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Influence of Formulation Parametres on Liquid Detergent formulation and Performance: A Design of Experiments Approach

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الملخص

أظهرت هذه الدراسة أن أداء واستقرار منظفات غسل الأطباق السائلة يتأثران بشدة بنوع وتركيز مكونات التركيبة. وأظهرت النتائج أن حمض اللاكتيك سلفات الصوديوم (LABSA) هو المكون الأكثر تأثيرًا على درجة الحموضة، وقدرة الرغوة، واستقرار المستحلب، بينما يلعب كلوريد الصوديوم (NaCl) دورًا رئيسيًا في التحكم في الموصلية الكهربائية وسلوك التعكر. يساهم مركب CAPB في تنظيم درجة الحموضة واستقرار الرغوة، في حين يعزز كبريتات لوريل إثر الصوديوم (SLES) أداء الرغوة ولكنه قد يؤثر سلبًا على استقرار المستحلب. يحسن غلوكوزيد جوز الهند استقرار الرغوة، ونعومة المنتج، والتحكم في التعكر. بالإضافة إلى ذلك، وُجد أن ظروف التصنيع، مثل سرعة الخلط وترتيب إضافة المكونات، لها تأثير كبير على جودة المنتج النهائي. وقد حققت كلتا التركيبتين، الأكاديمية والصناعية، بنجاح نطاق درجة الحموضة المطلوب (6.5-7.5)، مما يؤكد ملاءمتهما لتطبيقات غسل الأطباق. بشكل عام، يتطلب تحسين التركيبة تحقيق توازن دقيق بين عدة عوامل متنافسة للحصول على منتج مستقر وفعال وعالي الجودة.

الكلمات المفتاحية: التركيبة، المواد الفعالة سطحياً، الرغوة، التعكر، التصميم التجريبي.

Abstract

This study demonstrated that the performance and stability of liquid dishwashing detergents are strongly influenced by both the type and concentration of formulation ingredients. The results showed that LABSA is the most influential component affecting pH, foaming ability, and emulsion stability, while NaCl plays a major role in controlling conductivity and clouding behavior. CAPB contributes to pH buffering and foam stabilization, whereas SLES enhances foaming performance but may negatively affect emulsion stability. Coco Glucoside improves foam stability, product mildness, and clouding control. In addition, processing conditions such as mixing speed and the order of ingredient addition were found to have a significant impact on the quality of the final product. Both academic and industrial formulations successfully achieved the desired pH range (6.5–7.5), confirming their suitability for dishwashing applications. Overall, formulation optimization requires a careful balance between several competing factors to obtain a stable, effective, and high-quality product.

Keywords: formulation, surfactants, foam stability, turbidity, experimental design.

Résumé

Cette étude a montré que les performances et la stabilité des détergents liquides pour vaisselle dépendent fortement de la nature et de la concentration des ingrédients de formulation. Les résultats ont révélé que le LABSA est le composant le plus influent sur le pH, le pouvoir moussant et la stabilité de l'émulsion, tandis que le NaCl joue un rôle majeur dans la conductivité et le comportement de trouble (clou ding). Le CAPB contribue à l'effet tampon du pH et à la stabilisation de la mousse, alors que le SLES améliore le pouvoir moussant mais peut avoir un effet négatif sur la stabilité de l'émulsion. Le Coco Glucoside améliore la stabilité de la mousse, la douceur du produit et le contrôle du trouble. De plus, les paramètres de procédé, tels que la vitesse d'agitation et l'ordre d'ajout des ingrédients, influencent significativement la qualité du produit final. Les formulations académique et industrielle ont toutes deux atteint la plage de pH souhaitée (6,5–7,5), confirmant leur aptitude pour les applications de lavage de vaisselle. Globalement, l'optimisation de la formulation nécessite un équilibre entre plusieurs facteurs afin d'obtenir un produit stable, efficace et de haute qualité.

Mots clés : formulation, tensioactifs, mousse, turbidité, plan d'expériences.

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Listed des abbreviations:

Abbreviation	Signification
SLES	Sodium Lauretha Sulfate
LABSA	Linear Alkyl Benzene Sulfonic Acid
CAPB	Cocamidopropyl Betaine
NaCl	Sodium Chloride
CG	Coco Glucoside
CA	Citric Acid
SB	Sodium Benzoate
pH	Potential of Hydrogen
DOE	Design of Experiments
RSM	Response Surface Methodology
CMC	Critical Micelle Concentration
ANOVA	Analysis of Variance
Rpm	Revolutions Per Minute
°C	Degree Celsius
G	Gram
mL	Milliliter
%	Percentage

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General Introduction

General Introduction

Liquid dishwashing detergents are among the most widely used cleaning products in everyday life due to their effectiveness in removing grease, food residues, and various types of dirt from kitchen utensils. Their performance mainly depends on the nature and proportion of surfactants as well as the interactions between the different formulation ingredients. Therefore, the development of an efficient and stable detergent requires a good understanding of the physicochemical properties of its components and the factors influencing its performance [18].

In recent years, formulation studies have increasingly relied on experimental design methods to optimize product composition while reducing the number of experiments, time, and cost. These methods allow the evaluation of the effect of different formulation variables and their interactions on the final properties of the product. [3,8]

The present work focuses on the formulation and characterization of liquid dishwashing detergents using two different approaches: an academic formulation and an industrial formulation. Various raw materials, including SLES, LABSA, CAPB, Coco Glucoside, and NaCl, were used to prepare the formulations. The influence of these components on several physicochemical properties, such as pH, conductivity, turbidity, foam stability, and emulsification capacity, was investigated. The objective of this study is to compare the two formulations, evaluate their performance, and identify the most suitable composition for obtaining an effective and stable liquid dishwashing detergent. [1,2]

Chapter 1

Surfactants

1.1. Introduction

Surfactants lie at the heart of every liquid detergent formulation, serving as the primary functional ingredients that drive cleaning efficiency and overall product performance. Their distinctive amphiphilic molecular architecture, consisting of a water-loving (hydrophilic) head and an oil-loving (hydrophobic) tail, enables them to occupy interfaces, lower surface and interfacial tension, and interact effectively with a wide spectrum of soils. Through these capabilities, surfactants facilitate essential processes such as wetting, emulsification, dispersion, and micelle formation, which collectively allow detergents to remove dirt, grease, and oily residues from a variety of substrates [3,8] .

The versatility of surfactants extends beyond soil removal. They strongly influence a formulation's foam profile, rheology, stability, mildness, biodegradability, and compatibility with other components such as enzymes, builders, solvents, and fragrances. Modern liquid detergent systems rarely rely on a single type of surfactant; instead, they commonly incorporate strategic blends of anionic, nonionic, cationic, and amphoteric classes. Each category offers distinct strengths—such as high detergency, good solubilization capacity, skin mildness, or antimicrobial activity—and combining them enables formulators to fine-tune cleaning performance while meeting cost, regulatory, and consumer expectations. [3,5]

A deep understanding of surfactant chemistry is therefore essential for designing effective and sustainable liquid detergents. This chapter provides a comprehensive overview of the structures, classifications, mechanisms of action, and functional roles of surfactants within liquid detergent systems. By building a clear foundation in these concepts, readers will be better equipped to understand formulation strategies, evaluate ingredient choices, and optimize product performance for diverse household and industrial applications. [1,2]

1.2. General Structure

The molecular architecture of a surfactant can be simplified as: **Hydrophilic head – Hydrophobic tail [3]**

This dual structural arrangement allows the molecule to orient itself strategically at boundaries such as water/air, water/oil, or solid/liquid interfaces. In aqueous solution, the hydrophilic head associates with water molecules, while the hydrophobic tail avoids water and seeks nonpolar environments. This interfacial positioning is fundamental to the ability of surfactants to:

Reduce surface and interfacial tension: By accumulating at interfaces and disrupting cohesive forces between water molecules.

Promote wetting: Enabling water to spread more easily over surfaces and soils.

Initiate micelle formation: At concentrations above the critical micelle concentration (CMC), surfactant molecules aggregate into micelles, with hydrophobic tails inward and hydrophilic heads outward. These micelles solubilize oily soils and suspend them in the wash solution.

Enhance emulsification and dispersion: Surfactants stabilize oil droplets within water, preventing them from coalescing.[3]

The combination of structural features and these functional properties makes surfactants indispensable in liquid detergent formulations. Their molecular design determines not only detergency but also foaming behavior, solubilization capacity, chemical stability, and environmental compatibility. [3,9]

1.3 Classification of Surfactants

Surfactants are commonly classified according to the nature of the hydrophilic (polar) head group, as this greatly influences their interfacial behavior, solubility, performance in formulations, and compatibility with other ingredients. The four major categories are: anionic, cationic, nonionic, and amphoteric surfactants. Each group displays distinct chemical properties and fulfills specific functional roles within liquid detergent systems.[3,8]

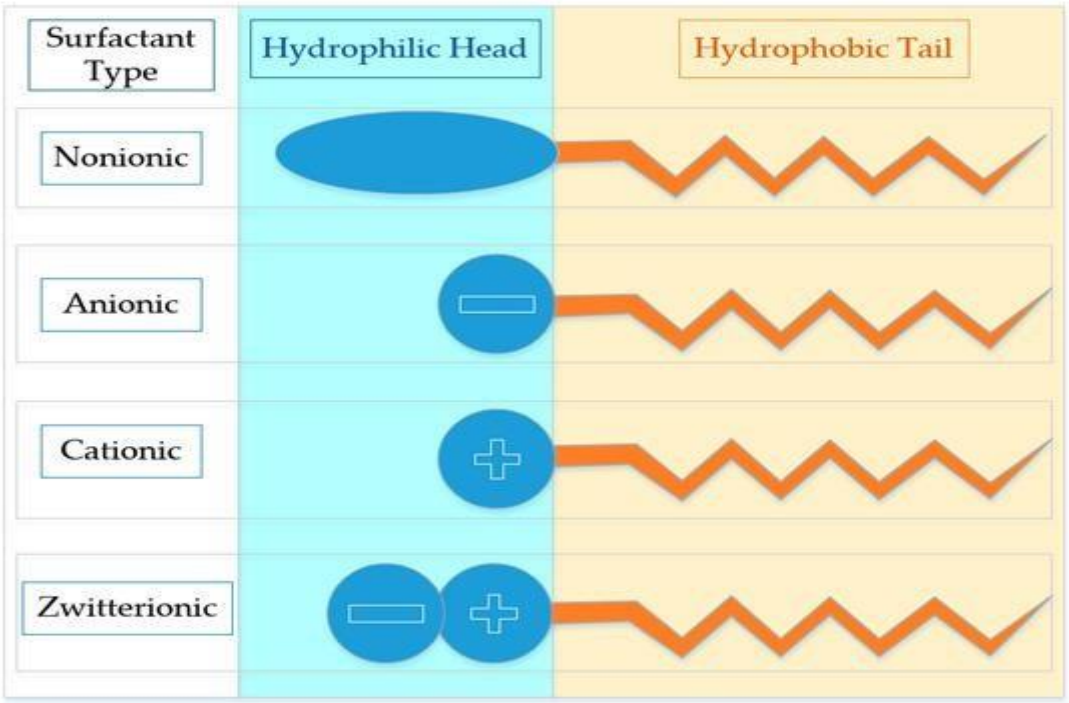


Figure 1: Classification of Surfactants

1.3.1 Anionic Surfactants

Definition: Anionic surfactants possess a negatively charged hydrophilic head when dissolved in water. They constitute more than 60% of global surfactant consumption, particularly in household and industrial detergent formulations. [3,6]

Key Chemical Characteristics

- High detergency due to strong interaction with oily and particulate soils

- Superior foaming capability, making them ideal for consumer-oriented cleaning products
- Good chemical stability under moderate pH and temperature conditions
- Cost-effective synthesis from petrochemical or oleochemical feedstocks
- Common hydrophobic chains include C12–C18 alkyl groups

Industrial Advantages

- High cleaning power in hard and soft water
- Wide availability and established manufacturing processes
- Easily biodegradable variants available (e.g., linear alkylbenzene sulfonates)

Common Examples

Table 1: examples about common surfactant

Chemical Name	Abbreviation	Role in Formulation
Linear Alkylbenzene Sulfonate	LAS	Primary detergent, strong degreaser
Sodium Lauryl Ether Sulfate	SLES	Rich foam, good solubilizing power
Sodium Lauryl Sulfate	SLS	Strong foamed, high detergency
Soaps (fatty acid salts)	—	Basic detergency, viscosity modifier

Applications

- Dishwashing liquids (high foam + strong grease removal)
- Household surface cleaners
- Shampoos and personal wash products (especially SLES due to mildness compared to SLS).

- Laundry detergents, including heavy-duty industrial formulas

1.3.2 Cationic Surfactants

Definition: Cationic surfactants carry a positive charge on their hydrophilic head. They exhibit strong interaction with negatively charged surfaces such as textiles, hair fibers, and microbial cell membranes. [3,16]

Key Chemical Characteristics

- Excellent antimicrobial and biocidal activity due to membrane disruption
- Strong adsorption onto negatively charged surfaces, providing softening or conditioning effects
- Incompatible with anionic surfactants due to ionic neutralization
- Often based on quaternary ammonium or pyridinium structures

Industrial Advantages

- Provide long-lasting surface modification (e.g., anti-static, softening)
- Effective at low concentrations
- Essential for disinfectant formulations

Examples

Quaternary ammonium compounds (“Quats”); Cetyltrimethylammonium chloride (CTAC); Benzalkonium chlorides (BACs)

Applications

- Disinfectants and sanitizing agents
- Fabric softeners (conditioning effect on fibers)
- Antistatic treatments for plastics, textiles, and industrial surfaces

- Hair conditioners (adsorption to keratin)

1.3.3 Nonionic Surfactants

Definition: Nonionic surfactants contain no net charge, making them highly compatible with all other classes and stable under a wide range of process conditions. [3,9]

Key Chemical Characteristics

- Excellent degreasing and solubilizing capability
- Low foaming—ideal for industrial and mechanical cleaning applications
- High stability to electrolytes, acids, alkalis, and hard water
- Lower skin irritation potential
- Often based on ethylene oxide, propylene oxide, or sugar-derived moieties

Industrial Advantages

- Ideal for low-foam detergents used in automatic dishwashers, industrial washers, and clean-in-place (CIP) systems
- Useful in high-temperature processes due to thermostability

Examples

Ethoxylated fatty alcohols (AE)

Alkyl polyglucosides (APGs) – biodegradable, plant-derived

Fatty acid alkanolamides

Applications

- Eco-friendly detergents (APGs widely used in green formulations)
- Industrial degreasing and metal-cleaning products

- Low-temperature laundry detergents
- Food industry CIP cleaners

1.3.4 Amphoteric Surfactants

Definition: Amphoteric (or zwitterionic) surfactants can carry either a positive or negative charge depending on the pH. In acidic conditions they behave like cationic surfactants; in alkaline conditions they resemble anionic surfactants. [3,11]

Key Chemical Characteristics

- Very mild on skin and mucous membranes
- Excellent foam stabilization—improves the quality and persistence of foams
- Highly compatible with anionic, cationic, and nonionic surfactants
- Good biodegradability and favorable environmental profile
- Common structures include betaine, sultane, and amphoacetate derivatives

Industrial Advantages

- Improve viscosity, foam stability, and mildness of formulations
- Buffer harshness of strong anionic surfactants
- Ideal for high-foaming personal care and specialized cleaning products

Examples

Cocamidopropyl betaine (CAPB); Hydroxysultaines; Amphoacetates and amphopropionates

Applications

- Sensitive-skin and baby detergents
- Shampoos and body washes (mild, stable foam)
- Liquid hand soaps

- Premium household cleaners requiring both gentleness and performance

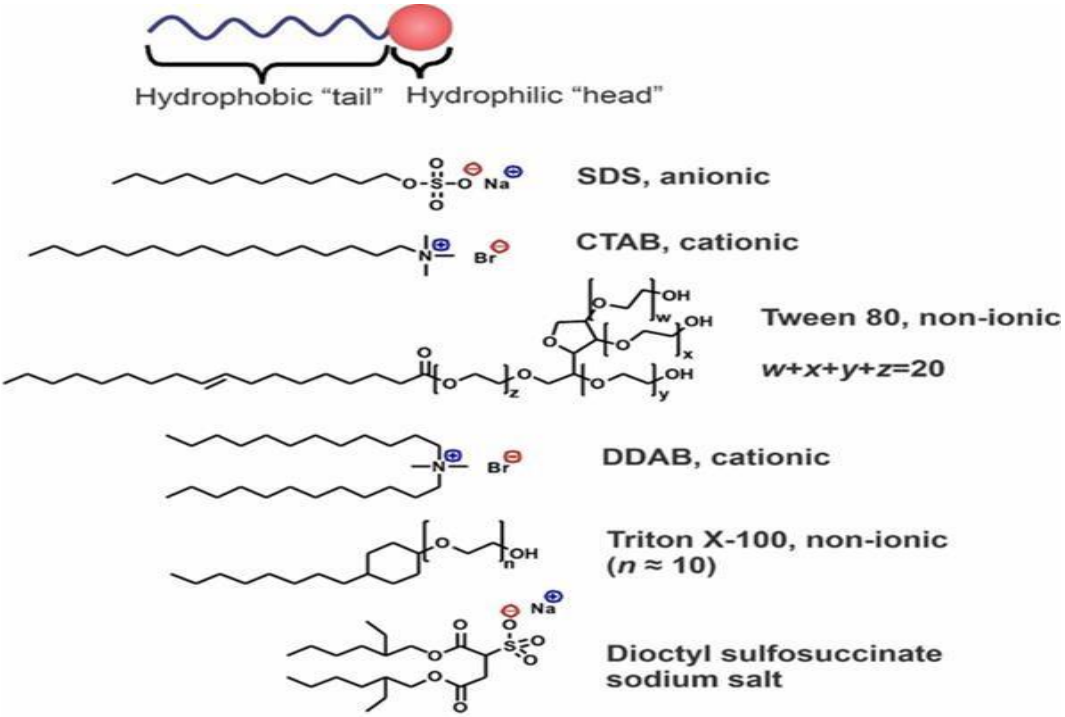


Figure 2: examples about different surfactants types

1.4 Physicochemical Properties of Surfactants

1.4.1 Reduction of Surface Tension

Surfactants reduce the surface tension of water from approximately 72 $mN \cdot m^{-1}$ to values as low as 25–30 $mN \cdot m^{-1}$. This reduction enhances wetting, spreading, and penetration of aqueous solutions on solid and particulate surfaces, thereby facilitating soil detachment.[11]

1.4.2 Critical Micelle Concentration (CMC)

At the CMC, surfactant molecules transition from interfacial adsorption to aggregate formation. Above this threshold: surface tension becomes nearly constant, micelles proliferate in solution, and oil solubilization and detergency increase dramatically. The CMC is influenced

by surfactant structure, ionic strength, temperature, and the presence of cosurfactants or solvents.[17]

1.4.3 Micelle Formation and Structure

Micelles are thermodynamically stable aggregates in which hydrophobic tails assemble into a nonpolar core surrounded by hydrophilic headgroups. Micelles solubilize hydrophobic soils such as grease, oils, and sebum by incorporating them within their cores. The structure, shape, and size of micelles (spherical, rod-like, or worm-like) are determined by surfactant geometry and interactions with additives.[14,17]

1.4.4 Foaming and Foam Stability

Foam generation results from the stabilization of air–water interfaces by surfactant monolayers. Anionic surfactants typically produce abundant foam, whereas nonionic generate minimal foam. Amphoteric act as foam stabilizers by reinforcing the elasticity of interfacial films.[17]

1.4.5 Determinants of Detergency

Cleaning efficiency arises from a complex interplay among:

surfactant structure and chain length, micelle morphology, solution pH and ionic strength, water hardness, and interactions with polymers, enzymes, and builders.[14]

1.5 Functional Roles of Surfactants in Liquid Detergents

Surfactants perform several key functions:

Wetting: lowering surface tension allows rapid penetration of aqueous solutions into porous soils and textile fibers.[11]

Degreasing: hydrophobic tails solubilize oily residues through micelle encapsulation.

Emulsification: surfactants disperse oils into stable droplets, preventing coalescence.[11]

Suspension: particulate matter is kept dispersed in solution, inhibiting redeposition on surfaces.

