured drainage volume data and dilatational air-water interfacial viscoelasticity parameters was examined through regression analysis. Linear regression equations for the drainage rate were derived from the drainage volume-time curves shown in Figure 3, and the average drainage rate was calculated based on the slope of each equation. The calculated average drainage rates are presented in Table 3.

Table 3. Average drainage rates and dilatational viscoelasticity at the air-water interface.

Average drainage rates (mL/s)	Dilatational elasticity *E'* (mN・m^{-1})	Dilatational viscosity *E"* (mN・m^{-1})
0.0245	9.3	9.0
0.0228	11.6	10.2
0.0241	9.2	8.1
0.0224	10.3	8.5
0.0230	16.3	7.3
0.0211	19.2	7.3

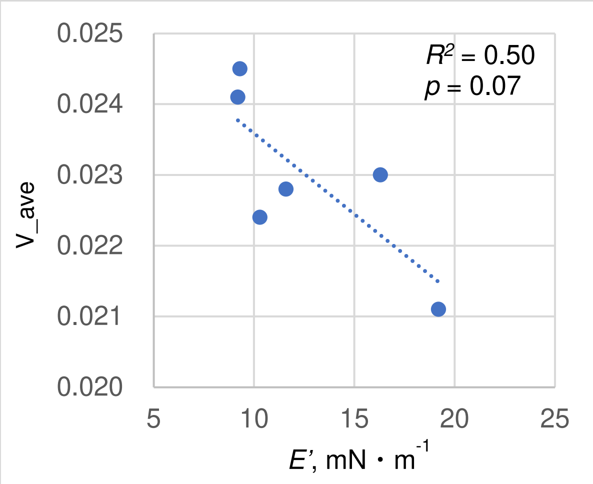
Using the data shown in Table 3, a regression analysis was performed with the average drainage rate (V_ave) as the dependent variable and *E'* (dilatational elasticity) and *E"* (dilatational viscosity) as independent variables. The following regression model was used:

$$Y(V\_ave) = \alpha E' + \beta E'' + e,$$

where V_ave = average drainage rate; *E'* = dilatational elasticity; *E"* = dilatational viscosity

The results of the regression analysis using *E'* as the independent variable are shown in Figure 5 as the regression scatter plot. Regression analysis revealed that the increase in dilatational elasticity *E'* lowered the mean drainage velocity ($p = 0.07 < 0.10$), with an impact of t = 2.455** > t; 0.05, 2.447 with adjusted R-square (R^2) = 0.50.

The results of the regression analysis with *E"* as the independent variable are presented in Figure 6 as the regression scatter plot. The analysis showed that an increase in dilatational viscosity *E"* had no significant effect on the average drainage rate (p = 0.52).



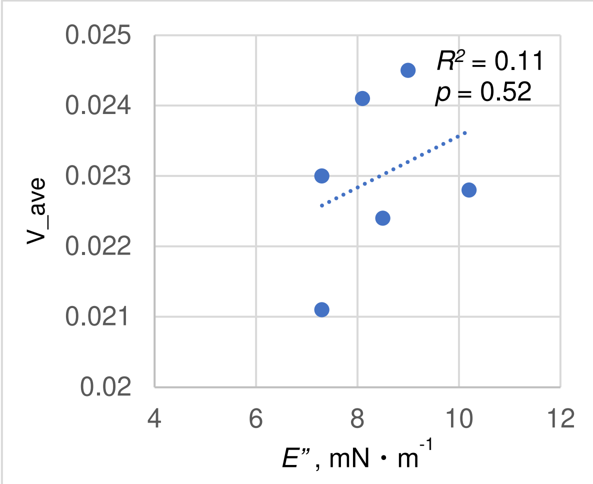


Figure 5. The scatter plots showing the relationship between V_ave and *E'*. The dashed line indicates the fitted linear regression line.

Figure 6. The scatter plots showing the relationship between V_ave and *E"*. The dashed line indicates the fitted linear regression line.

In studies on the stability of emulsions, the ratio of *E'* to *E"* has been analyzed, and it has been reported that *E"/E'* ≤ 1 is preferable for stabilization, indicating that *E'* should dominate over *E"* [12]. Therefore, *E"/E'* was calculated from the dilatational viscoelasticity results obtained in this study (Table 3), and a regression analysis was conducted using *E"/E'* as the independent variable, and the result is shown in Figure 7 as the regression scatter plot. The analysis showed that an increase in *E"/E'* lowered the mean drainage rate (p = 0.05 < 0.10), with an impact of t = 2.768 > t; 0.05, 2.447 with an adjusted R-square (R^2) = 0.57.