Formulation stabilization: surfactants contribute to viscosity development, solubilization of fragrances, and stabilization of dyes and dispersed phases.[11]

1.6 Criteria for Industrial Selection of Surfactants

The industrial selection of surfactants for liquid detergent formulations is a multifactorial process that requires a balanced evaluation of performance efficiency, physicochemical compatibility, safety and environmental considerations, and economic viability. Because surfactants govern both the cleaning function and the structural behavior of the formulation, their selection must be optimized not only for detergency but also for stability, processing characteristics, and end-use requirements.[19]

1.6.1 Performance-Related Criteria

The primary determinant in surfactant selection is cleaning performance. This encompasses several interrelated parameters:

Detergency and Soil-Removal Efficiency: Formulators assess the ability of surfactants to remove a wide range of soils, including hydrophobic grease, particulate matter, proteinaceous stains, and body oils. Molecular structure particularly chain length, degree of branching, and headgroup chemistry strongly influences adsorption at interfaces and micelle formation, which in turn determines cleaning efficiency in cold, warm, or hard water conditions.[19]

Foam Characteristics: Foaming behavior is critical in applications such as hand dishwashing liquids and personal care cleansers, where foam height, foam density, and foam persistence affect consumer perception. Surfactants must be selected based on the desired foam profile:

high and stable foam (anionic surfactants), controlled moderate foam (amphoteric), or low foam for automated processes (nonionic).[19]

Kinetics of Action: The speed of wetting, emulsification, and solubilization determines how rapidly visible cleaning occurs. Surfactants with fast adsorption dynamics and low surface tension reduction times are preferred for high-performance household and industrial formulations.[19]

1.6.2 Physicochemical Criteria

Surfactants must also be evaluated based on their behavior in the complex chemical environment of a detergent formulation:

Solubility and Temperature Stability: Surfactants must remain soluble and stable across a wide temperature range to prevent cloudiness, phase separation, or precipitation. Nonionic surfactants with high ethoxylation degrees, for example, exhibit cloud points that influence clarity and stability.[19]

Viscosity and Rheological Contribution: Some surfactants interact with salts, polymers, and cosurfactants to modify viscosity. Anionic–amphoteric mixtures often provide desirable thickening behavior. Formulators must anticipate how a surfactant contributes to the rheological profile of the final product.[19]

Electrolyte Tolerance and Water Hardness Resistance: Hard water tolerance is crucial for detergency. Surfactants must operate efficiently in the presence of calcium and magnesium ions, either inherently (nonionic) or with the support of builders (anionics).[19]

Compatibility with Other Ingredients: Surfactants must be chemically compatible with enzymes, fragrances, dyes, preservatives, and additives. Incompatibilities such as the

precipitation between anionics and cationic—limit formulation options and require careful selection or structural modification.[19]

1.6.3 Safety, Toxicological, and Environmental Criteria

Increasingly stringent environmental regulations and consumer expectations require surfactants to meet safety and sustainability benchmarks:

Biodegradability: Surfactants must degrade readily under environmental conditions to minimize ecological impact. Linear surfactants (e.g., LAS) are preferred over branched analogues due to superior biodegradability.[19,14]

Dermal and Ocular Compatibility: Products intended for skin contact must use surfactants with low irritation potential. Amphoteric and nonionic surfactants are commonly blended with anionics to mitigate harshness.[19]

Ecotoxicity: Toxicity toward aquatic organisms is a critical constraint in surfactant choice. Regulatory frameworks (REACH, EU Detergent Regulation) enforce strict limits on persistent and bio accumulative compounds.[19]

1.6.4 Economic and Industrial Processing Criteria

Beyond performance and safety, the commercial viability of a surfactant plays a decisive role:

Raw Material Cost and Availability: Surfactants must be economically sustainable at industrial scales. High-volume anionic surfactants (LAS, SLES) remain dominant due to their low cost-of-manufacture and widespread global availability.[17]

Processing and Manufacturability: Surfactants must be suitable for large-scale production and integration into high-speed manufacturing lines. Factors such as pourability, viscosity behavior, and resistance to shear or temperature fluctuations influence industrial handling.

Supply Chain Robustness: Surfactants derived from renewable feedstocks (e.g., APGs, fatty alcohol ethoxylates) are increasingly appealing due to supply stability and reduced dependency on petrochemical sources.[17]

1.7 Chemical Interactions Between Surfactants and Additives

The performance of a detergent formulation is shaped by the interactions between surfactants and other chemical components.[5]

1.7.1 Surfactant–Builder Interactions

Builders enhance detergency by sequestering hard water ions, thereby preventing the formation of insoluble surfactant salts. By reducing calcium and magnesium interference, builders increase micelle stability and improve soil emulsification. [5,2]

1.7.2 Surfactant–Solvent Interactions

Solvents modify the polarity of the aqueous medium, improving the solubility and dispersion of nonionic surfactants, perfumes, and hydrophobic additives. They also influence viscosity, clarity, and low-temperature stability.[5]

1.7.2 Surfactant–Salt Interactions

Salts adjust micelle size and shape by altering electrostatic interactions. In anionic surfactant systems, moderate salt addition increases viscosity through micelle growth, but excessive salt can induce phase separation. [5,1]

1.7.3 Surfactant–Polymer Interactions

Polymers interact with surfactants through both hydrophobic binding and electrostatic interactions. These associations enhance soil suspension, modify rheology, and improve stability against phase separation.[5]

1.7.4 Surfactant–Enzyme Interactions

Enzymes require a stabilizing environment to maintain activity. Surfactant selection influences enzyme stability; nonionic and amphoteric surfactants are preferred due to their low denaturing potential.[5]

1.7.5 Surfactant–Perfume and Surfactant–Dye Interactions

Fragrance oils and dyes are solubilized within micelles. Mixed surfactant systems (e.g., anionic–nonionic blends) often provide superior solubilization due to enlarged or more flexible micellar cores.[5]

Chapter 2

Design of Experiments

2.1 Introduction

In engineering and formulation sciences, systems impacted by several variables acting simultaneously are frequently the subject of experimental inquiry. Because they ignore interaction effects and necessitate numerous experimental trials to draw valid findings, classical experimental approaches—especially the one-factor-at-a-time method—are limited in their capacity to define complex systems. Systematic approaches that can effectively extract useful information from experimental data are becoming more and more necessary as industrial processes and formulations get more complicated. A rigorous statistical framework known as Design of Experiments (DoE) has been developed to address these issues by facilitating the organized planning and analysis of experiments when multiple variables are manipulated simultaneously. [1,2]

By incorporating statistical concepts into the process of designing experiments, DoE offers a logical foundation for experimentation. DoE makes it easier to identify essential variables, quantify their impacts, and create prediction models through organized data analysis and controlled variation of input parameters. DoE is an essential tool for comprehending system behavior and directing optimization efforts in formulation-based systems, like liquid detergents, where performance qualities are controlled by complex physicochemical interactions among constituents. [1,2]

2.2 Definition of Design of Experiments (DoE)

Design of Experiments is formally defined as a statistical methodology used to plan, conduct, analyze, and interpret experiments in a systematic manner, with the objective of determining the relationships between factors affecting a process and the responses of interest. This methodology emphasizes efficiency and rigor by ensuring that experimental data are collected in a way that maximizes information content while

minimizing experimental effort. In DoE, experiments are not conducted arbitrarily; instead, factor levels and combinations are selected according to predefined statistical designs that allow for unbiased estimation of effects and interactions [1,2]

From a theoretical standpoint, DoE is grounded in probability theory and statistical inference. It provides tools for estimating model parameters, assessing experimental uncertainty, and testing hypotheses regarding factor significance. By employing DoE, researchers can construct empirical models that describe system behavior over a defined experimental domain and use these models to predict responses under new conditions. Consequently, DoE serves both descriptive and predictive functions in experimental research. [1,2,13]

2.3 Objectives and Importance of DoE

DoE's primary objective is to generate reliable and understandable data about a system with the fewest experimental runs feasible. One of its prim ary goals is to identify the elements that significantly affect the responses and quantify the magnitude and direction of these effects. DoE is specifically made to identify interaction effects, which happen when one factor's influence is dependent on another's level, in addition to primary effects. These interactions are common in chemical and formulation systems and often regulate system performance. [1,2]

In an industrial setting, the application of DoE results in lower development costs, shorter development timelines, and better product quality. For liquid detergent formulations, DoE offers a scientific foundation for optimizing performance [13,14]

characteristics while maintaining formulation stability and manufacturability. DoE also aims to improve experimental reproducibility and robustness by reducing variability and isolating noise factors. DoE ensures that conclusions drawn from

experimental data are statistically valid through randomization, replication, and blocking strategies.[15]

2.4 Fundamental Concepts of Experimental Design:

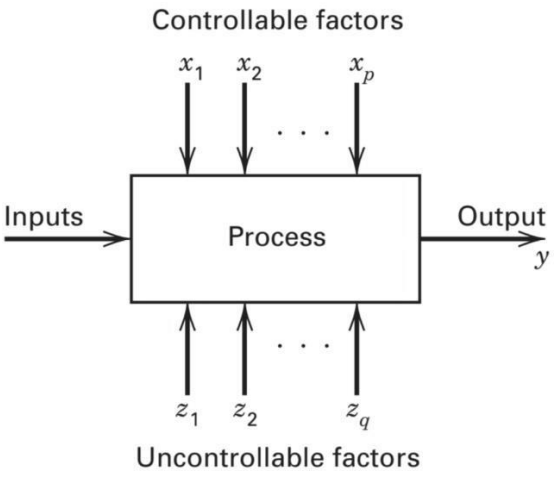


Figure 3: General model of a process or system.

2.4.1 Factors and Levels

During an experiment, factors are controllable input variables that are purposefully changed to see how they affect the replies. Factors can be qualitative, such material kind or processing technique, or quantitative, like concentration, temperature, or pH Every factor is examined at predetermined levels, or values. The experimental region in which the system is investigated is determined by the selection of factor levels. [2,1]

A crucial stage in DoE is choosing the right levels and elements. Prior knowledge, theoretical concerns, and practical relevance must all be taken into

account while selecting factors. Levels should be chosen to ensure experimental viability and safety while accurately reflecting the system's operational range.[13]

2.4.2 Responses

The measured outputs or performance indicators that come from experimental runs are called replies. Depending on the system being studied, responses could be mechanical, chem ical, physical, or functional characteristics. Performance, stability, and quality metrics are frequently included in formulation research replies. Meaningful statistical analysis and model building depend on accurate and exact response measurement. [14,13]

2.4.3 Main Effects and Interactions [13,14]

The average change in reaction when a factor is changed from one level to another, regardless of other factors, is known as the main effect of that factor. When the level of one element influences the impact of another on a response, interaction effects occur. One of DoE's key advantages is its ability to identify interactions, as in multivariable systems, interactions are often crucial in determining system behavior.

2.5 Classification of Experimental Designs

2.5.1 Full Factorial Designs

All potential combinations of factor levels are investigated in full factorial designs. This approach offers thorough information about key impacts and interactions for a system with various elements. Full factorial designs provide the most comprehensive characterization of system behavior, but their practical application may be limited to systems with few variables because the number of experimental runs grows exponentially with the number of factors. [13,1]

2.5.2 Fractional Factorial Designs

A methodical reduction of full factorial designs is represented by fractional factorial designs. These designs preserve important information about factor effects while drastically lowering experimental effort by carefully choosing a portion of the total experimental runs. Early-stage research frequently uses fractional factorial designs to screen factors and determine which have the biggest impact on answers.[14]

2.5.3 Screening Designs

. Screening designs are experimental designs used to identify the most influential factors among a large number of variables while minimizing the number of experimental runs. They are mainly applied during the early stages of experimentation to determine which factors significantly affect the response and should be included in further optimization studies. Fractional factorial and Plackett–Burman designs are among the most commonly used screening designs. [13,14]

2.5.4 Response Surface Methodology (RSM)

Response Surface Methodology is a collection of statistical and mathematical methods for modeling and analyzing systems where multiple variables affect responses. The goal of RSM is to create empirical models that characterize the response surface inside the experimental region. These models are usually second-order polynomial equations. These models are used to determine ideal operating conditions and investigate factor-response correlations. [15,2]

2.5.4.1 Central Composite Design (CCD)

Within RSM, Central Composite Design is one of the most popular designs. It allows for the estimation of linear, interaction, and quadratic effects by combining

factorial, axial, and center points. CCD is very useful for identifying curvature in the response surface and offers flexibility in experimental planning. [13,2]

2.5.4.2 Box–Behnken Design

An alternate RSM design that requires fewer experimental runs than CCD is the Box-Behnken Design. It stays away from extreme factor combinations and is thought to be appropriate for systems where it could be dangerous or unfeasible to operate at boundary conditions. Fitting quadratic models and determining the ideal factor levels inside the experimental zone are both made possible by this strategy.[15]

2.5.5 Mixture Designs

When experimental factors indicate component proportions in a mixture and their sum is limited, mixture designs are used. Responses in these systems rely on the relative ratios of components rather than their absolute amounts. Mixture designs are frequently employed in product development and are especially pertinent to formulation research.[30]

2.6 Statistical Analysis in DoE

2.6.1 Mathematical Modeling

DoE uses regression analysis to create mathematical models that explain how causes and responses relate to one another. These models serve as the foundation for prediction and optimization and offer quantitative insight into system behavior. Statistical criteria are used to evaluate model adequacy in order to guarantee validity and reliability. [2,13,20]

2.6.2 Analysis of Variance (ANOVA)

A key statistical approach used in DoE to assess the importance of factor effects and interactions is analysis of variance. ANOVA allows hypothesis testing to identify which effects are statistically significant by dividing the overall variability in the data into components attributed to various causes. [1,12,13]

2.7 Application of DoE in Liquid Detergent Formulation

DoE is used in liquid chemical formulation to methodically examine how formulation parameters affect performance attributes. Formulators can assess interactions between ingredients, identify essential factors, and optimize formulation qualities in an organized and repeatable way by using DoE. This approach facilitates the construction of logical formulations and improves comprehension of intricate formulation systems. [2,20,30]

2.7.1 Inputs (Independent Variables)

The formulation study was carried out by varying several parameters in order to evaluate their influence on the final product [30].

- Type of surfactants used
- Surfactant concentrations
- Presence or absence of secondary surfactants
- Sodium chloride (NaCl) concentration

- Mixing conditions (time and agitation)

2.7.2 Outputs (Measured Responses)

2.7.2.1 Turbidity (without oil)

Definition

Turbidity is a measure of the clarity or cloudiness of a solution, and it reflects the presence of dispersed particles**. [3,8,18]**

Interpretation

Low turbidity values indicate a clear and homogeneous solution, which means good stability of the formulation.

High turbidity values indicate poor homogeneity or the beginning of phase separation between components. [3,18]

2.7.2.2 Turbidity in the presence of oil

Definition

It is the measurement of turbidity after mixing the detergent with oil, used to evaluate the ability of the detergent to form an emulsion. [3,9,18]

Interpretation

An increase in turbidity after mixing indicates a good emulsification of oil, which means better cleaning efficiency.

Measurements were taken at 1, 3, and 5 minutes to follow the evolution of emulsification over time.

Stable values over time indicate a stable emulsion. [9,3,18]

2.7.2.3 Foam

properties Definition

It includes the measurement of foam height and its stability over time after shaking the solution. [7,8,28]

Interpretation

High foam height reflects a good ability of the detergent to produce foam, which is important for user acceptance.

Foam 6 s t a b i l i t y (half-life t i m e) i n d i c a t e s h o w s t a b l e t h e f o a m i s . High and stable foam is considered a sign of better quality.[28]

2.7.2.4 Conductivity

Definition

Conductivity is the ability of a solution to conduct electricity, reflecting the amount of dissolved ions. [10,11]

Interpretation

High conductivity values indicate a higher amount of salts and surfactants. Variations between formulations help to understand the effect of composition and concentration. [10,11,18]

2.7.2.5 Effect of temperature (Cloud Point / Stability)

Definition

It is the study of changes in the appearance of the solution when temperature decreases, especially the appearance of turbidity. [3,9,18]

Interpretation

The appearance of turbidity at a certain temperature indicates a decrease in stability. The lower the temperature at which turbidity appears, the better the stability of the formulation. [3,9,18]

Chapter 3

Materials and Methods

Introduction

This experimental work was carried out in the laboratory of Yahia Fares University of Medea. The objective of this study was to formulate a liquid dishwashing detergent and evaluate the effect of formulation components (SLES, LABSA, CAPB, CG and NaCl) on its physicochemical properties. Furthermore, two different formulations, namely an academic formulation and an industrial formulation, were prepared and compared in order to determine the most suitable composition and evaluate their performance.[30]

3. Synthesis of a dishwashing liquid

3.1 Materials and Products

3.1.1 Table 2. Materials and Equipment Used in the Experimental Studyfk

Device Name	Brand	Manufacturer
Magnetic Stirrer	IKA	IKA-Werke GmbH, Germany
pH Meter	EZ series	Generic manufacturer, china
Conductivity Meter	EZ series	Generic manufacturer, china
Turbidity meter	Hach	Hach Company, USA
Analytical Balance	OHAUS	OHAUS Corporation, USA
Thermometer	Testo	Testo SE & Co., Germany
Graduated cylinders (50 mL, 100 mL)	Pyrex	Corning Inc., USA
Electric mixer	IKA	IKA-Werke GmbH, Germany
Crystallizer	Pyrex	Corning Inc., USA
Beakers (100–500 mL)	Pyrex	Corning Inc., USA
Pipettes	Eppendorf	Eppendorf AG, Germany

3.1.2 Table 3. Chemical Products Used and Their Formulas

Product Name	Chemical Formula
SLES (Sodium Lauryl Ether Sulfate)	$C_{12}H_{25}SO_4Na$
LABSA (Linear Alkyl Benzene Sulfonic Acid)	$C_{18}H_{30}O_3S$
CAPB (Cocamidopropyl Betaine)	$C_{19}H_{38}N_2O_3$
NaCl (Sodium Chloride)	NaCl
CA(Citric Acid)	$C_6H_8O_7$
NaOH (Caustic soda)	NaOH
CG(Coco Glucoside)	$C_{16}H_{32}O_6$ (approx.)
SB(Sodium Benzoate)	$C_7H_5NaO_2$
Glycerin	$C_3H_8O_3$
Fragrance (Perfume)	Mixture
Colorant (Dye)	Mixture
Distilled Water	H_2O

3.2 Characteristics of the products used

- **Sulfonic acid:** Sulfonic acid is an anionic surfactant used in the formulation of liquid detergents. It has the general formula R–SO_3H, where R is an organic chain. After neutralization, it forms an active salt responsible for its cleaning and foaming power.
- **Caustic soda (NaOH):** Caustic soda is a strong base used to neutralize sulfonic acid and adjust the pH of the final product. It also contributes to improving detergent performance.[4]
- **Texapon (SLES):** Texapon is an anionic surfactant widely used in cleaning and hygiene products. It promotes foam formation and helps remove dirt.[16,8]
- **Sodium chloride (NaCl):** Sodium chloride is used as a thickening agent in liquid detergents. It allows for adjusting the viscosity of the final product.[4,6]
- **Cocamidopropyl Betaine (CAPB):** Cocamidopropyl betaine is a surfactant used in liquid detergents. It helps to improve foam and makes it more stable. It also makes the product less irritating and helps in cleaning.[11]

- **Citric acid (CA):** Citric acid is used to adjust the pH of the product. It helps to keep the pH in a suitable range. It also improves the stability of the solution.[6,9]
- **Coco glucoside (CG):** Coco glucoside is a mild surfactant. It is used for gentle cleaning and helps to improve the foam. It is also biodegradable and safe to use.[6,8]
- **Fragrance:** Fragrance is added in small quantities to enhance the product's scent and make it more pleasant to use.[4]
- **Colorant:** Colorant is incorporated to give the product an attractive appearance without affecting its chemical properties.[4]
- **Distilled Water:** Distilled water is the primary solvent in the formulation. It allows for the dissolution and homogenization of the various components.[6]

3.3 Procedure

In order to conduct this study, we used a mixed-type experimentation design with upper and lower constraints on the concentrations of each ingredient.

The use of specialized software facilitates the creation of the experiment plan.

Among these many programs, we have used STATISTICA and MODDE 6 for both the planning process and the interpretation of the results.

3.3.1 Classification of Experimental Formulations

The experimental work was divided into two distinct formulations:

Academic formulation: Formulated using SLES, LABSA, CAPB, and NaCl.

Industrial formulation: Formulated using SLES, CG, CAPB, and NaCl

Table 4. Concentration Levels of the Components Used in the Academic Formulation

Factor	Symbol	Low Level (-1)	High Level (+1)
SLES (70%)	**X1**	**12 %**	**18 %**
LABSA	**X2**	**3%**	**6%**
CAPB (35%)	**X3**	**2%**	**5%**
NaCl	**X4**	**0.2%**	**1%**

The other factors' concentrations are consistent with the suggested formula:

- Glycerin: 2.0 %

- Preservative: 0.5 %
- Fragrance: 0.3 %
- Water: q.s. to 100 %
- The pH is adjusted between 6.5 and 7.5 by adding NaOH

This results in a total of 8 effects in an random order.

Table 5. Experimental Design Matrix of the Academic Formulation

	SLES		LABSA		CAPB		NaCl	
Run	Real value	Coded value	Real value	Coded Value	Real value	Coded value	Real value	Coded value
01	12%	-1	3%	-1	2%	-1	0.2%	-1
02	18%	+1	3%	-1	2%	-1	1%	+1
03	18%	+1	3%	-1	2%	-1	1%	+1
04	18%	+1	3%	-1	2%	-1	1%	+1
05	18%	+1	6%	+1	2%	+1	1%	+1
06	12%	-1	6%	+1	2%	+1	1%	+1
07	12%	-1	6%	+1	2%	+1	1%	+1
08	12%	-1	6%	+1	2%	+1	1%	+1
09	18%	+1	6%	+1	2%	+1	0.2%	-1
10	12%	-1	3%	-1	5%	-1	1%	+1
11	12%	-1	3%	-1	5%	-1	1%	+1
12	12%	-1	3%	-1	5%	-1	1%	+1
13	18%	+1	3%	-1	5%	-1	0.2%	-1
14	12%	-1	6%	+1	5%	+1	0.2%	-1
15	18%	+1	6%	+1	5%	+1	1%	+1
16	18%	+1	6%	+1	5%	+1	1%	+1
17	18%	+1	6%	+1	5%	+1	1%	+1

3.3.3 Preparation of 500 g of Liquid Dishwashing Soap (Academic formulation)

1. Clean all glassware using distilled water before starting the experiment.

2. Weigh the required amounts of SLES, CAPB, LABSA, and NaCl, and keep them ready.

3. Heat the water used for dissolving SLES to a temperature between 30 and 35°C.

4. Dissolve SLES in the warm water under continuous stirring using an electric mixer for 45 minutes to 1 hour, while avoiding excessive foam formation.

5. Separately, dilute CAPB in water and mix well.

6. In another container, dilute LABSA in water.

7. Mix the diluted CAPB and LABSA solutions using a spatula, stirring in the same direction for about 15 minutes until a homogeneous mixture is obtained.

8. Gradually add this mixture to the SLES solution under continuous stirring for about 20 minutes until complete homogenization.

9. Leave the mixture to rest for about 10 minutes to reduce foam.

10. Prepare separate solutions of SB , NaCl, and NaOH by dissolving each in a small amount of water.

11. Add the SB solution to the main mixture and stir until well combined.

12. Measure the pH of the mixture.

13. Adjust the pH by adding NaOH drop by drop until it reaches between 6.5 and 7.

14. Add the NaCl solution gradually to adjust the viscosity, with continuous stirring.

15. Add colorant and fragrance, then mix gently.

16. Leave the final mixture to rest for a short time until the product becomes stable and ready for use.

Table 6. Concentration Levels of the Components Used in the Industrial Formulation

Factor	Symbol	Low Level (-1)	High Level (+1)
SLES (70%)	**X1**	**20%**	**25 %**
CAPB (35%)	**X2**	**2.5%**	**4%**

CG	**X3**	**2%**	**4%**
NaCl	**X4**	**0.3%**	**1%**

The other factors' concentrations are consistent with the suggested formula:

- Glycerin: 2.0 %
- Preservative: 0.5 %
- Fragrance: 0.3 %
- Water: q.s. to 100 %
- The pH is adjusted between 6.5 and 7.5 by adding citric acid

This results in a total of 8 effects in an Random order.

Table 7. Experimental Design Matrix of the Industrial Formulation

	SLES		**CG**		**CAPB**		**NaCl**	
Run	Real value	Coded value	Real Value	Coded Value	Real value	Coded value	Real value	Coded value
01	20%	-1	2%	-1	2.5%	-1	0.3%	-1
02	25%	+1	2%	-1	4%	-1	1%	+1
03	25%	+1	2%	-1	4%	-1	1%	+1
04	25%	+1	2%	-1	4%	-1	1%	+1
05	20%	-1	2%	-1	2.5%	+1	1%	+1
06	20%	-1	2%	-1	2.5%	+1	1%	+1
07	20%	-1	2%	-1	2.5%	+1	1%	+1
08	25%	+1	2%	-1	2.5%	+1	0.3%	-1
09	20%	-1	4%	+1	2.5%	-1	1%	+1
10	20%	-1	4%	+1	2.5%	-1	1%	+1
11	20%	-1	4%	+1	2.5%	-1	1%	+1

12	25%	+1	4%	+1	2.5%	-1	0.3%	-1
13	20%	-1	4%	+1	4%	+1	0.3%	-1
14	25%	+1	4%	+1	4%	+1	1%	+1
15	25%	+1	4%	+1	4%	+1	1%	+1
16	25%	+1	4%	+1	4%	+1	1%	+1

3.3.5 Preparation of 500 g of Liquid Dishwashing Soap (Industrial formulation)

1. Clean all glassware using distilled water before starting the experiment.
2. Weigh the required amounts of SLES, CAPB, CG, and NaCl, and keep them ready.
3. Heat the water used for dissolving SLES to a temperature between 30 and 35°C.
4. Dissolve SLES in the warm water under continuous stirring using an electric mixer for 45 minutes to 1 hour, while avoiding excessive foam formation.
5. Separately, dilute CAPB in water and mix well.
6. In another container, dilute CG in water.
7. Mix the CAPB and CG solutions using a spatula, stirring in the same direction for about 15 minutes until a homogeneous mixture is obtained.
8. Gradually add this mixture to the SLES solution under continuous stirring for about 20 minutes until complete homogenization.
9. Leave the mixture to rest for about 10 minutes to reduce foam.
10. Prepare separate solutions of sodium benzoate, NaCl, and citric acid by dissolving each in a small amount of water.
11. Add the sodium benzoate solution to the main mixture and stir until well combined.
12. Measure the pH of the mixture.
13. Adjust the pH by adding citric acid gradually until it reaches a value between 6.5 and 7.5.
14. Add the NaCl solution gradually to adjust the viscosity, with continuous stirring.
15. Add colorant and fragrance, then mix gently.

Leave the final mixture to rest for a short time until the product becomes stable and ready for use.

3.4 Experimental Methods for Liquid Dishwashing Soap Characterization

3.4.1 Turbidity Measurement

3.4.1.1 Direct Measurement

1. A volume of 10 mL of the liquid soap was taken and placed directly into the turbidity meter. The turbidity value was measured and recorded for each sample.

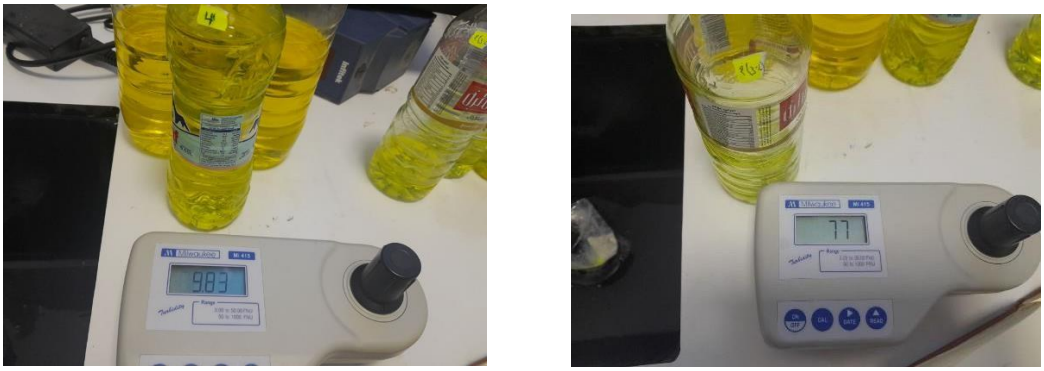


Figure 3.1. Turbidity Measurement

3.4.1.2 Emulsification Test

1. A diluted solution was prepared by taking 1 mL of liquid soap and diluting it in 250 mL of **tap water**. Then, 2 mL of oil was added to 8 mL of the diluted solution. The mixture was shaken manually (180° inversion) for about 30 times.

The turbidity was measured after 1 minute, 3 minutes, and 5 minutes, and the values were recorded.



Figure 3.2. Turbidity Measurement in the Presence of Oil

3.4.2 Cloud Point Test

- A quantity of the previously prepared liquid dishwashing soap was placed in a beaker. The beaker was covered with an insulating material to maintain the temperature.
- It was then placed in a glass bath containing water and ice to decrease the temperature.
- During cooling, the solution was observed, and the time at which turbidity appeared was noted. The temperature was measured at each stage.
- The same procedure was repeated for all samples, and the results were recorded.

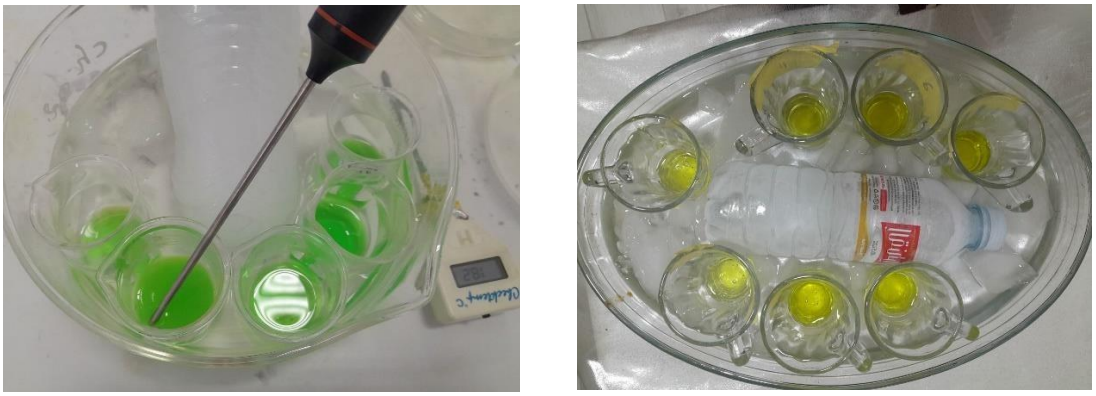


Figure 3.3. Cloud Point Test

3.4.3 Foam Stability Test

- A volume of 5 mL of liquid dishwashing detergent was transferred into a 100 mL graduated cylinder and diluted with distilled water to a final volume of 20 mL
- The cylinder was closed and shaken well until foam was formed.
- The foam height was measured immediately using a ruler.
- The time required for the foam to decrease to half of its initial height was also recorded.

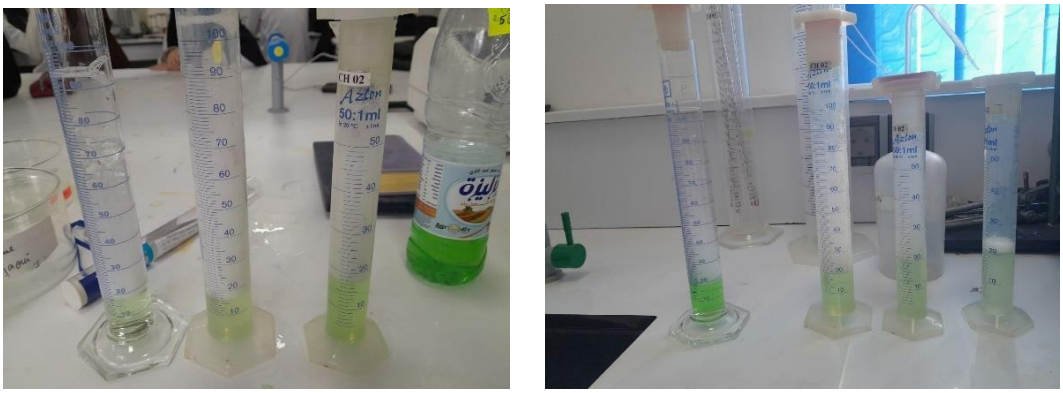


Figure 3.4. Foam Stability Test

3.4.4. Acidity Teste

The pH of each formulation was measured using a pH meter to ensure compatibility with skin and product stability.



Figure 3.5. Acidity Teste

3.4.5. Conductivity Measurement:

Conductivity was measured using a conductivity meter to evaluate the ionic content of the solution.



Figure 3.6 . Conductivity Measure

3.5 Introduction

During the preparation of the liquid detergent formulations, several practical observations were made that contributed to a better understanding of the formulation process. It was found that the mixing conditions had a significant influence on the quality and stability of the final product [6]. When the stirring speed was too high, excessive foam was generated, making the incorporation of ingredients more difficult and affecting the homogeneity of the mixture. In contrast, moderate stirring at a constant direction facilitated the dispersion of the components and resulted in a more uniform formulation [4]. Furthermore, allowing sufficient time for each ingredient to dissolve before the addition of the next component improved the stability and consistency of the detergent [6]. The order of addition of raw materials was also found to be important, as it affected properties such as viscosity, turbidity, and overall appearance [8]. These observations highlight the importance of controlling the preparation conditions in addition to optimizing the formulation composition. Therefore, both the formulation factors and the processing parameters must be carefully considered to obtain a stable and high-quality liquid detergent [4,6].

3.6 Table8. Experimental Results of the Academic Formulation

	Sles	**Labs**	**Capb**	**NaCl**	**Ph**	**condi**	**terbi**	**p.m**	**P.t**	**p.e1**	**p.e3**	**p.e5**
01	-1	-1	-1	-1	7.17	18.3	10.88	7min	1.0	151	51.0	28.82
02	+1	-1	-1	+1	7.10	41.1	663.0	23min	5.6	132	58.0	51.0
03	+1	-1	-1	+1	6.89	46.0	102.0	20min	5.4	297	169.0	152.0
04	+1	-1	-1	+1	7.10	55.1	1000.0	22min	6.3	217	71.0	52.0
05	+1	-1	+1	+1	6.89	84.9	205.0	24min	7.0	214	115.0	103.0
06	-1	+1	+1	+1	6.5	60.0	96.0	32min	4.9	966	236.0	181.0
07	-1	+1	+1	+1	6.5	60.4	199.0	33min	5.1	622	324.0	260.0
08	-1	+1	+1	+1	6.5	70.7	1000.0	30min	3.8	1000	380.0	233.0

09	+1	+1	+1	-1	6.60	24.8	258.0	32min	3.2	118	89.0	15.0
10	-1	-1	-1	+1	7.17	44.3	26.57	14min	5.6	365	78.0	63.0
11	-1	-1	-1	+1	7.17	61.9	17.65	12min	6.0	134	45.94	44.72
12	-1	-1	-1	+1	7.17	75.1	30.84	15min	4.6	101	37.92	36.52
13	+1	-1	-1	-1	7.00	28.4	15.69	36min	5.2	583	110.0	85.5
14	-1	+1	+1	-1	6.83	18.5	679.0	32min	4.5	538	166.0	113.0
15	+1	+1	+1	+1	6.80	40.0	684.0	37min	4.1	617	58.0	59.0
16	+1	+1	+1	+1	6.80	50.2	120.0	25min	5.0	170	87.0	62.0
17	+1	+1	+1	+1	6.80	65.8	1000.0	23min	3.2	90	67.0	48.0

3.7 Correlation Between Formulation Components and Physicochemical Properties

The correlation matrices express in figure 1, obtained from the two independent experimental studies were identical, demonstrating excellent reproducibility of the formulation design and analytical measurements. The studied formulations consisted of mixtures of Sodium Lauryl Ether Sulfate (SLES), Cocamidopropyl Betaine (CAPB), Linear Alkylbenzene Sulfonic Acid (LABSA), sodium chloride (NaCl), and sodium hydroxide (NaOH). These ingredients represent a typical surfactant system used in liquid detergents and household cleaning products. The correlation analysis provides valuable insight into how each component influences the physicochemical properties and performance characteristics of the formulations.



Figure 4.1: correlation matrix mapping for the first and second case.

The strongest correlations observed were associated with LABSA and NaCl, suggesting that these ingredients play dominant roles in controlling the acidity, foaming behavior, conductivity, and emulsion characteristics of the formulations.

3.7.1 Influence of Formulation Components on pH

Among all variables, pH exhibited the strongest negative correlation with LABSA (r = –0.84), indicating that increasing LABSA concentration substantially decreases the pH of the formulations. This behavior is expected because LABSA is a strong anionic surfactant precursor containing a sulfonic acid group. Before neutralization, LABSA contributes acidic protons to the solution, thereby lowering pH. Conversely, CAPB showed a moderate positive correlation with pH (r = 0.34). CAPB is an amphoteric surfactant containing both positive and negative functional groups. Its zwitterionic nature provides buffering behavior and reduces the acidity generated by LABSA-rich formulations. Similar synergistic interactions between CAPB and anionic surfactants have been reported in detergent formulations where CAPB contributes to improved formulation mildness and pH stabilization.[20]

The weak correlation observed between pH and NaOH (r = –0.15) appears counterintuitive because NaOH is a strong base. However, this likely reflects the experimental design where NaOH was used primarily to neutralize increasing amounts of LABSA rather than independently raising alkalinity. Therefore, formulations with higher LABSA concentrations may also contain higher NaOH concentrations, producing an apparent negative relationship.

SLES and NaCl showed negligible effects on pH, with correlation coefficients of 0.02 and 0.10, respectively. This observation agrees with their chemical nature because SLES is generally supplied in a neutralized form and NaCl is a neutral electrolyte. Overall, pH was primarily governed by the balance between acidic LABSA and amphoteric CAPB, with LABSA acting as the dominant controlling factor.

3.7.2 Influence on Electrical Conductivity:

Conductivity exhibited its strongest positive correlation with NaCl (r = 0.55), confirming that electrolyte concentration is the primary determinant of ionic conductivity in the studied systems. Sodium chloride dissociates completely in water according to:

$$NaCl \rightarrow Na^{+} + Cl^{-}$$

The resulting increase in ionic concentration enhances charge transport through the solution and consequently increases conductivity. Similar conductivity increases in surfactant-electrolyte systems have been widely reported in studies involving ionic surfactants and mixed micellar solutions.[21]

LABSA exhibited a weaker positive correlation (r = 0.16). Upon neutralization, LABSA forms sulfonate ions that contribute additional mobile charge carriers to the aqueous phase. Thus, increasing LABSA concentration contributes modestly to conductivity. The weak negative correlations observed for SLES (r = –0.08) and CAPB (r = –0.10) may be explained by micellization phenomena. As surfactant concentration increases, a portion of the ions become associated with micellar aggregates, reducing the number of freely mobile ions available for electrical conduction. This effect has been described extensively in conductivity studies of surfactant systems. The small positive contribution of NaOH (r = 0.06) suggests that hydroxide ions contribute to conductivity but to a much lesser extent than NaCl.

3.7.3 Influence on Foaming Capacity (p_ moussant)

Foaming capacity exhibited the strongest positive correlation with LABSA (r = 0.71), indicating that LABSA is the primary contributor to foam generation within the studied formulations. LABSA-derived surfactants possess excellent surface activity and rapidly adsorb at the air-water interface, reducing surface tension and facilitating

foam formation. Previous studies have reported LABSA as one of the most effective foaming anionic surfactants used in commercial formulations.[22]

SLES also displayed a substantial positive correlation (r = 0.43). SLES is widely used as a primary foaming surfactant because of its ability to generate large foam volumes while maintaining good detergency [25]. CAPB exhibited a weaker but positive effect (r = 0.19). CAPB is generally recognized as a foam booster rather than a primary foam generator. It stabilizes foam films and reduces bubble coalescence, resulting in improved foam persistence [28]

NaOH showed a moderate positive relationship (r = 0.27), likely because neutralization of LABSA increases the concentration of active anionic surfactants capable of participating in interfacial adsorption. The weak negative effect of NaCl (r = –0.19) may be attributed to salt-induced foam destabilization. Excessive electrolyte concentrations accelerate liquid drainage from foam lamellae and promote bubble collapse.[29]

3.7.4 Influence on Cloud Point (p_ trouble)

The parameter p_ trouble appears related to clouding or opacity formation. The strongest positive correlation was observed with NaCl (r = 0.57), indicating that salt concentration is the primary factor controlling cloudiness. This behavior is consistent with the well-known "salting-out" effect. Increasing NaCl concentration reduces surfactant hydration and solubility, promoting aggregation and phase separation. Several studies have shown that NaCl decreases cloud point temperatures and increases cloud formation in surfactant systems.

SLES exhibited a weak positive effect (r = 0.21), suggesting that higher surfactant concentrations facilitate the formation of larger aggregates capable of scattering light. LABSA displayed a slight negative correlation (r = –0.16), indicating that LABSA-rich systems may remain relatively homogeneous under the studied conditions. Therefore, clouding behavior appears to be controlled predominantly by electrolyte-induced changes in surfactant aggregation.

3.7.5 Influence on Emulsion Stability

3.7.5.1 Emulsion Stability After 1 minute (p_emulsion1)

The strongest positive correlation was observed with LABSA (r = 0.40). LABSA is known to reduce oil-water interfacial tension and facilitate the formation of stable emulsions through adsorption at the interface. The aromatic hydrophobic chain and sulfonate head group provide effective stabilization mechanisms.

Negative correlations were observed with NaOH (r = –0.45), SLES (r = –0.37), NaCl (r = –0.21), and CAPB (r = –0.15). High ionic strength and elevated alkalinity can compress electrical double layers surrounding dispersed droplets, reducing electrostatic stabilization and promoting coalescence[21,22] .