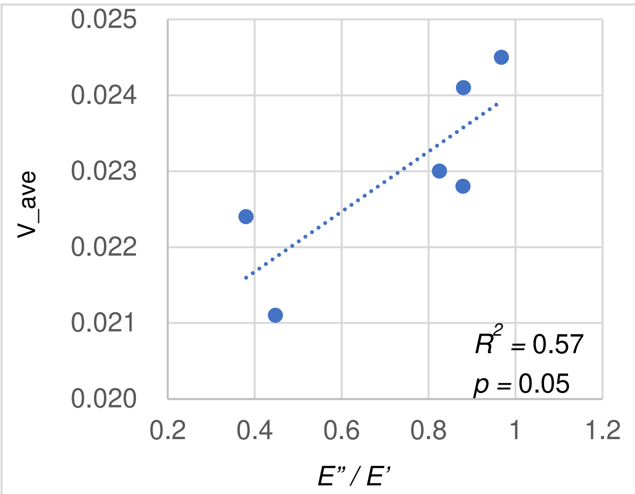


Figure 7. The scatter plots showing the relationship between V_ave and *E"/E'*. The dashed line indicates the fitted linear regression line.

The finding of a decrease in average draining velocity associated with an increase in *E'* is in line with the findings of Koolivand-Salooki et al. [7] and Aono et al. [8, 9] who showed that an increase in *E'* improves foam stability. Our results establish that *E'* is an important factor for foam stability and explain why *E"* was not emphasized in previous studies on foam stability.

Moreover, the present study demonstrated that *E'* is effective for foam stability, while *E"* is not. However, the adjusted coefficient of determination (R^2) values (Tables 4-6) show that

$$R^2(E''/E') = 0.57 > R^2(E') = 0.50 > R^2(E'') = 0.11,$$

indicating that the *E"/E'* provides the best fit to the foam drainage rates. These results suggest that the effect of dilatational interfacial viscoelasticity on foam stability may support the hypothesis that foam stability improves when *E'* increases and *E"* decreases simultaneously. Furthermore, using *E"/E'* as an indicator of foam stability—by incorporating both *E"* and *E'* into account—may offer a more accurate assessment than using *E'* alone.

Table 4 summarizes the foam volume data of each condition shown in Figure 4 and corresponding values of *E'*, *E"*, and *E"/E'*, which were calculated based on values from Table 3. These data indicate a stronger relationship between foam volume enhancement and *E"/E'* than with *E'* alone, further suggesting that the Gibbs–Marangoni effect plays an important role.

Table 4. Summary of data on foam volume and dilatational viscoelasticity at the air-water interface.

		Sample measured			
		Blank	+ PQ-7 (0.2% (w/w))	+ Inulin (0.2% (w/w))	Combination of PQ-7 and Inulin
Foam volume	Sensory score (Ave.)	3.0	4.0	3.9	4.7
	Cylinder test (mL. Ave.)	63	80	76	95
Dilational viscoelasticy of cleanser	*E'* (Dilational elasticity: $mN \cdot m^{-1}$)	9.3	11.6	9.2	10.3
	E" (Dilational viscosity: $mN \cdot m^{-1}$)	9.0	10.2	8.1	8.5
	E"/E' value	0.97	0.88	0.88	0.83

A possible mechanism underlying the observed increase in *E'* (dilatational elasticity) with the addition of PQ-7 is the formation of complexes between the cationic polymer PQ-7 and anionic surfactants, such as cocoyl glycine potassium (cocoylglycine K). Previous reports have indicated that such oppositely charged polymer–surfactant complexes can enhance *E'* [7]. It is speculated that these complexes adsorb at the air-water interface, thereby reinforcing the interfacial film and increasing *E'*.

Regarding the tendency of inulin to decrease *E"* (dilatational viscosity), one plausible mechanism is its influence on the hydration state and solubility of the surfactant. Inulin, a non-ionic polysaccharide, may alter micelle formation dynamics. Previous studies have shown that the addition of sugars can reduce the critical micelle concentration of anionic surfactants, such as sodium dodecyl sulfate, potentially lowering *E"* [13].

5. Conclusion

This study evaluated the roles of both dilatational elasticity (*E'*) and dilatational viscosity (*E"*) in foam stabilization through the Gibbs–Marangoni effect, focusing on their relationship with foam drainage behavior. The findings suggest that foam stability tends to increase with a decrease in the *E"*/*E'* ratio, highlighting not only the influence of elasticity (*E'*) but also the significance of viscosity (*E"*) in stabilizing foam. The insights may be valuable for the development of cleansing formulations that generate more stable and voluminous foam.

While the regression analysis results did not show statistically clear significant effects, the observed trends imply a potential relationship. Given the complexity and sensitivity of dilatational interfacial viscoelasticity measurements using the rising drop method, further experiments with stricter control of experimental conditions and an increased number of samples are necessary to validate these findings.

This study introduces a novel approach to foam-enhancing technology through the control of dilatational viscoelasticity at the air-water interface. We believe that these results may contribute to the development of wash products that offer enhanced user comfort and sensory satisfaction, improved cleansing performance, and reduced skin irritation through lower friction. Additionally, optimizing surfactant usage based on dilatational interfacial viscoelastic properties may help minimize both skin irritation and environmental burden.

6. References

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