3.7.5.2 Emulsion Stability After 3 minute (p_emulsion2)

LABSA again showed the strongest positive influence (r = 0.47), confirming its importance as the primary emulsifying component. The negative effects of CAPB (r = –0.44), SLES (r = –0.38), and NaOH (r = –0.36) suggest that excessive concentrations of these ingredients interfere with the optimal interfacial film required for emulsion stabilization.

3.7.5.3 Emulsion Stability After 5 minute (p_emulsion3)

A similar trend was observed:

1. LABSA: + 0.39
2. SLES: – 0.36
3. CAPB: – 0.40
4. NaOH: – 0.44

The consistency across all three emulsion parameters strongly supports the hypothesis that LABSA is the principal emulsifying agent in the studied formulations.

3.8 Table 9. Experimental Results of the Industrial Formulation

	Sles	**CG**	**Capb**	**NaCl**	**Ph**	**Condi**	**terbi**	**p.m**	**P.t**	**P .e1**	**P .e3**	**p.e5**
01	-1	-1	-1	-1	6.92	40.1	70.0	55min	3.6	89.0	72.0	59.00

02	+1	-1	-1	+1	7.00	47.6	626.0	40min	4.00	46.65	19.59	18.17
03	+1	-1	-1	+1	7.00	57.3	328.0	35min	4.4	59.0	50.0	45.33
04	+1	-1	-1	+1	7.00	74.2	111.0	25min	5.1	62.0	36.20	32.76
05	-1	+1	+1	+1	6.59	44.8	88.0	30min	6.2	73.0	52.0	35.43
06	-1	+1	+1	+1	6.59	59.5	74.0	23min	4.2	108.0	57.0	34.49
07	-1	+1	+1	+1	6.59	65.8	154.0	26min	4.9	161.0	126.0	126.0
08	+1	+1	+1	-1	7.13	34.4	12.4	47min	6.2	70.0	37.49	26.09
09	-1	-1	-1	+1	6.62	32.4	621.0	43min	3.2	74.0	62.0	61.0
10	-1	-1	-1	+1	6.62	55.4	1000.0	40min	4.5	62.0	33.32	21.94
11	-1	-1	-1	+1	6.62	53.1	1000.0	38min	5.3	68.0	35.03	29.27
12	+1	-1	-1	-1	7.10	30.6	298.0	45min	5.4	78.0	38.33	32.96
13	-1	+1	+1	-1	6.70	29.6	56.0	39min	6.7	65.0	62.0	64.0
14	+1	+1	+1	+1	6.60	70.7	96.0	30min	4.4	98.0	55.0	36.25
15	+1	+1	+1	+1	6.60	52.2	256.0	35min	4.1	67.0	63.0	56.0
16	+1	+1	+1	+1	6.60	48.6	117.0	43min	3.00	212.0	63.0	63.0

3.9 Correlation Between Formulation Components and Physicochemical Properties

The correlation matrices expressed in Figure 4.2 and Figure 4.3, obtained from two independent experimental sets studies, reveal the distinct behaviors of two different surfactant formulation strategies designed for liquid detergents and household cleaning products. Rather than being identical, the two matrices represent distinct chemical systems:

First Experimental System (Figure **4.2**): Consists of Sodium Lauryl Ether Sulfate (SLES), Cocamidopropyl Betaine (CAPB), Linear Alkylbenzene Sulfonic Acid (LABSA), sodium chloride (NaCl), and sodium hydroxide (NaOH).

Second Experimental System (Figure 4.3): Substitutes the strong acid/base neutralization pair with alternative conditioning agents, tracking SLES, CAPB, NaCl, Coconut diethanolamine (coco), and Citric Acid.

The correlation analysis provides valuable insight into how each component uniquely influences the physicochemical properties and performance characteristics across both formulation sets.

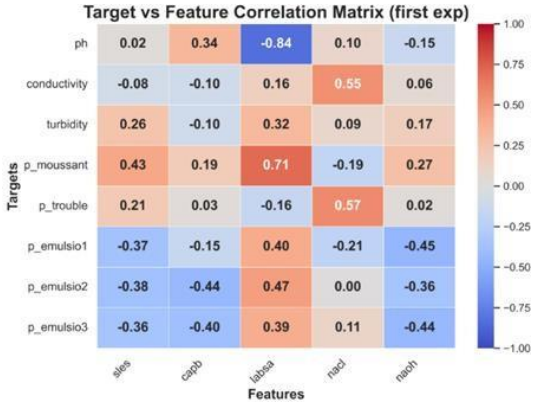


Figure 4.2: Correlation matrix for first experiment sets

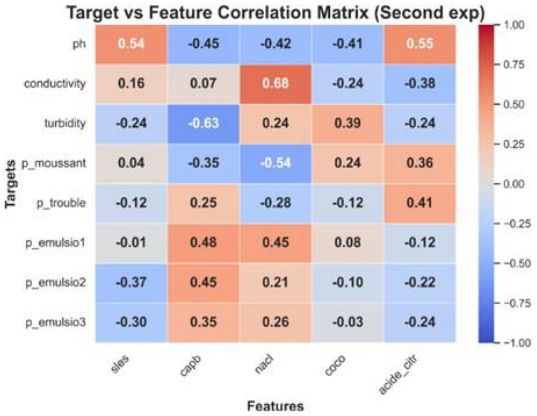


Figure 4.3*:* Correlation matrix for second experiment sets

3.9.1 Influence of Formulation Components on pH

The mechanisms governing pH regulation differ fundamentally between the two experimental series due to the shifting acidic components.

First Experiment (LABSA/NaOH System): Among all variables, pH exhibited the strongest negative correlation with LABSA (r = -0.84), indicating that increasing LABSA concentration substantially decreases the pH of the formulations. This behavior is expected because LABSA is a strong anionic surfactant precursor containing a sulfonic acid group which, before neutralization, contributes acidic protons to the solution. Conversely, CAPB showed a moderate positive correlation with pH (r = 0.34).

Its zwitterionic nature provides buffering behavior and reduces the acidity generated by LABSA-rich formulations. Similar synergistic interactions between CAPB and anionic surfactants contribute to pH stabilization. The weak correlation observed between pH and NaOH (r = -0.15) likely reflects the experimental design where NaOH was used primarily to neutralize increasing amounts of LABSA rather than independently raising alkalinity. SLES and NaCl showed negligible effects on pH, with correlation coefficients of 0.02 and 0.10, respectively, due to their neutral chemical nature.

Second Experiment (Citric Acid System): In this system, pH dynamics alter due to the organic acid framework. Citric acid exhibits a strong positive correlation (r = 0.55) within the matrix space, while SLES strongly correlates with higher pH values (r = 0.54). Conversely, CAPB (r = -0.45), NaCl (r = -0.42), and coco (r = -0.41) display moderate-to-strong negative correlations, indicating a radically different buffering equilibrium compared to the sulfonic acid system.

3.9.2 Influence on Electrical Conductivity:

Ionic concentration remains a primary driver of electrical conductivity, though the dominant ionic species shift between the two datasets.

First Experiment: Conductivity exhibited its strongest positive correlation with NaCl (r = 0.55), confirming that electrolyte concentration is the primary determinant of ionic conductivity in this system. Sodium chloride dissociates completely in water, enhancing charge transport. LABSA exhibited a weaker positive correlation (r = 0.16), as its neutralized sulfonate ions contribute additional mobile charge carriers. The weak negative correlations observed for SLES (r = -0.08) and CAPB (r = -0.10) are explained by micellization phenomena, where ions become associated with micellar aggregates, slightly reducing the number of freely mobile ions.

Second Experiment: The conductivity dynamics shift, with NaCl becoming an exceptionally dominant driver (r = 0.68). SLES maintains a mild positive correlation (r = 0.16), while coco (r = -0.24) and **Citric acid** (r = -0.38) display notable negative correlations, suggesting that the presence of these organic additives potentially alters micellar assembly or suppresses overall ionic mobility.

3.9.3 Influence on Cloud Point (p_ moussant):

Foam generation and boosting behaviors depend heavily on which primary surfactant dominates the formulation matrix.

First Experiment: Foaming capacity exhibited the strongest positive correlation with LABSA (r = 0.71), indicating that LABSA9[0 is the primary contributor to foam generation within these formulations due to its high surface activity at the air-water interface. SLES also displayed a substantial positive correlation (r = 0.43), as it is widely used to generate large foam volumes, SLES is widely used as a primary foaming surfactant because of its ability to generate large foam volumes while maintaining good detergency [25] .CAPB exhibited a weaker but positive effect (r = 0.19), consistent with its role as a foam booster that stabilizes foam films rather than acting as a primary generator. NaOH showed a moderate positive relationship (r = 0.27) , while NaCl showed a weak negative effect (r = -0.19) likely due to salt-induced foam destabilization. Excessive electrolyte concentrations accelerate liquid drainage from foam lamellae and promote bubble collapse[29].

Second Experiment: With LABSA removed, the foaming dynamics alter completely. SLES shows nearly no linear correlation with foaming (r = 0.04), while CAPB drops into a negative correlation (r = -0.35). Crucially, NaCl exerts a heavy penalty on foam capacity (r = -0.54). Instead, **Citric acid** (r = 0.36) and the foam-stabilizing co-surfactant coco (r = 0.24) emerge as the primary positive drivers of the foaming properties in this organic acid blend.

3.9.4 Influence on Clouding Behavior and Turbidity:

The parameters p_ trouble and turbidity map aggregate formation and solution clarity across the different formulation spaces.

First Experiment: The parameter p_ trouble (clouding) showed its strongest positive correlation with NaCl (r = 0.57), indicating that salt concentration is the primary factor controlling cloudiness. This is consistent with the "salting-out" effect where NaCl reduces surfactant hydration, promoting aggregation. SLES exhibited a weak positive effect (r = 0.21) , while LABSA displayed a slight negative correlation (r = -0.16), indicating that LABSA-rich systems remain relatively homogeneous under these conditions.

Second Experiment: In this system, turbidity is strongly reduced by CAPB (r = -0.63), revealing that the amphoteric surfactant acts as an effective hydro trope or clarifying agent in this matrix. NaCl maintains its positive correlation with turbidity (r = 0.39), verifying that salt consistently promotes aggregate growth across both experiments. For the p. trouble metric, **Citric acid** (r = 0.41) and CAPB (r = 0.25) correlate positively, highlighting how organic components shift the aggregation balance.

3.9.5 Influence on Emulsion Stability

Evaluating emulsion stability across parameters 1, 2, and 3 reveals contrasting stabilization mechanisms depending on the primary surfactant backbone.

3.9.5.1 Emulsion Stability After 1 minute (p_emulsio1)

First Experiment: The strongest positive correlation was observed with LABSA (r = 0.40), which reduces oil-water interfacial tension through its aromatic hydrophobic chain and sulfonate head group. Negative correlations were observed with NaOH (r = -0.45), SLES (r = -0.37), NaCl (r = -0.21), and CAPB (r = -0.15), where high ionic strength and alkalinity compress electrical double layers and promote droplet coalescence. reducing electrostatic stabilization and promoting coalescence[22,21].

Second Experiment: In the absence of LABSA, the emulsification burden shifts. CAPB (r = 0.48) and NaCl (r = 0.45) display strong positive correlations, stabilizing the emulsion phase. SLES (r = -0.01) showing zero impact, and coco (r = 0.08) showing a slight positive impact.

3.9.5.2 Emulsion Stability After 3 minute (p_emulsion2)

First Experiment: LABSA again showed the strongest positive influence (r = 0.47), while negative effects were sustained by CAPB (r = -0.44), SLES (r = -0.38), and NaOH (r = -0.36).

Second Experiment: CAPB maintains its strong positive correlation (r = 0.45), followed closely by NaCl (r = 0.21). SLES negatively correlates with stability (r = -0.37), and **Citric acid** exhibits a negative effect (r = -0.22).

3.9.5.3 Emulsion Stability After 5 minute (p_emulsio3)

First Experiment: The identical trend persists: LABSA (+0.39), SLES (-0.36), CAPB (-0.40), and NaOH (-0.44). This consistency strongly supports the hypothesis that LABSA is the principal emulsifying agent in the first system.

Second Experiment: CAPB remains the primary stabilizer (r = 0.35), supported by NaCl (r = 0.26). SLES (-0.30), coco (-0.03), and (-0.24) continue to demonstrate negative relationships with emulsion persistence.

GENERAL CONCLUSION

GENERAL CONCLUSION

This work focused on the formulation and characterization of liquid dishwashing detergents using two different approaches: an academic formulation and an industrial formulation. An experimental design methodology was applied to investigate the influence of the main formulation factors on the physicochemical properties of the final product, allowing a better understanding of the role of each component in improving detergent performance. Several formulations were prepared using different proportions of surfactants and additives, and their properties were evaluated through pH, conductivity, turbidity, foam stability, and emulsification measurements.[1,2,4,6]

The obtained results demonstrated that the formulation composition had a significant impact on the characteristics of the liquid dishwashing detergents. Surfactants played a key role in foam generation, emulsification efficiency, and grease removal performance, while other ingredients contributed to the adjustment of the physicochemical properties of the product. In addition, the preparation conditions, including the mixing procedure and the order of ingredient addition, were found to influence the homogeneity and stability of the formulations.[3,4,6,8]

Furthermore, the comparison between the academic and industrial formulations highlighted differences in their performance and physicochemical behavior, making it possible to evaluate the effectiveness of each formulation and identify the most suitable composition. Overall, this study confirmed that the appropriate selection of raw materials, combined with the application of experimental design techniques, is an effective approach for developing stable and efficient liquid dishwashing detergents with satisfactory cleaning performance and desirable physicochemical properties.[30,8,4]

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ANNEXES

In [30]:

```
solution = np.array([1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17])

sles = np.array([60,90,90,90,90,60,60,60,90,60,60,60,90,60,90,90,90])

capb = np.array([10,10,10,10,10,10,10,10,10,25,25,25,25,25,25,25,25])

labsa = np.array([15,15,15,15,30,30,30,30,30,15,15,15,15,30,30,30,30])

nacl =
np.array([1.0,5.0,10.0,7.5,15.0,2.5,2.5,3.75,1.0,2.5,2.5,3.75,1.0,1.0,2.5,2.5,3.75])

naoh =

np.array([1.5,2.5,2.5,2.5,2.5,2.0,2.0,2.0,4.0,2.5,2.5,2.5,1.5,2.0

,3.0,3.0,3.0]) ph =

np.array([7.17,7.10,6.89,7.10,6.89,6.50,6.50,6.50,6.60,
       7.17,7.17,7.17,7.00,6.83,6.80,6.80,6.80])

conductivity = np.array([18.3,41.1,46.0,55.1,84.9,60.0,60.4,70.7,
             24.8,44.3,61.9,75.1,28.4,18.5,np.nan,np.nan,np.nan])

                      turbidity =
np.array([10.88,663.0,102.0,1000.0,205.0,96.0,199.0,1000.0,
          258.0,26.57,17.65,30.84,15.69,679.0,684.0,120.0,1000.0])

p_moussant = np.array([
   7,23,20,22,24,32,33,
   30,32,14,12,15,36,36,
   np.nan,np.nan,np.nan
])

p_trouble = np.array([1.0,5.6,5.4,6.3,7.0,4.9,5.1,3.8,3.2,
                5.6,6.0,4.6,5.2,4.5,4.1,5.0,3.2])

p_emulsio1 = np.array([151,132,297,217,214,966,622,1000,118,
                365,134,101,583,538,617,170,90])

p_emulsio2 = np.array([51.0,58.0,169.0,71.0,115.0,236.0,324.0,380.0,
                89.0,78.0,45.94,37.92,110.0,166.0,58.0,87.0,67.0])

p_emulsio3 = np.array([28.82,51.0,152.0,52.0,103.0,181.0,260.0,233.0,
                15.0,63.0,44.72,36.52,85.5,113.0,59.0,62.0,48.0])

# Create
DataFrame df =
pd.DataFrame({
   'solution':
   solution, 'sles':
   sles,
   'capb':
   capb,
   'labsa':
   labsa,
   'nacl':
   nacl,
   'naoh': naoh,
   'ph': ph,
   'conductivity':
   conductivity, 'turbidity':
   turbidity, 'p_moussant':
```

```
    p_moussant, 'p_trouble':
    p_trouble, 'p_emulsio1':
    p_emulsio1, 'p_emulsio2':
    p_emulsio2, 'p_emulsio3':
    p_emulsio3
})
```

```
print(df.head())
```

```
   solution  sles  capb  labsa  nacl  naoh ph  conductivity  turbidity  \
0         1    60    10     15   1.0   1.5  7.17          18.3      10.88
1         2    90    10     15   5.0   2.5  7.10          41.1     663.00
2         3    90    10     15  10.0   2.5  6.89          46.0     102.00
3         4    90    10     15   7.5   2.5  7.10          55.1    1000.00
4         5    90    10     30  15.0   2.5  6.89          84.9     205.00

   p_moussant  p_trouble  p_emulsio1  p_emulsio2  p_emulsio3
0         7.0        1.0         151        51.0       28.82
1        23.0        5.6         132        58.0       51.00
2        20.0        5.4         297       169.0      152.00
3        22.0        6.3         217        71.0       52.00
4        24.0        7.0         214       115.0      103.00
```

In [29]:

```
features = ['sles','capb','labsa','nacl','naoh','ph']
targets = ['conductivity','turbidity','p_moussant','p_trouble','p_emulsio1','p_emulsio2','p_emulsio3']

sns.set(style="whitegrid")

# Loop through features and targets
for feature in features:
    for target in targets:

        plt.figure(figsize=(6, 5))

        # Scatter + regression line
        sns.regplot(
            data=df,
            x=feature,
            y=target,
            scatter_kws={'alpha': 0.6},
            line_kws={'color': 'red'}
        )

        # Calculate correlation coefficient
        # Drop NaNs to avoid errors
        valid_idx = df[[feature, target]].dropna()
        corr_coef = np.corrcoef(valid_idx[feature], valid_idx[target])[0,1]

        # Add correlation coefficient to figure
        plt.text(
            0.05, 0.95,
            f'r = {corr_coef:.2f}',
            transform=plt.gca().transAxes,
            fontsize=10,
            verticalalignment='top',
            bbox=dict(boxstyle="round,pad=0.3", facecolor='white', alpha=0.5)
        )

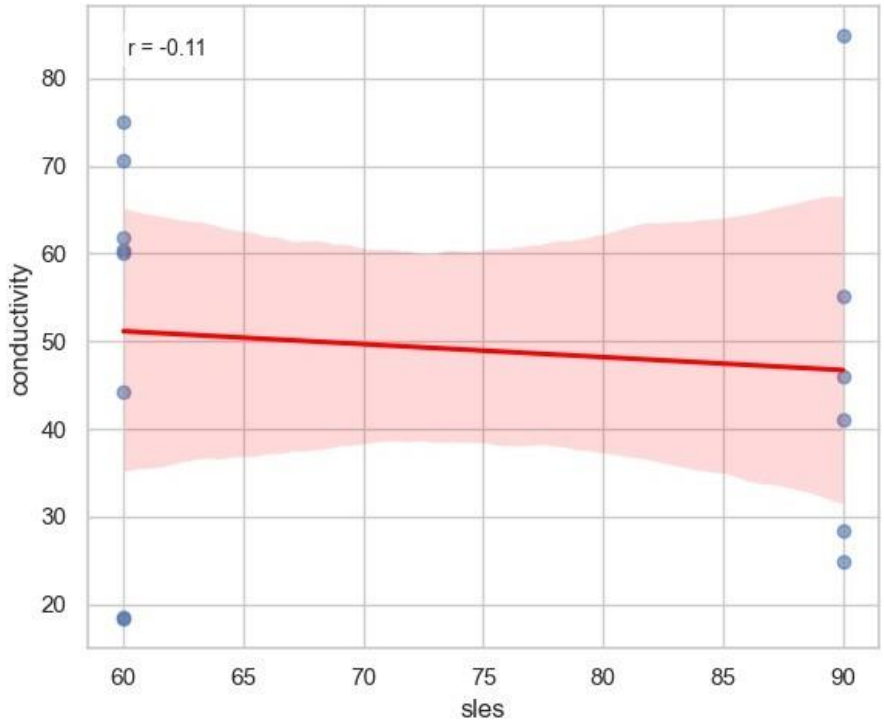
        plt.xlabel(feature)
        plt.ylabel(target)
        plt.tight_layout()

        # File names per feature-target pair
        filename_base = f"Fig_{feature}_vs_{target}"

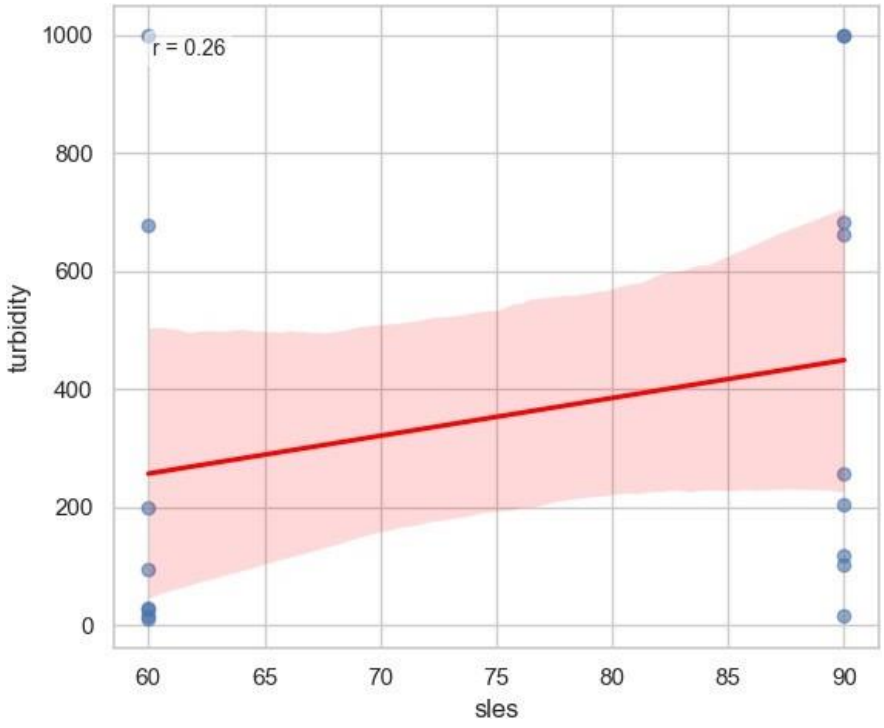
        # Save figures
        plt.savefig(f"{filename_base}.tif", format="tiff", dpi=800, bbox_inches="tight")
        plt.savefig(f"{filename_base}.eps", format="eps", bbox_inches="tight")

        plt.show()
        plt.close()
```

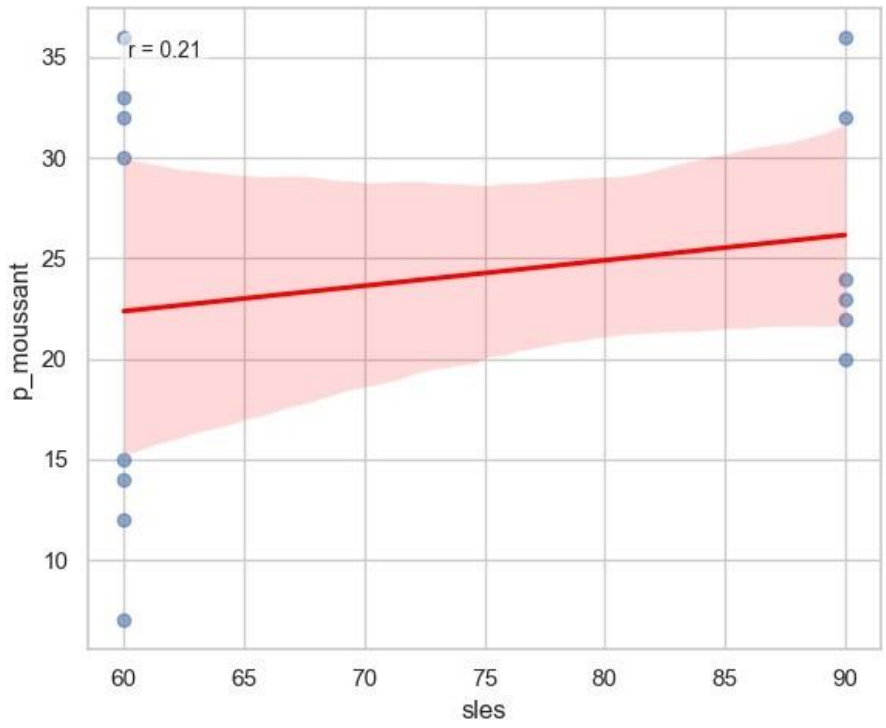
```
The PostScript backend does not support transparency; partially transparent artists will be rendered opaque.
```



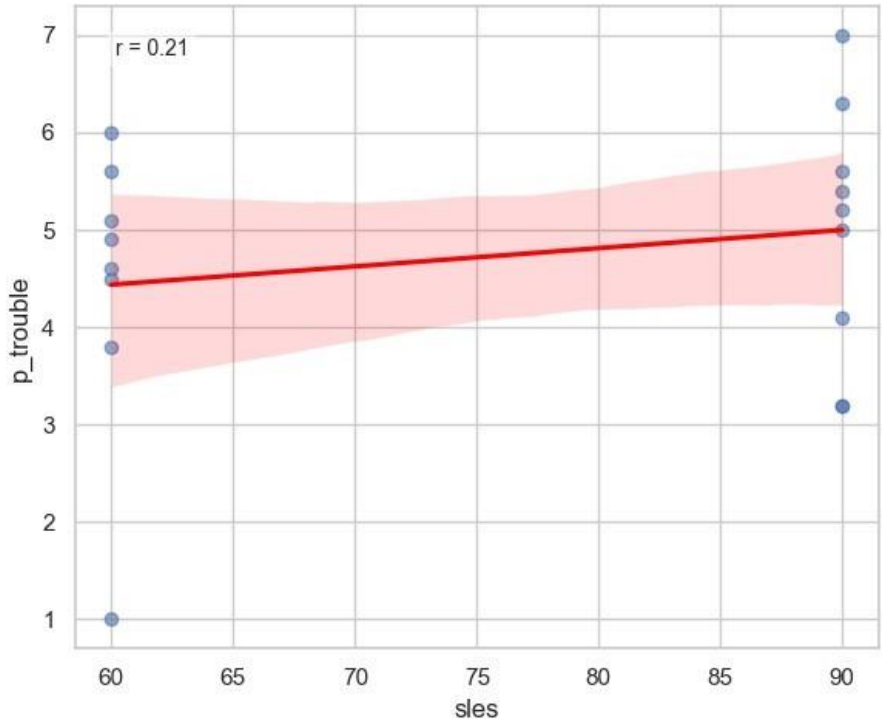

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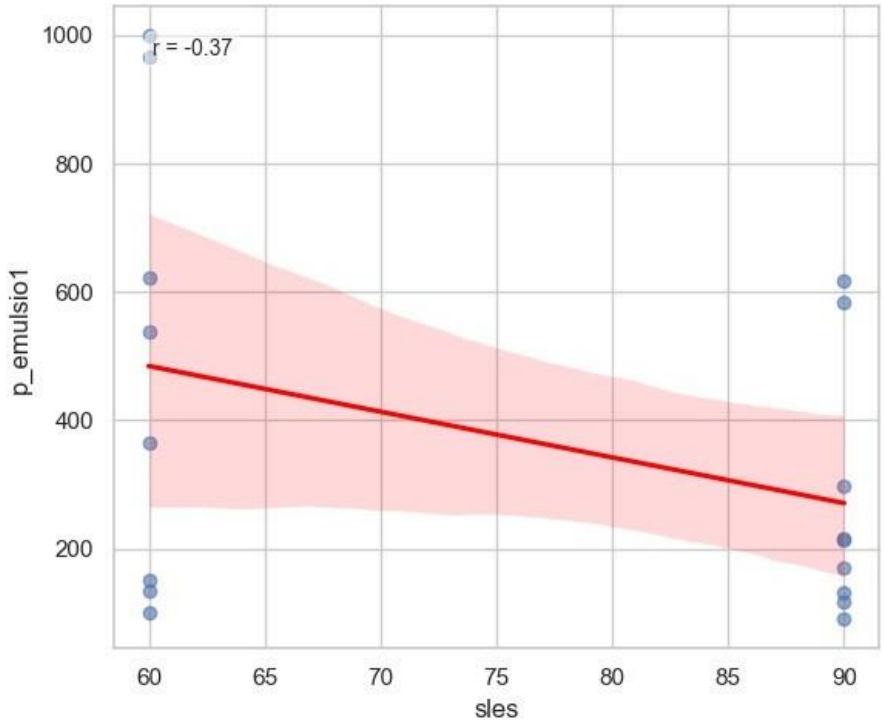

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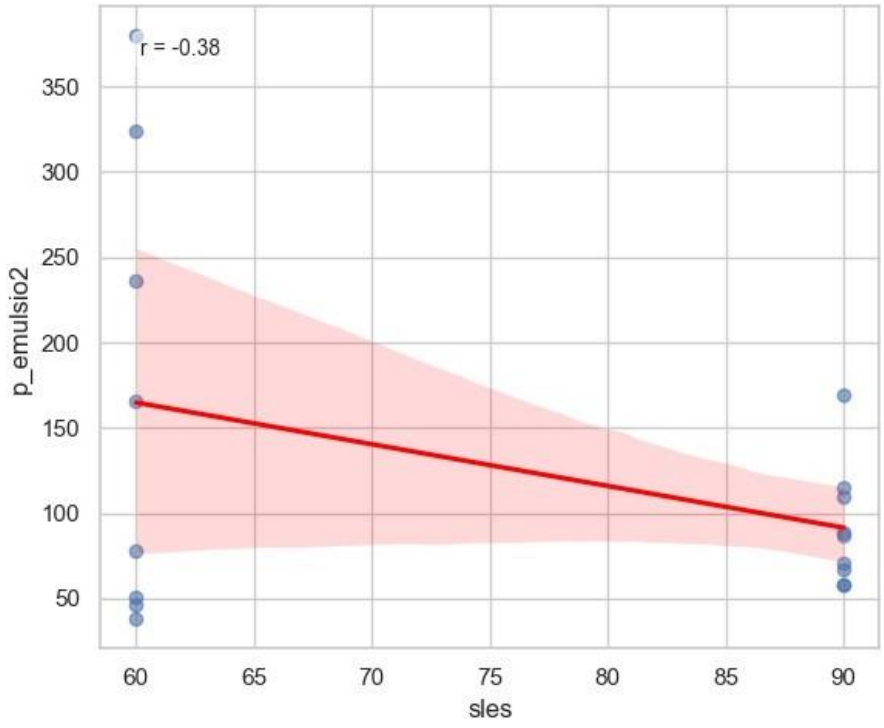

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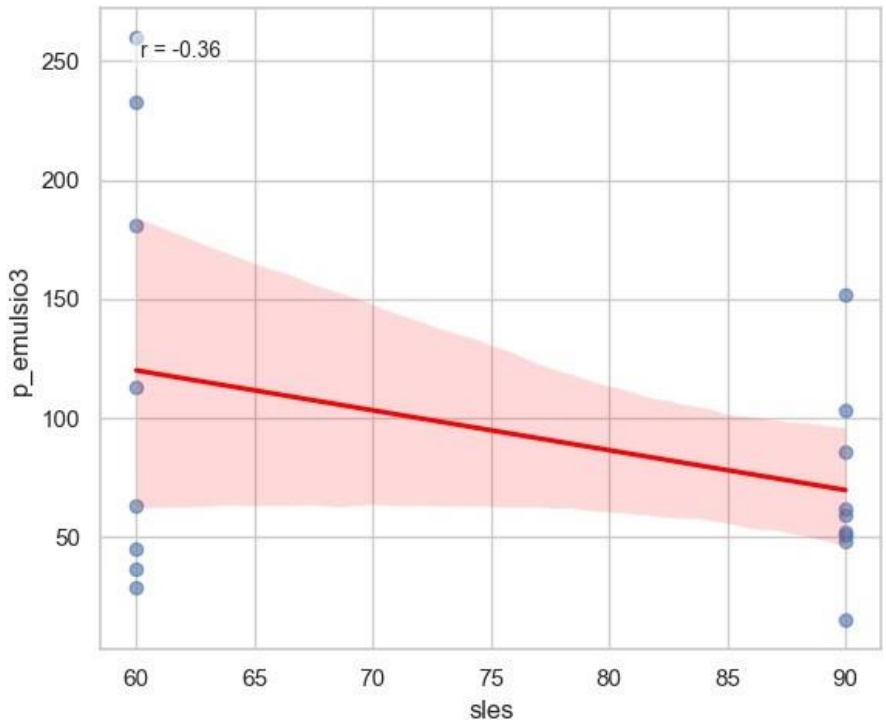

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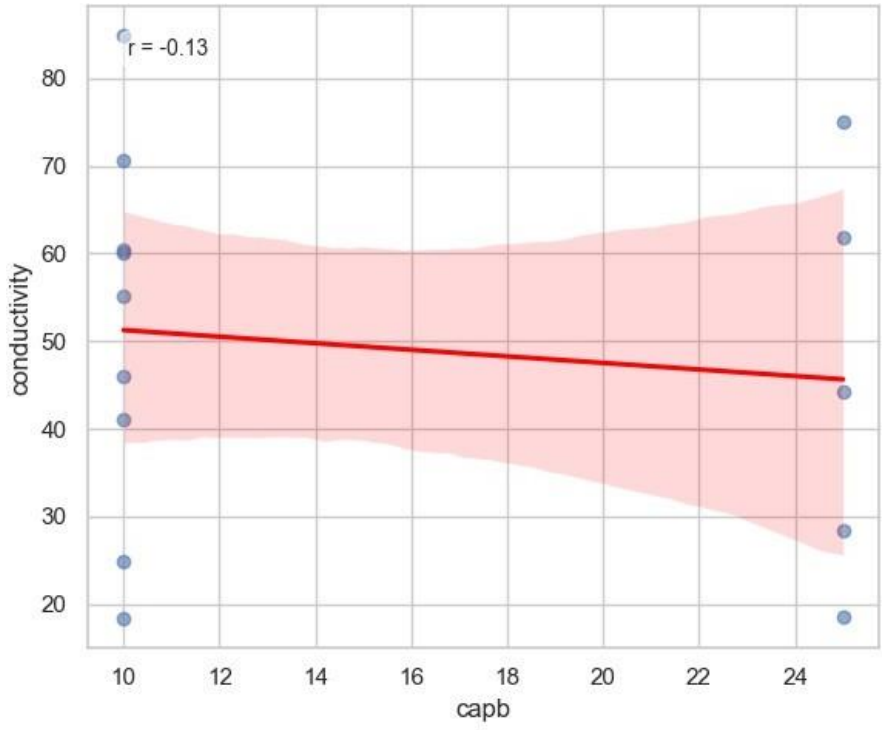

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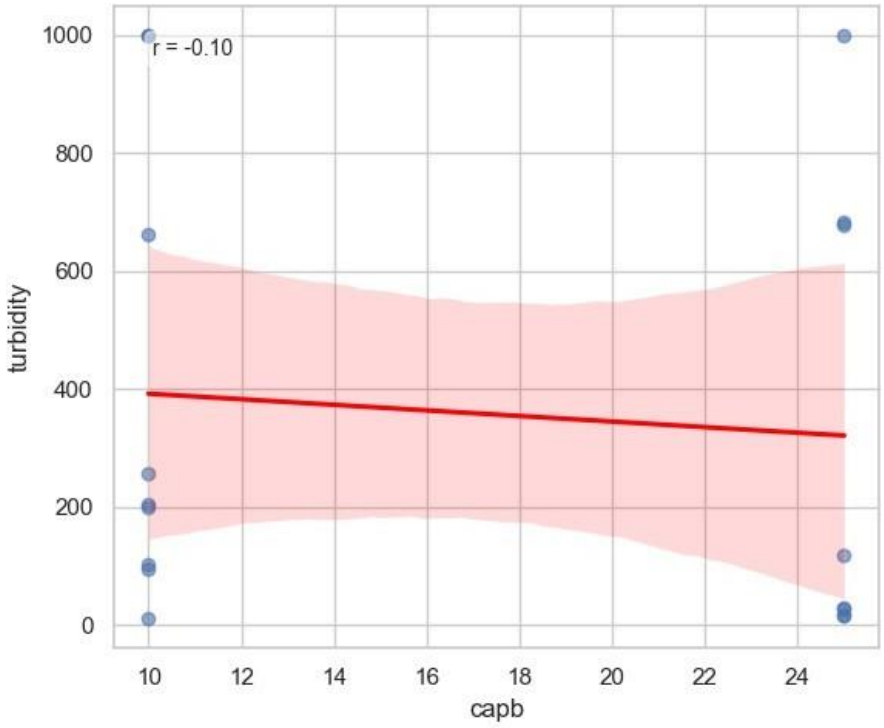

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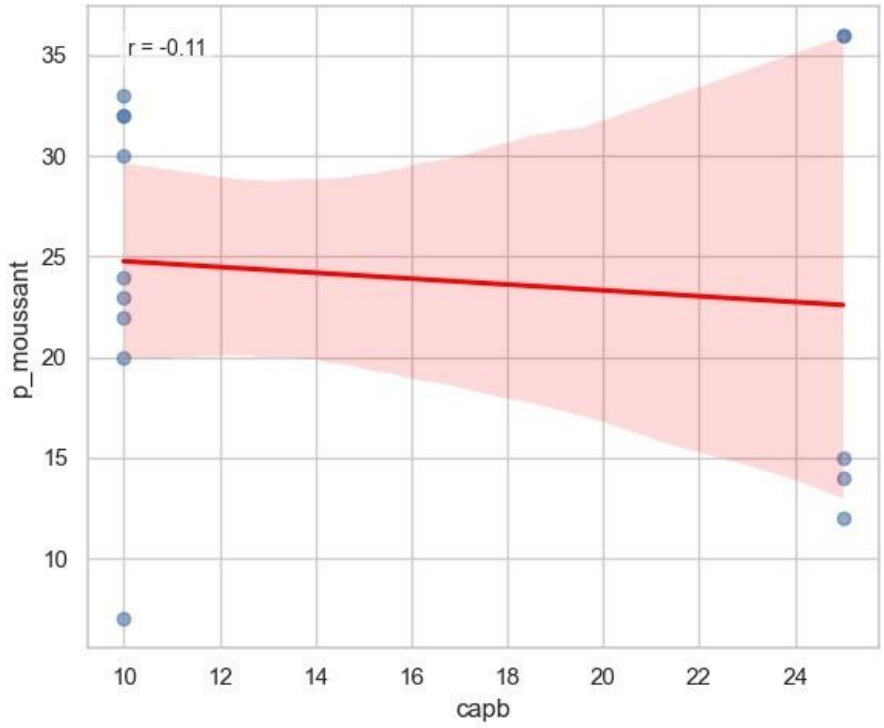

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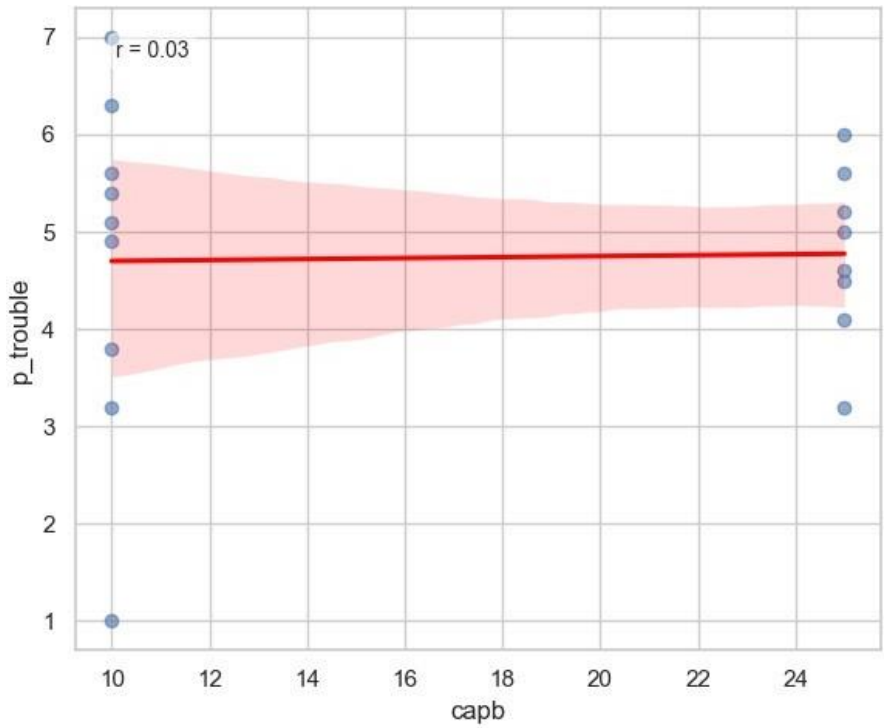

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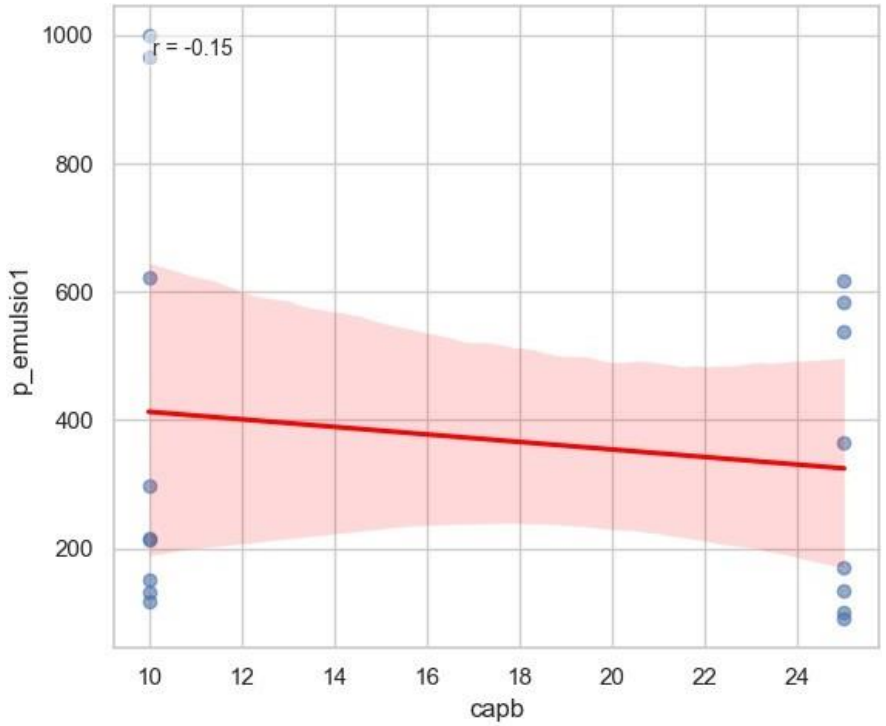

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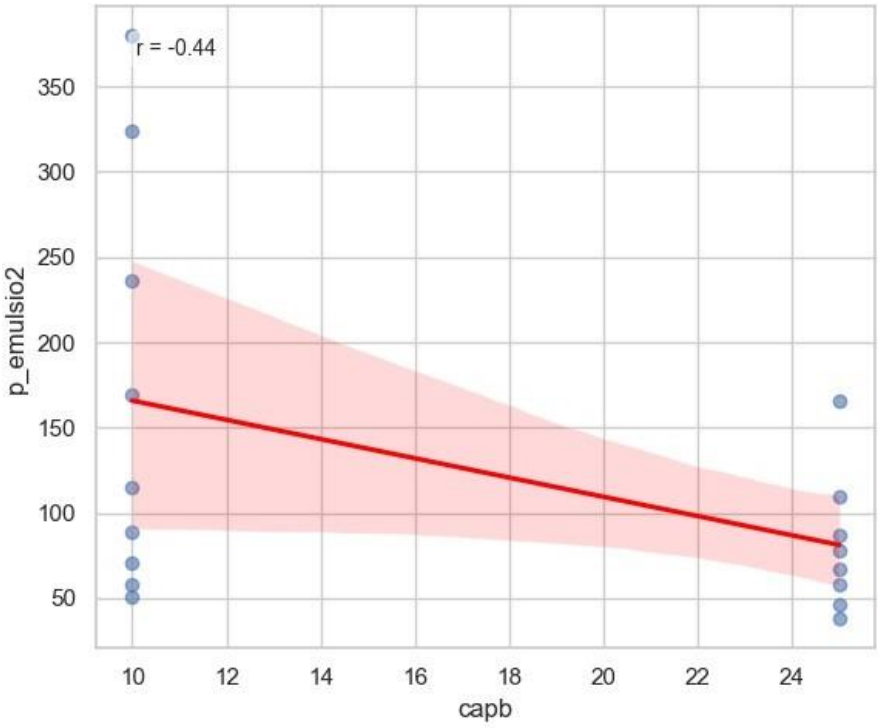

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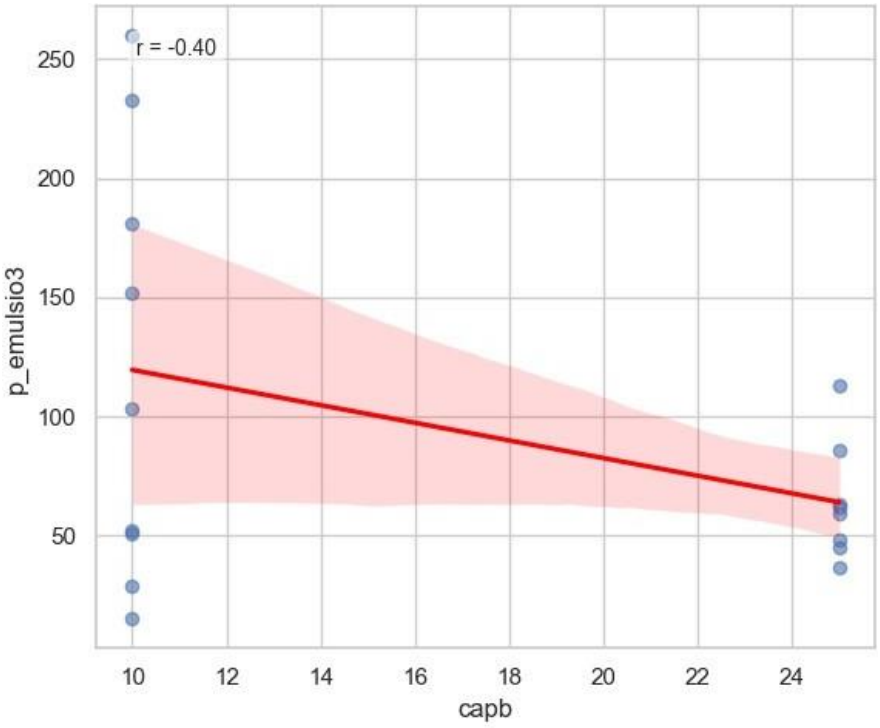

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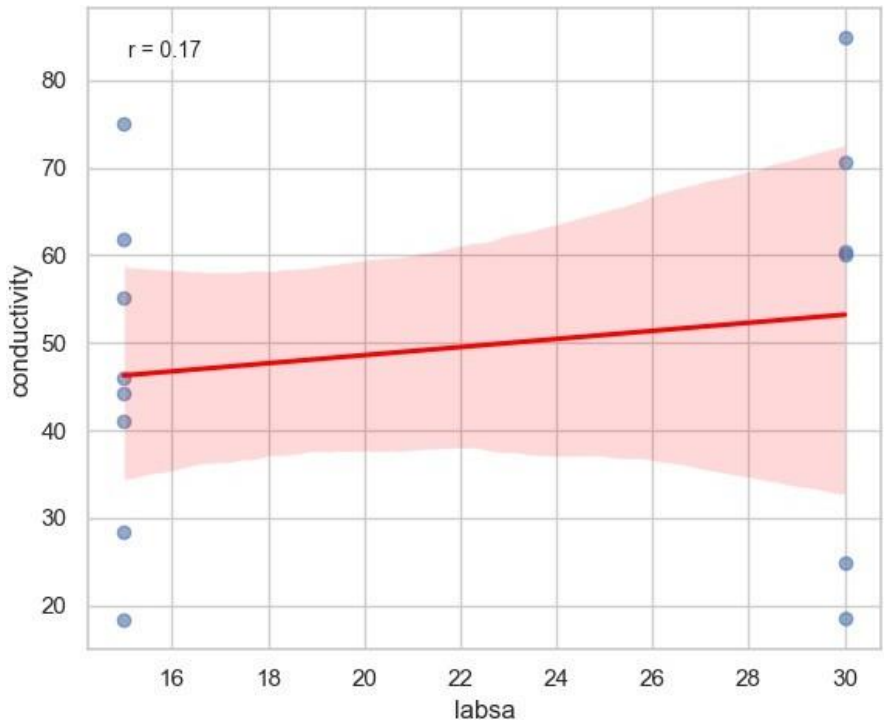

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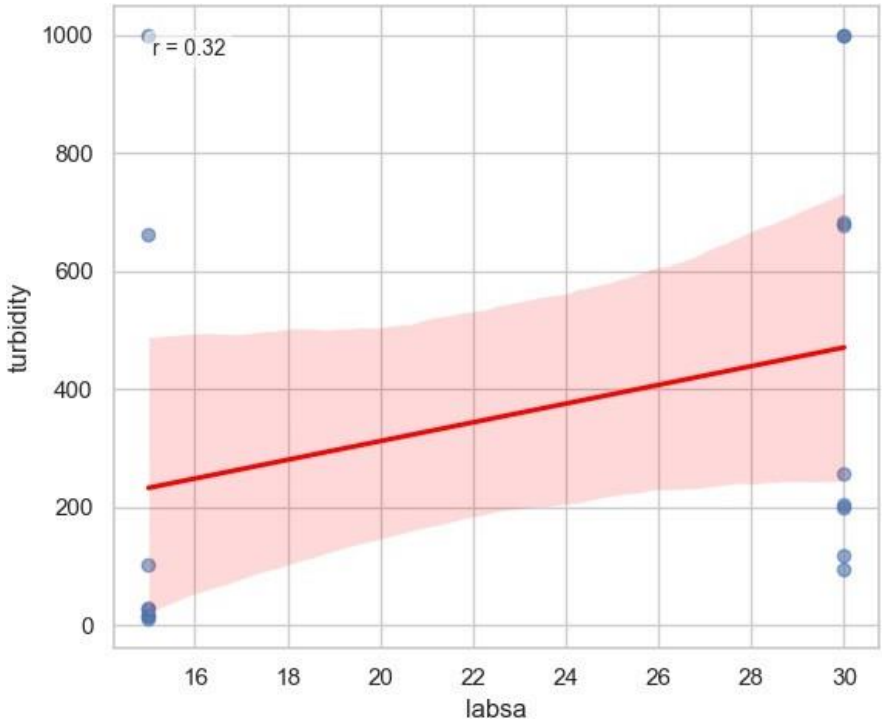

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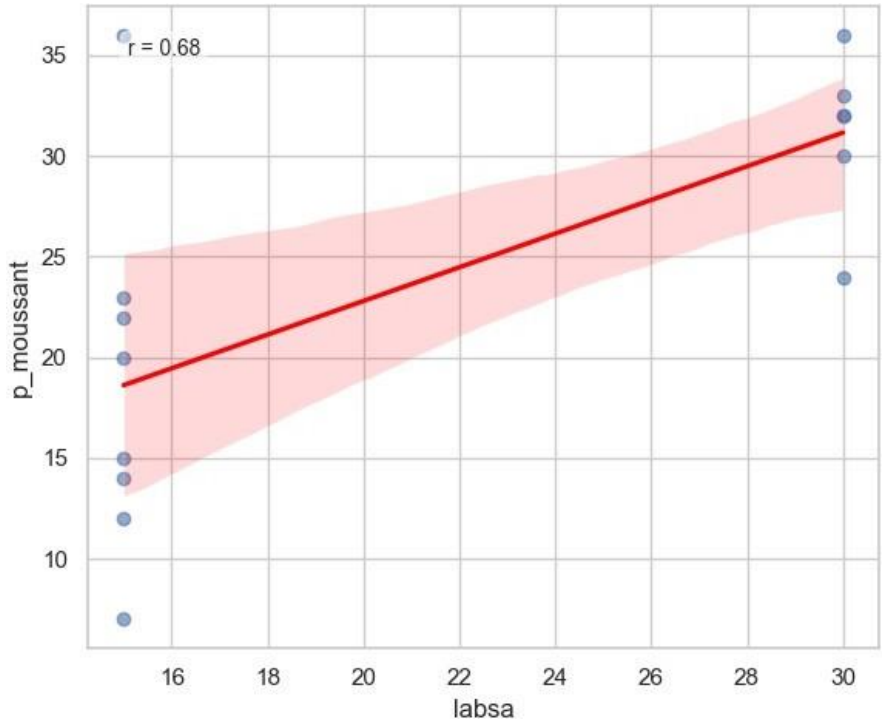

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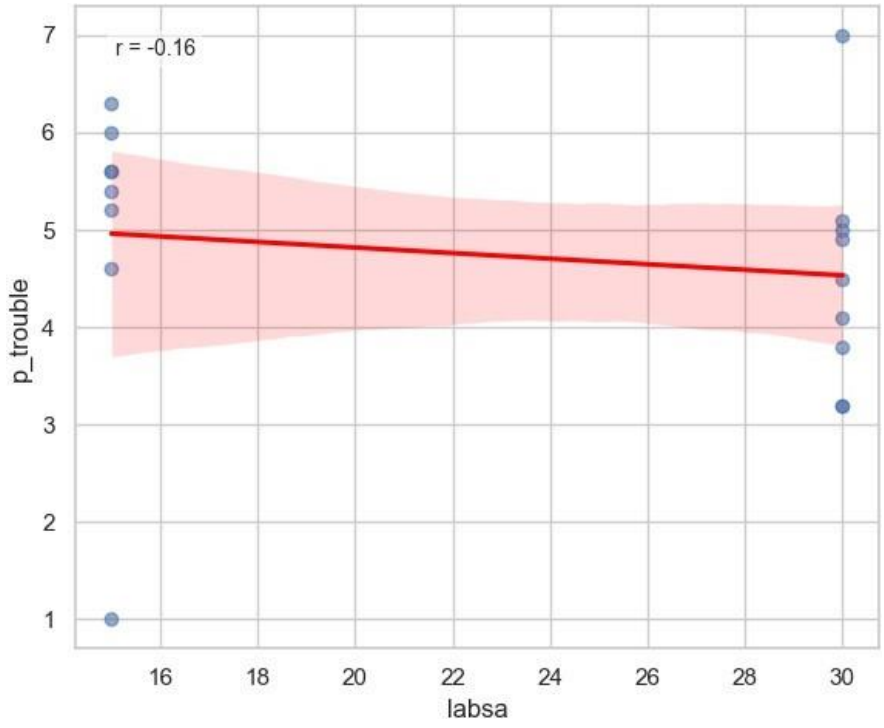

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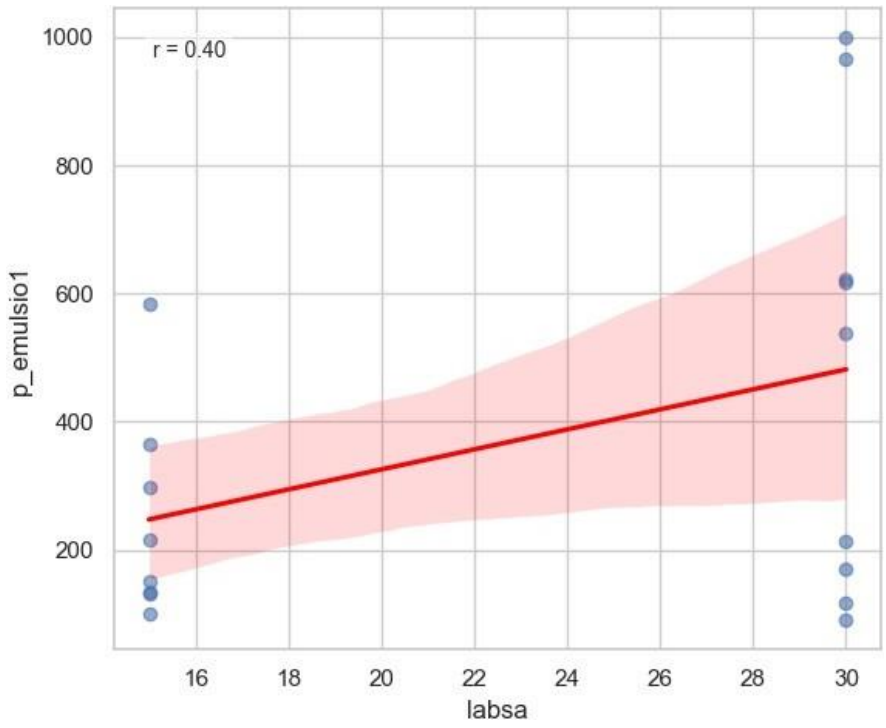

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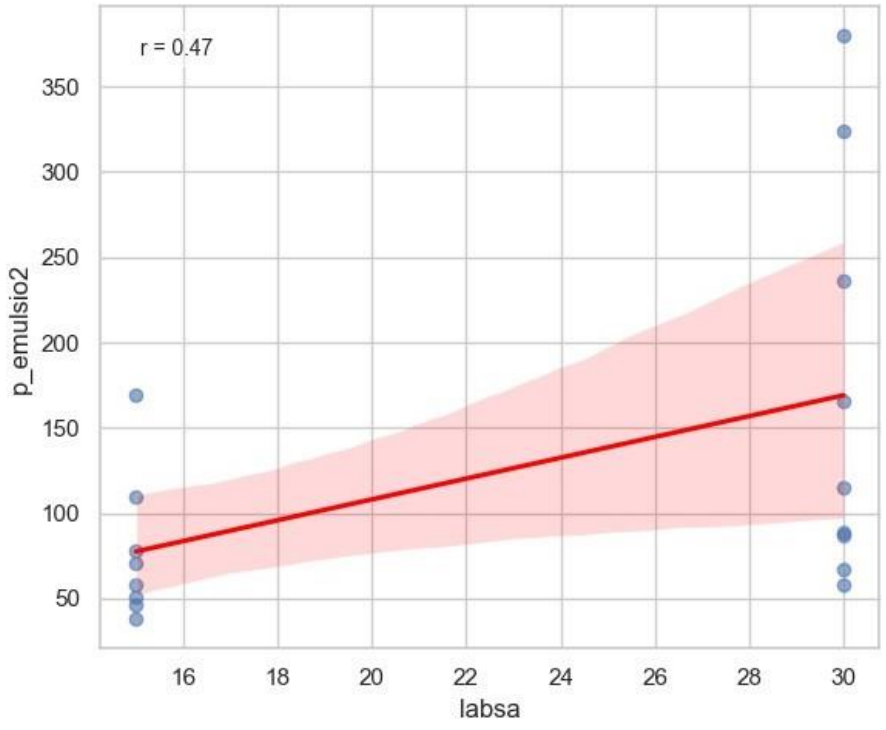

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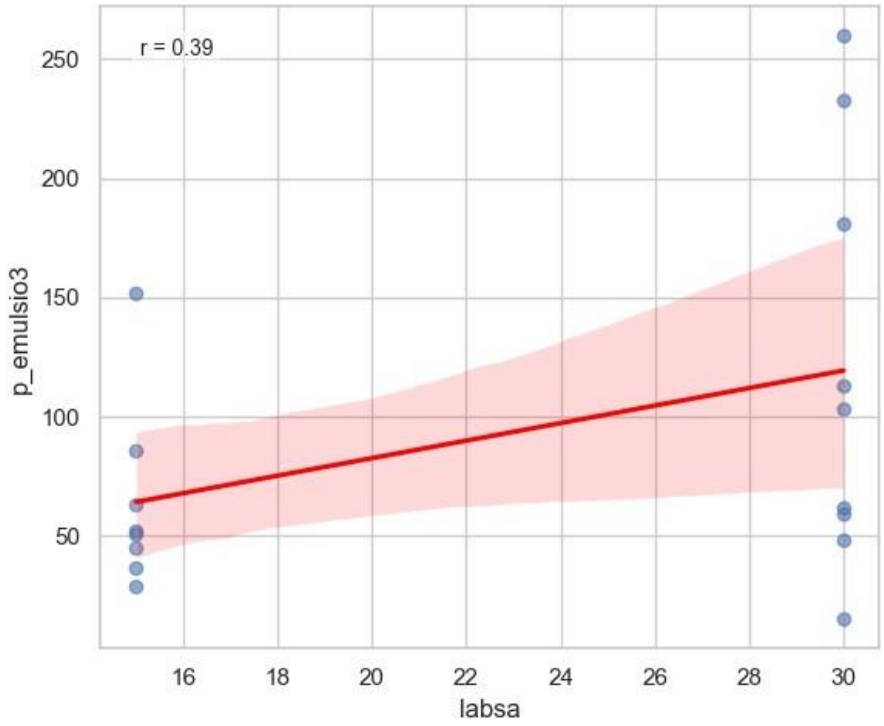

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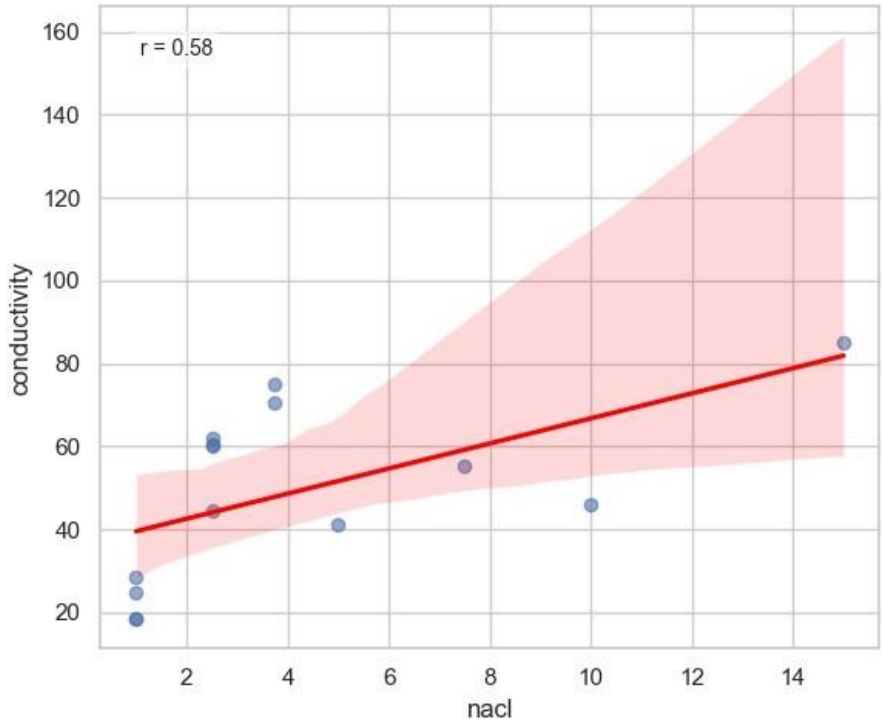

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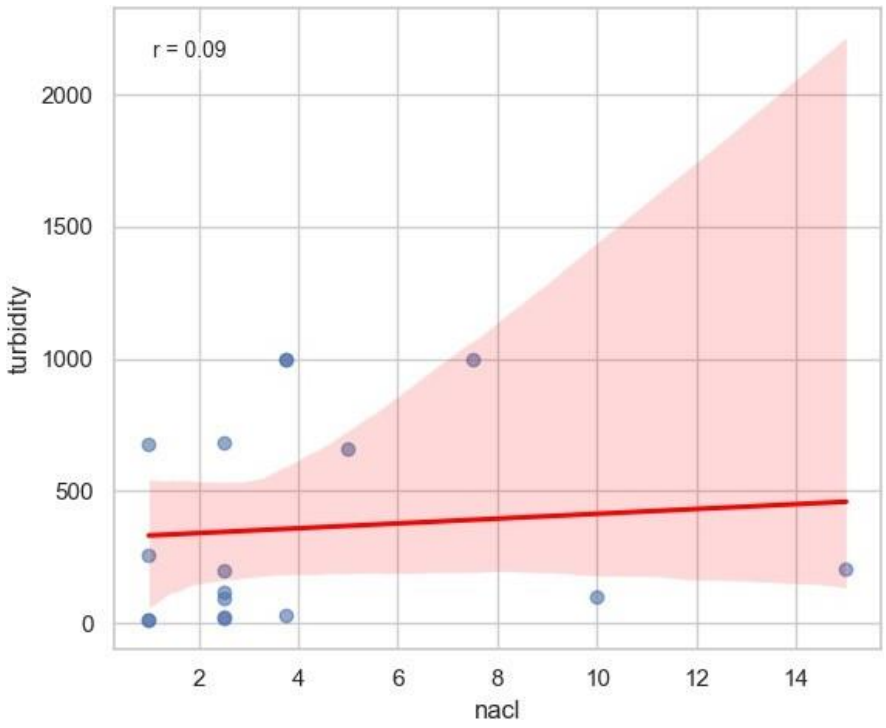

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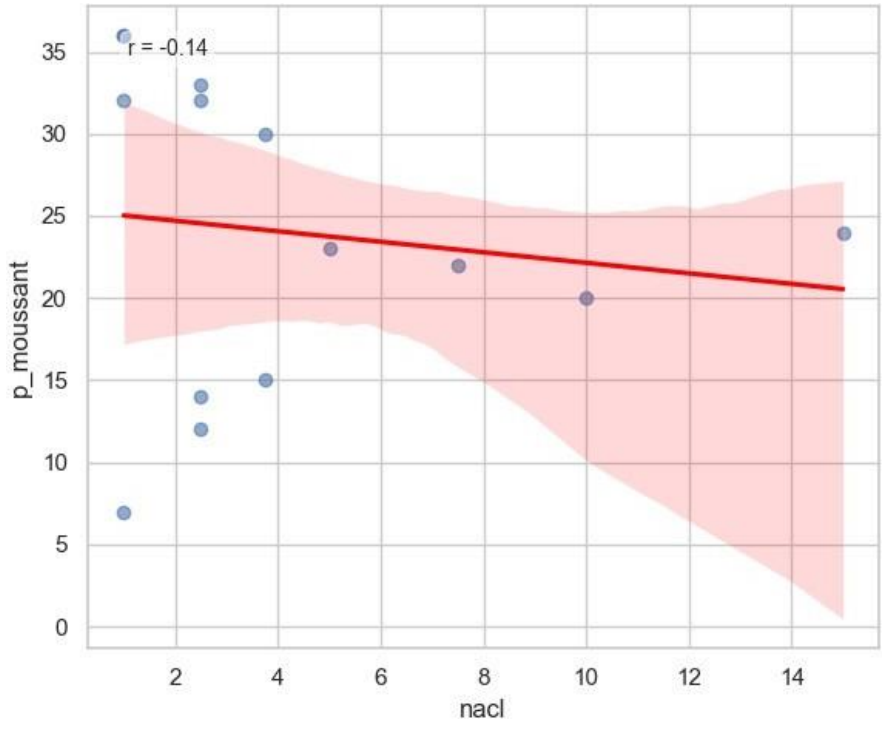

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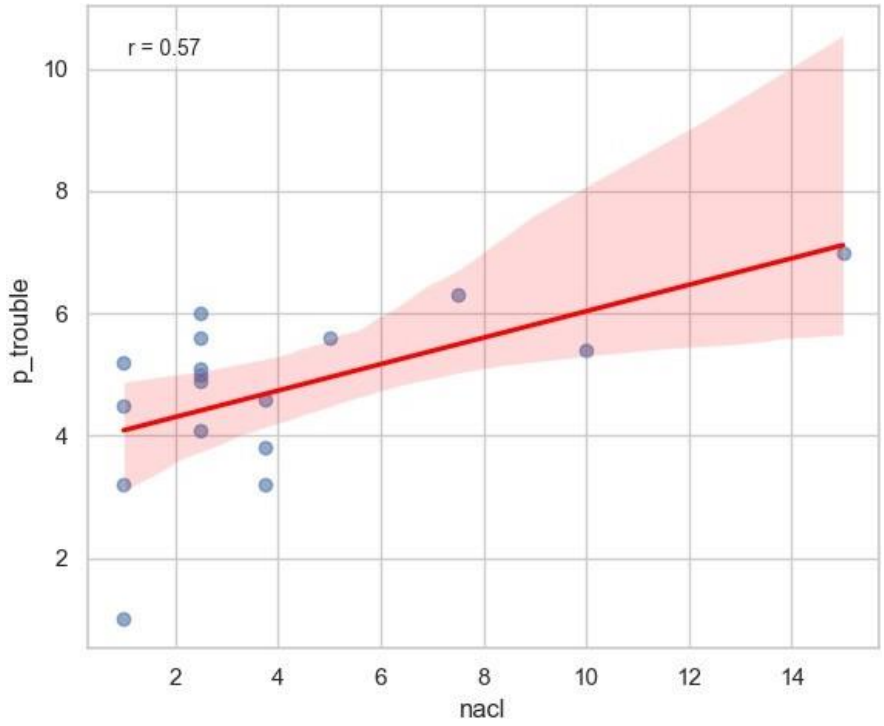

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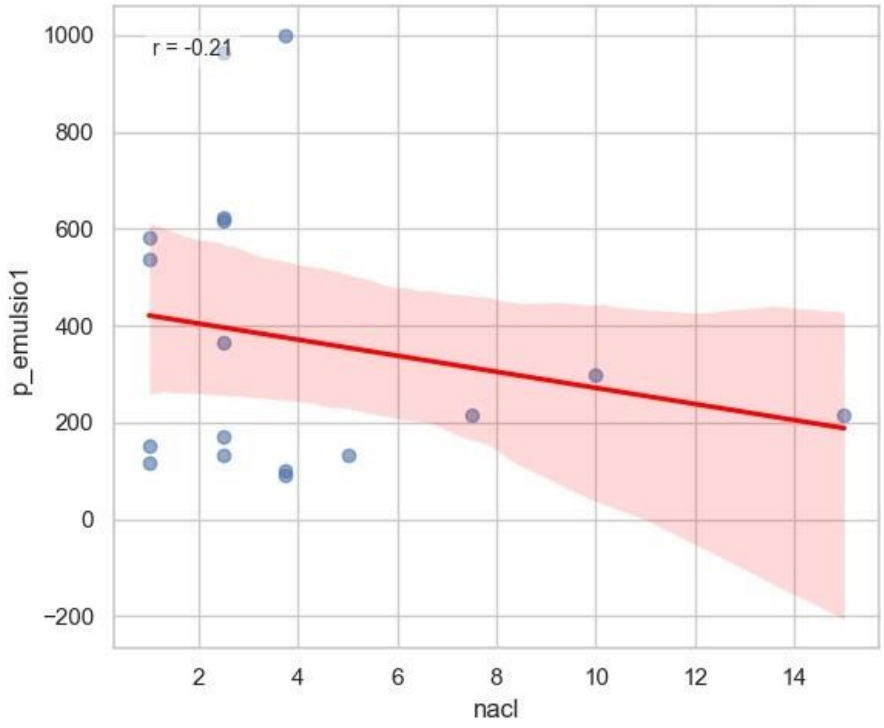

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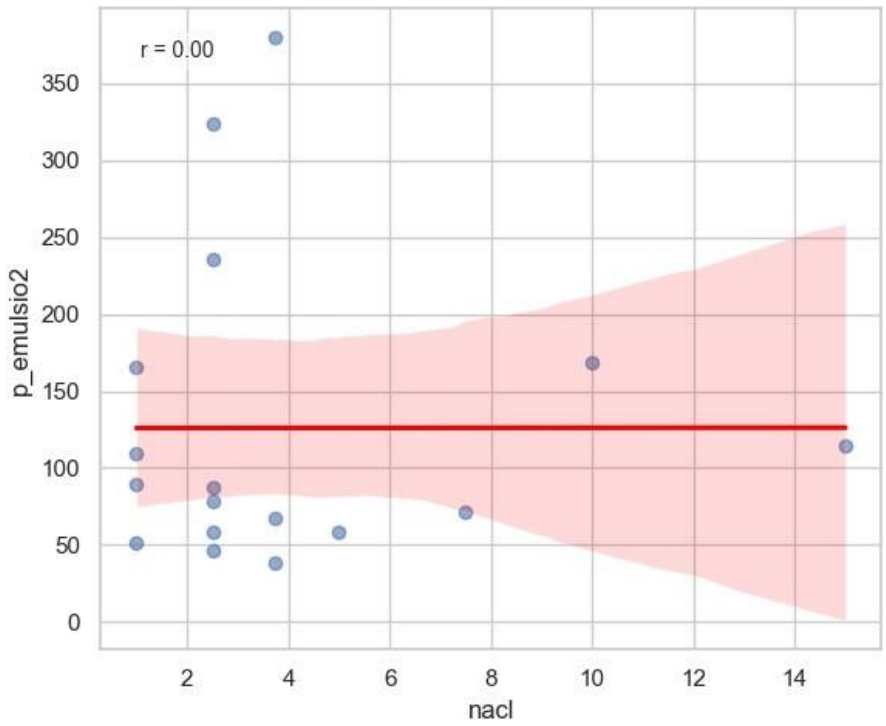

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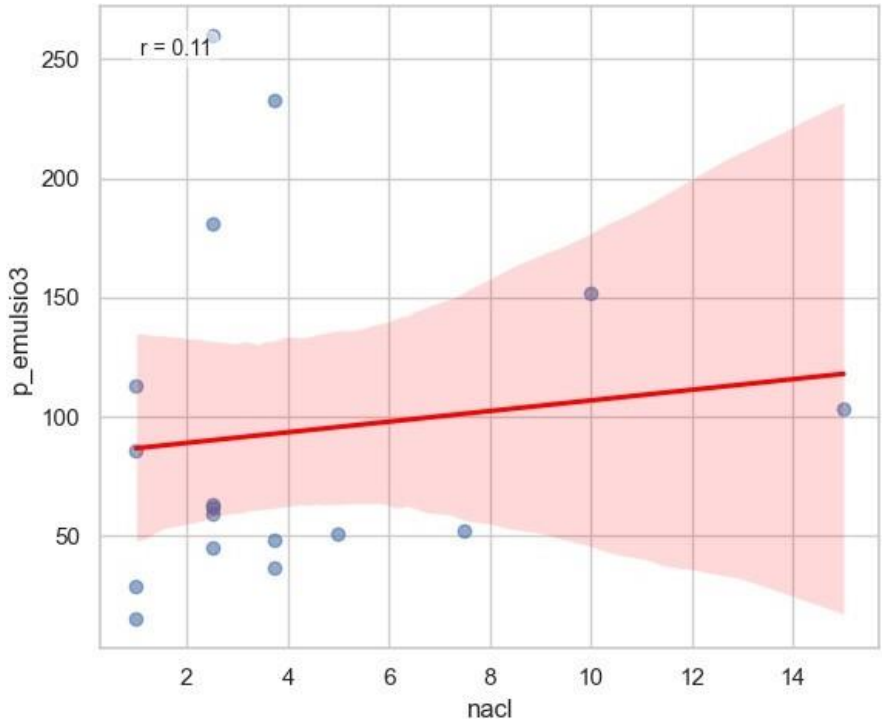

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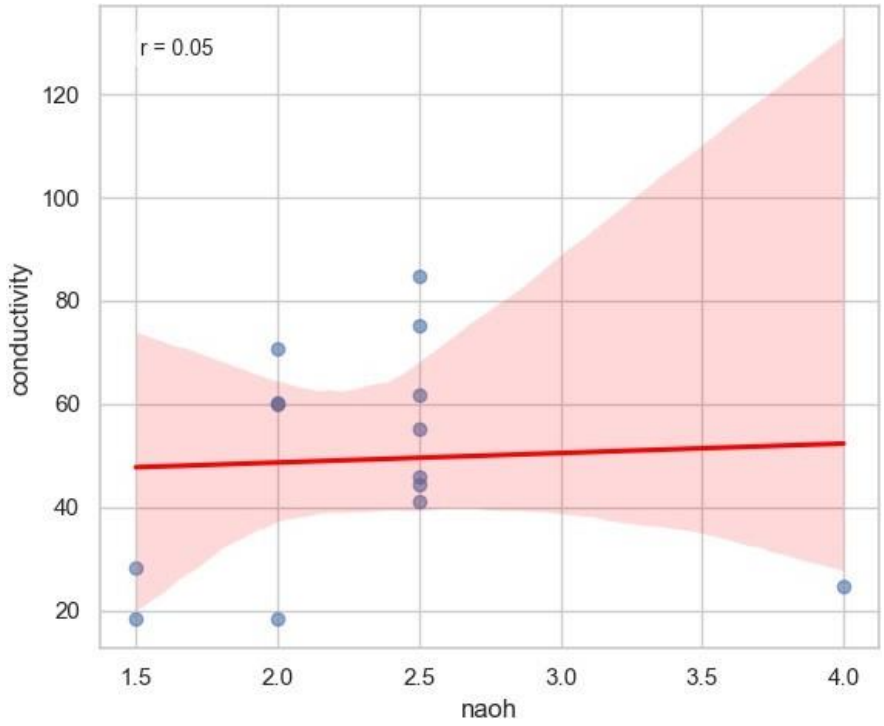

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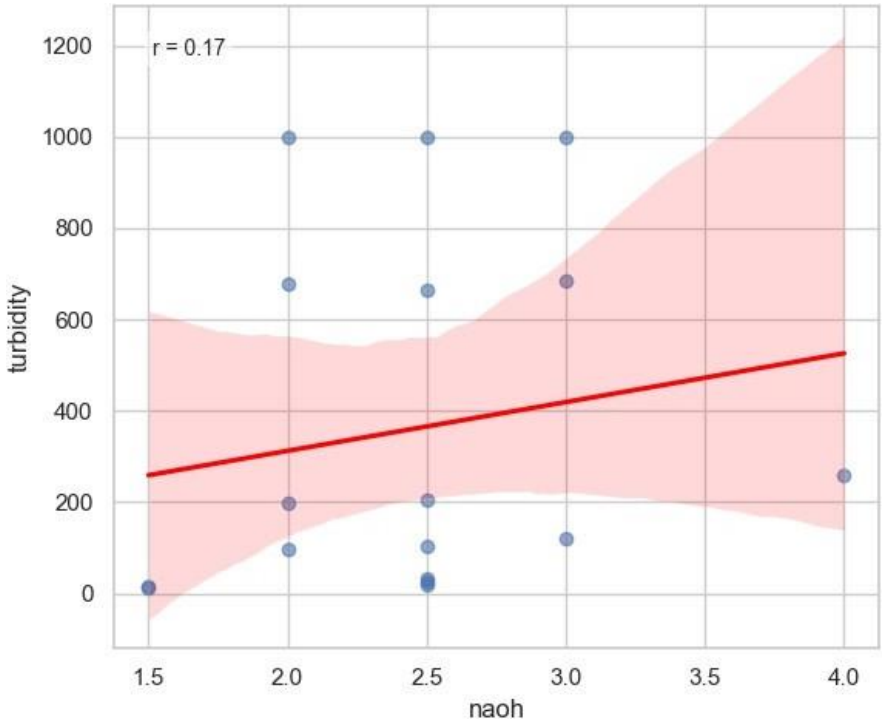

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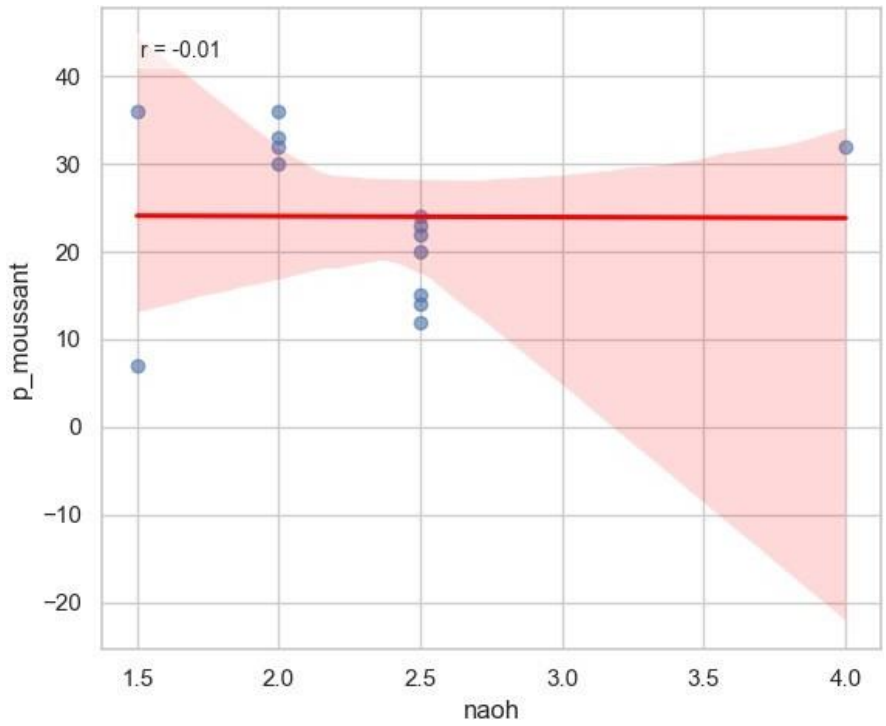

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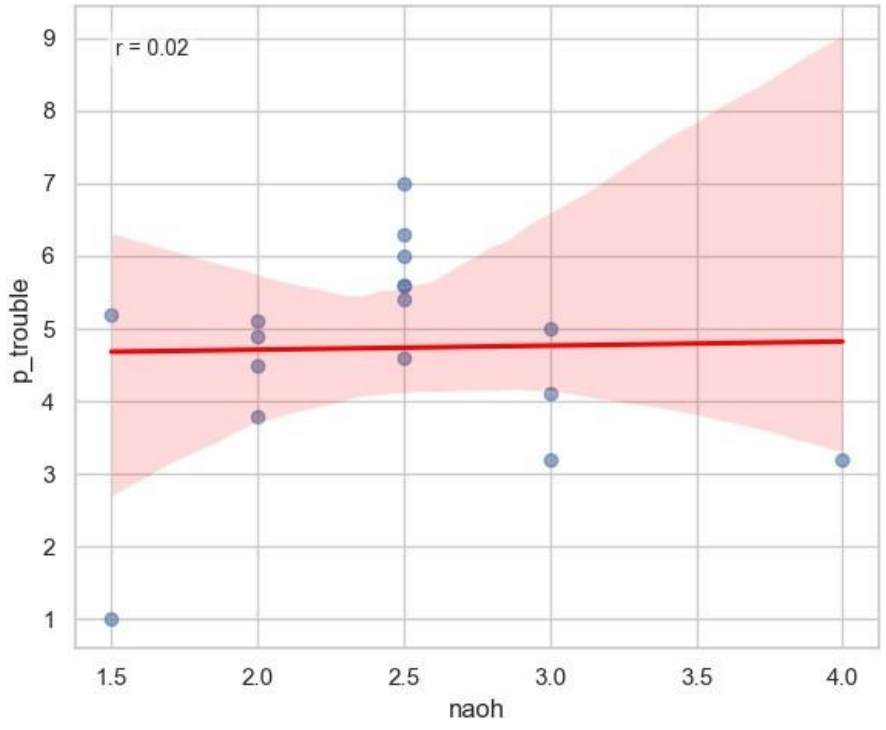

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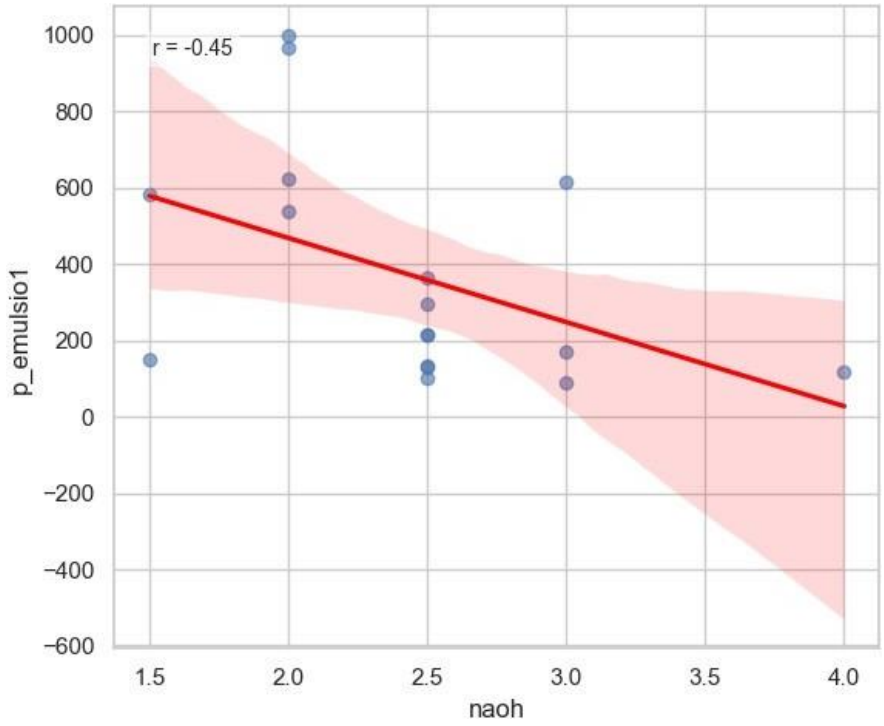

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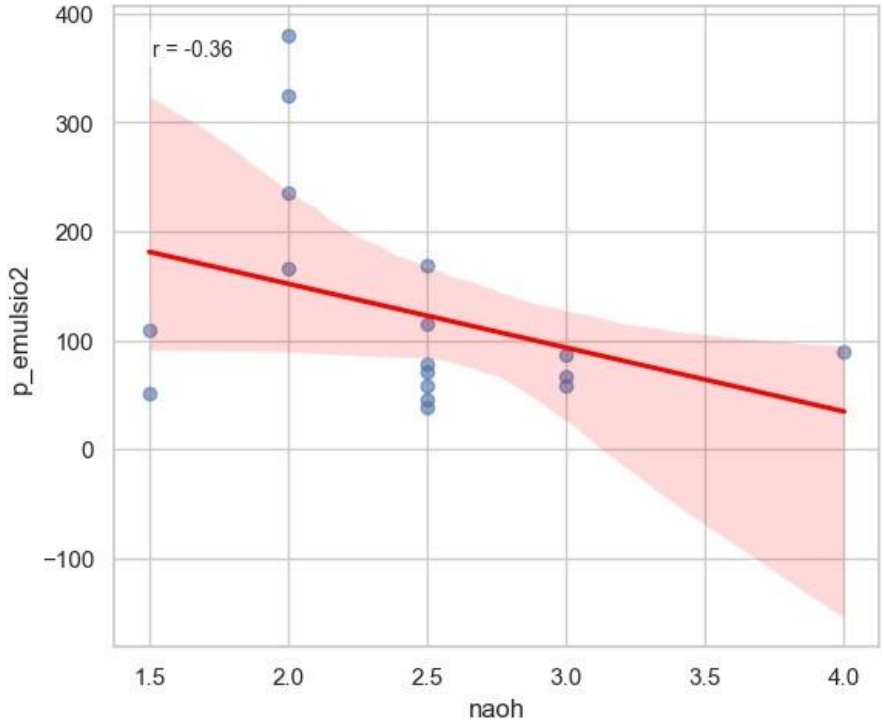

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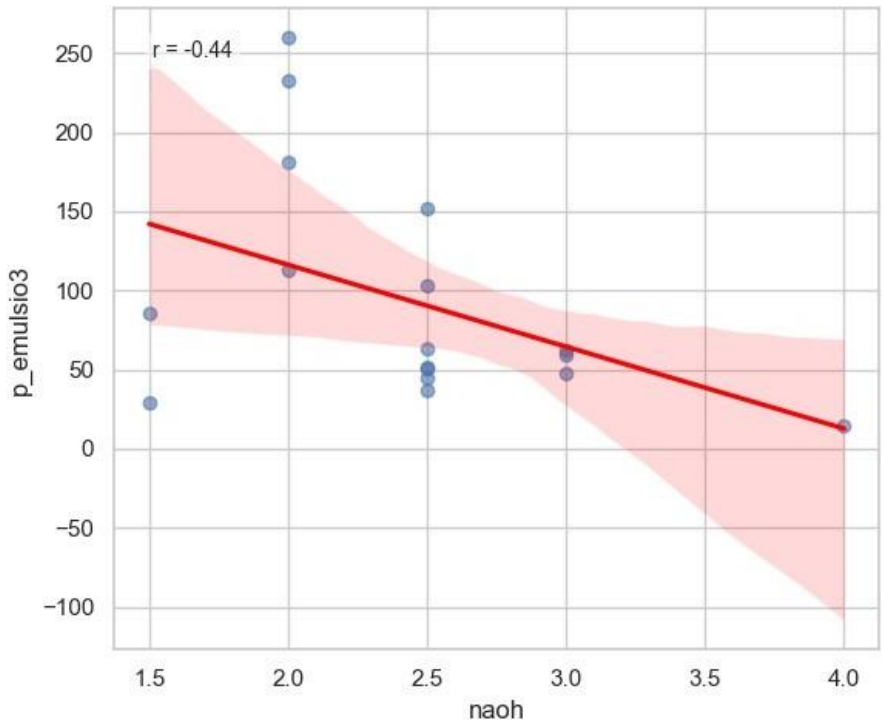

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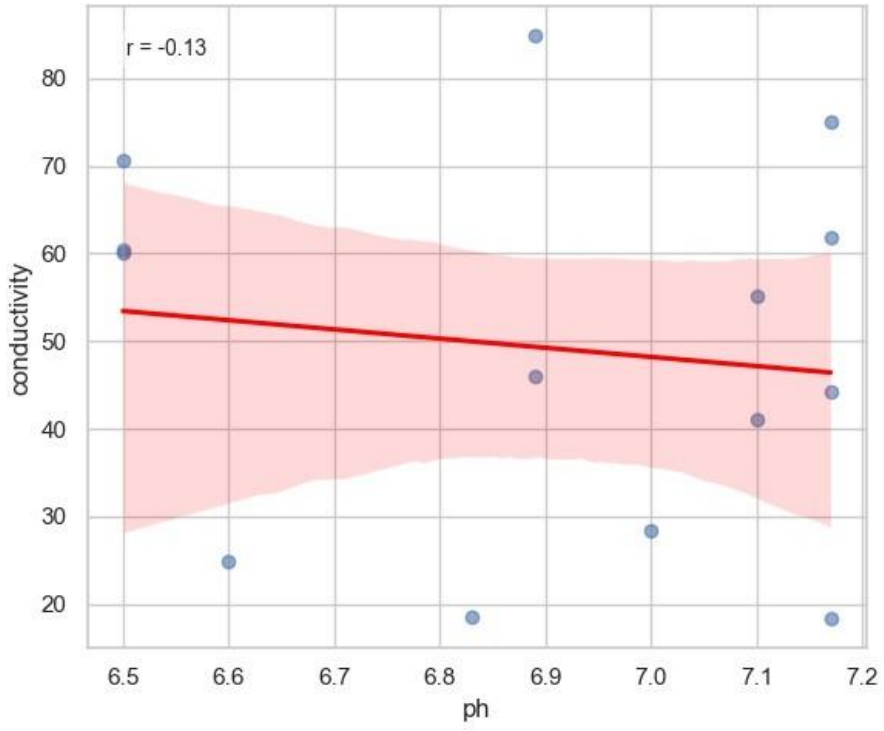

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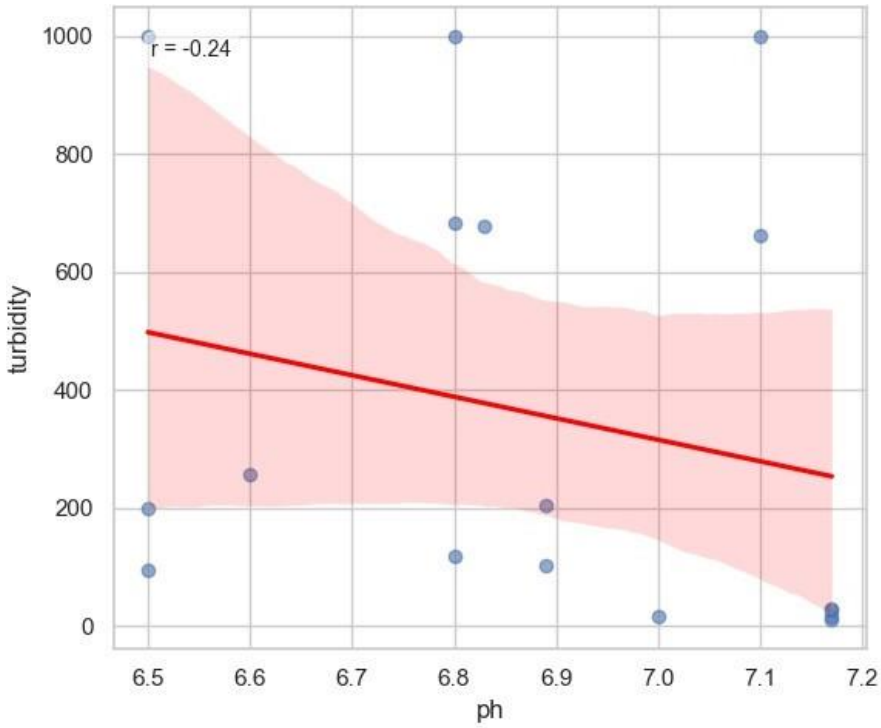

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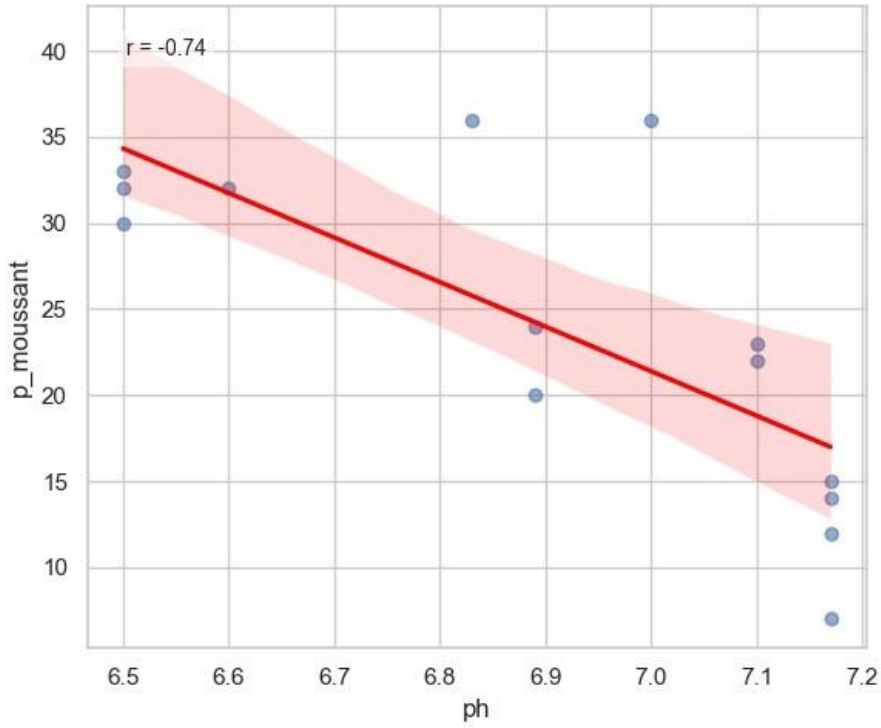

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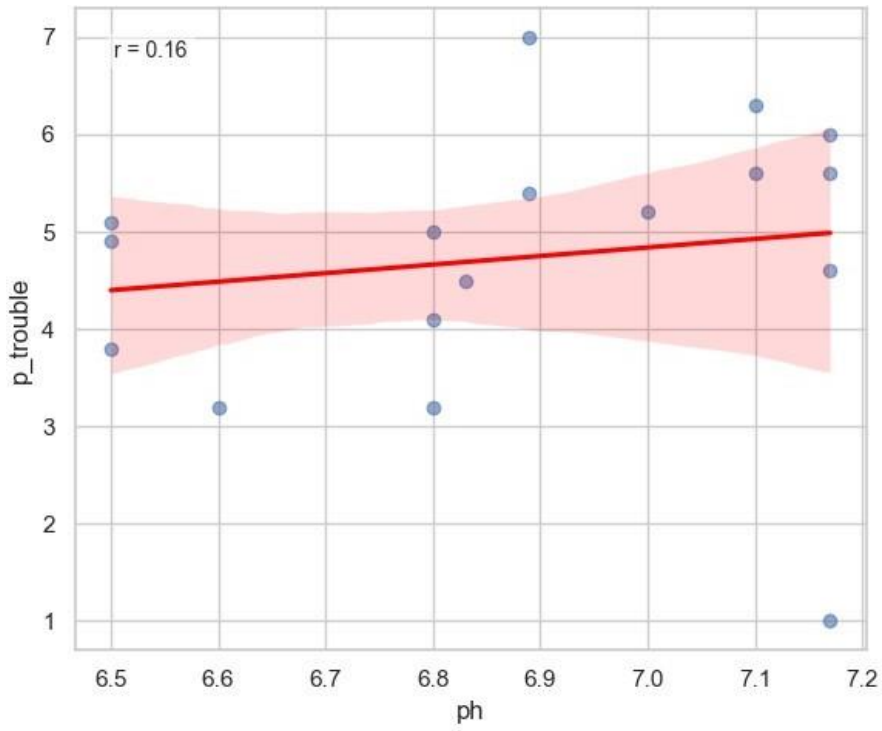

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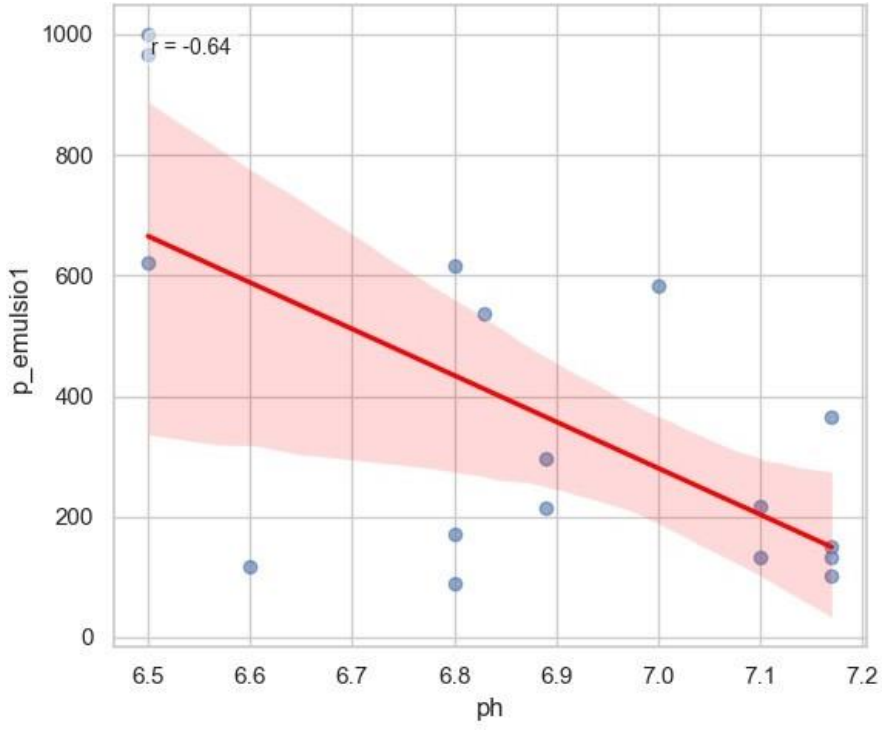

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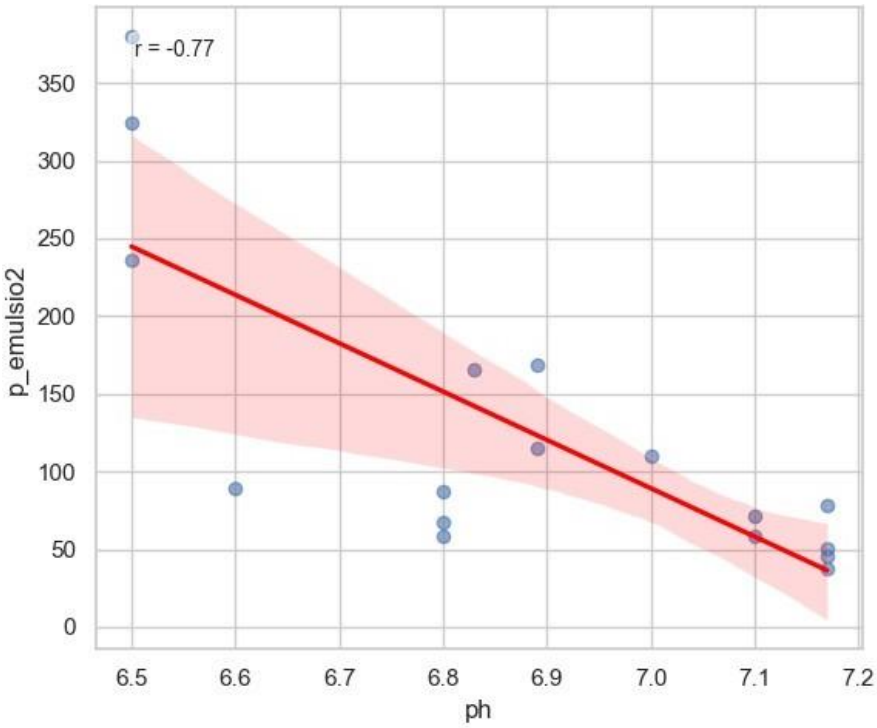

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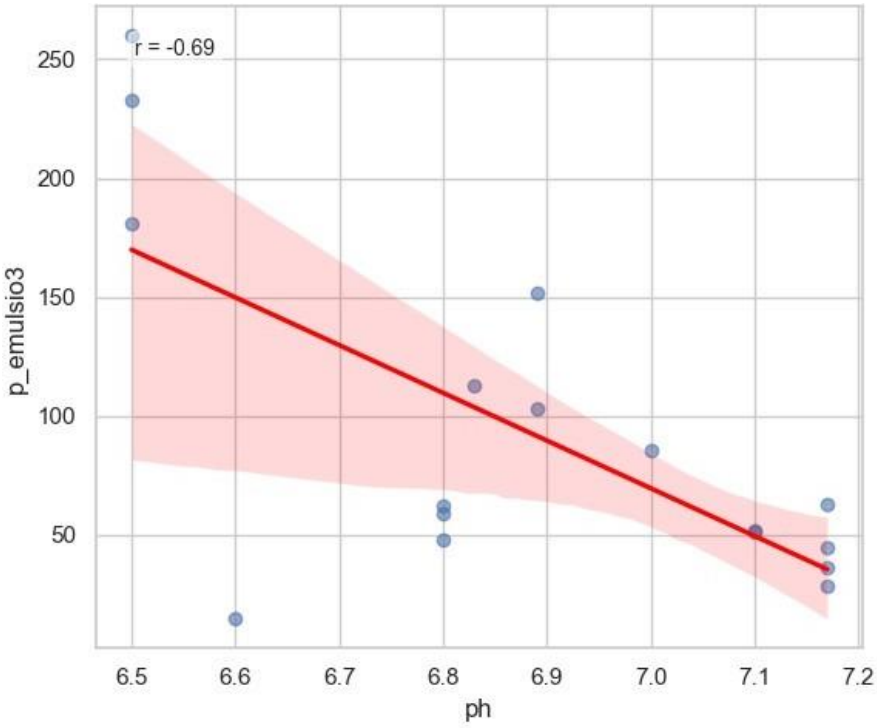

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In [ ]: