CHARACTERIZATION OF LANGMUIR MONOLAYERS OF COSMETICS SURFACTANTS

Juliana Martins Amado

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Orientadores: Helen Conceição Ferraz
Frederico Wanderley Tavares

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To my big hero (in memoriam),
To my mother and my brother,
With gratitude.

“Give up... I have already thought seriously about it, but never took me seriously. It is that there's more ground in my eyes than the tiredness on my legs, more hope in my steps, than sadness on my shoulders, more road in my heart than fear in my head."

(Cora Coralina)

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Orientadores: Helen Conceição Ferraz
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Programa: Engenharia Química

Emulsões possuem um papel fundamental em diversas aplicações industriais. Estão presentes na indústria alimentícia, farmacêutica, do petróleo, de cosméticos, entre outras. Apesar do grande trabalho do meio científico para elucidar o comportamento desses sistemas complexos, o campo do empirismo ainda domina o mercado. Por serem sistemas termodinamicamente instáveis, um dos grandes desafios da indústria é o desenvolvimento de produtos estáveis. O objetivo dessa pesquisa foi avaliar os filmes monomoleculares de Langmuir e Langmuir-Blodgett (LB) de surfactantes estudados na literatura e usados na indústria de cosméticos: cetil fosfato de potássio, lauril sulfato de sódio (SDS) e dioctil sulfosuccinato de sódio (DSS). Foram estudadas isotermas pressão superficial versus área molar em várias condições. Os filmes na interface ar-água foram investigados quanto às possíveis transições de fases bidimensionais. Em menores temperaturas, 4ºC, por exemplo, os filmes ficam mais rígidos e, consequentemente, mecanicamente mais estáveis. Para as temperaturas de 4 ºC, 25 ºC, 45ºC e 55ºC, o perfil das isotermas obtido implica que a transição líquido expandido-líquido condensado é de segunda-ordem. Em concentrações maiores, o filme apresenta-se mais condensado em maiores áreas molar como observado em 1%. A isoterma pressão superficial versus área molar em pH 7 mostrou a transição gás-líquido condensado. Porém a transição foi observada para pressão de superfície muito baixa mostrando que o filme possui, qualitativamente, um comportamento mais expandido. Foi demonstrado que o modelo termodinâmico baseado na equação de estado PC-SAFT consegue descrever as transições de fases com boa correlação dos dados experimentais.

Palavras-chave: Cetil fostato de potássio, filmes de Langmuir e Langmuir-Blodgett, PC-SAFT,compressibilidade de monocamadas.

Abstract of Dissertation presented to COPPE/UFRJ as a partial fulfillment of the requirements for the degree of Master of Science (M.Sc.)

CHARACTERIZATION OF LANGMUIR MONOLAYERS OF COSMETICS SURFACTANTS

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Emulsions play a significant role in several industrial applications. They are present in the food, pharmaceutical, petrochemical industry, cosmetics industry, among others. Despite the great work of the scientific community to elucidate the behavior of these complex systems, the field of empiricism still dominates the market. As emulsions are thermodynamically unstable systems, one of the industrial's major challenges is the development of stable products. The objective of this research was to evaluate the Langmuir and Langmuir-Blodgett (LB) monomolecular films of surfactants studied in the literature and used in the cosmetics industry: potassium cetyl phosphate, sodium lauryl sulfate (SDS) and sodium dioctyl sulfosuccinate (DSS). Surface pressure versus molar area isotherms were studied under various conditions. The films at the air-water interface were investigated for possible transitions of two-dimensional phases. The study of isotherms showed that, at lower temperatures, 4ºC for example, the films become more rigid and, consequently, mechanically more stable. For the temperatures of 4 ºC, 25 ºC, 45ºC and 55ºC, the isotherm profile obtained implies that the transition between expanded liquid and condensed liquid are second-order. At higher concentrations, the film is more condensed over larger molar areas as seen in 1%. The surface pressure versus molar area isotherm at pH 7 showed the condensed gas-liquid transition. However, the transition was observed for extremely low surface pressure showing that the film has, qualitatively, a more expanded behavior. It was demonstrated that the thermodynamic model based on the PC-SAFT state equation can describe the phase transitions with good correlation of the experimental data.

Keywords: Potassium cetyl phosphate, Langmuir and Langmuir-Blodgett films, PC-SAFT, monolayer compressibility.

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CHAPTER 1

INTRODUCTION AND OBJECTIVES

1.1 Cosmetics emulsions and their behavior

The last panorama of the personal care, perfumery and cosmetics sector released by the Brazilian Association of Personal Hygiene, Perfumery and Cosmetics Industry, ABIHPEC, of 2019, shows that in 2019 Brazil occupied the 4th world position in the consumption of cosmetic products, having made $30.0 billion in 2019. Considering the sector's performance in the economy, the panorama shows that until 2014 the cosmetics sector had more vigorous growth than the industry in general. Another economic scenario presented in this report is the sector's contribution to the movement of the economy. Today it is the industry that invests the most in advertising, being the 3rd global market in product launches per year. Regarding the Research and Development (R&D) investment, that represent the incentive in science by cosmetic companies, in Brazil in the last years 10 year it increased 380% as shown in the Figure 1.1. Besides that, the sector increased 4.3% from 2017 to 2018 in direct jobs (ABIHPEC, 2019).

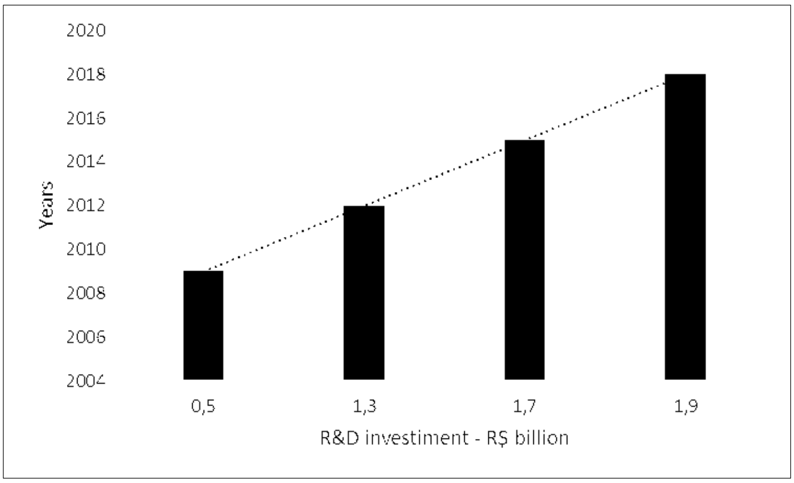


Figure 1.1. Research and Development (R&D) investment in the last 10 years
Source: Adapted from ABIHPEC, 2019

As mentioned, the cosmetics market is large and different types of products such as products for protection (sunscreens), hygiene (soaps, bath, and hair products), treatment (acids, vitamin C, antiaging, healing) exist. Therefore, companies need to develop new products to meet consumers' needs, that deliver differentiated treatments and are safe at the same time.

A large market containing many different products and several ingredients, in Brazil, Law nº. 6,360, of September 23, 1976, determines for health surveillance to be responsible for cosmetics. ANVISA, the National Health Surveillance Agency, created in 1999, regulates cosmetic products for use in humans.

ANVISA has the purpose of promoting the protection of the population's health, through the sanitary control of the production and consumption of products and services submitted to sanitary surveillance. All procedures related to technical requirements of cosmetics are set out in Collegiate Board Resolutions known as RDC. The RDC nº 07/2015 is considered the reference for all the others cosmetic RDCs. This resolution presents the definition of cosmetic products, classification (grade 1/grade 2) and definition of each technical requirements for regularizing cosmetic products (Annex III), among other information ("Portal Anvisa", [s.d.]).

One of the updates of RDC nº 07/2015 became RDC nº 288/2019 with the change of Annex III (mandatory requirements for regularization of cosmetics). For example, one of the changed items was the stability study with the determination of the range of variation of the concentration of UV filters in sunscreens (dosage). In the list of mandatory requirements in this same Annex III, the item 10 mentions the product stability data. To meet the stability data required by them, ANVISA created in 2012 a Cosmetic Product Stability Guide to provide subsidies and guidelines for carrying out stability studies on cosmetic products ("Portal Anvisa", [s.d.]).

The challenge of having a stable final product for a highly dynamic, competitive, and thirsty market for innovation is significant. Therefore, there is an increasing demand for studies that elucidate the interactions between the ingredients of the formulation, understanding the factors that lead to an emulsion destabilization, by the companies. Even though the stability guide presents, the technical explanations to verify the influence of several external factors such as humidity, temperature, and light over time, the point is that as the formula contains many ingredients together, it is crucial to understand who in the formula or which interaction the external factor destabilizes. Interpreting what happens microscopically is fundamental to looking for solutions and reworking improvements. And of course, the sooner we anticipate problems that can be identified only after a few months of accelerated stability study, sooner we will work in solutions (ANVISA, 2004).

Most cosmetic formulations are oil-in-water emulsions types, which must be stable until the expiration date of the product. Macroscopically, the most common emulsion-instability indicators are the appearance of oil droplets around the neck of the product packaging and changes in product color and odor.

The Van der Waals forces between identical bodies in a medium are always attractive. Between different bodies, they can be attractive or repulsive, depending on the properties of the materials. From an energetic point of view, this will define the unstable nature of colloidal systems (HOEK; AGARWAL, 2006). The DLVO (Derjarguin-Landau-Verwey-Overbeek) theory proposes that stable systems must have an energy barrier to bypass the attraction between the molecules and thus minimize phase separation.

Surfactants, substances that act on the surface and organize spontaneously due to intermolecular interactions with the medium, are mainly used adhere to surfaces creating a film between two surfaces of different polarities (MILLER; JOOS; FAINERMAN, 1994). Due to these properties, there is a monomolecular surfactant film-forming that provides mechanical stability for emulsions (LEE et al., 2013). Ionic surfactants also offer an electrostatic barrier to the droplets’ approach.

Surfactants orient themselves in medium by having their head maintaining contact with the polar part of the solution and non-polar chain in contact with the non-polar solution medium. The resulting interfacial film formed has as its thickness as a molecule thickness and is commonly called a "monomolecular layer" or simply "monolayer". The name “Langmuir monolayer” was given in honor of scientist Irving Langmuir, whose work in this area was pioneering (LEE, 2008).

The group of the Laboratory of Engineering of Interfacial Phenomena, LABEFIT, from the Chemical Engineering Program of the Alberto Luiz Coimbra Institute of Postgraduate Studies and Engineering Research, COPPE, has been working and developing strong expertise in the last 10 years in the elucidation of isotherms of Langmuir for different applications. GUIMARÃES, 2009, prepared mixed films of COx/S layer proteins and DPPC/S layer proteins. The appropriate surface pressure to transport film to a support was defined by obtaining Langmuir monolayers. ALMEIDA, 2012, evaluated the mechanical stability and compressive strength of DSS films, arabic gum and corn starch in beverage emulsions. It was observed that gum and starch helped to increase the mechanical stability of the film and avoiding coalescence. DSS also impacted the film by madding it more elastic. GASPAR, 2015, evaluated the mechanical stability and compressive strength of DSS films, arabic gum and whey protein isolate (WPI) also for beverage emulsions. She did not identify arabica gum as a good emulsifier and DSS made the film more elastic. MACHADO, 2019, analyzed the green pea isolated protein film and verified the formation of a condensed liquid film, indicating that this protein must form dense and elastic films.

On the surface, a molecule makes fewer intermolecular interactions when comparing the intermolecular interactions, it makes in the bulk phase. Consequently, the entropy of the surface is always positive. Langmuir films can be generated using the Langmuir trough. In the experiment to obtain Langmuir films, a solution is applied in the aqueous subphase with a micropipette. Once the film is formed, it can be compressed or decompressed (changing the area by moving the barriers) at a constant speed. The measure obtained is the surface pressure by molecular area, generating an isotherm (π-A) where the surface pressure is on the y-axis and molecular area is on the x-axis. These isotherms show the phases (solid, liquid, and gas) and their transitions in the monomolecular film.

Thermodynamically, these phases can be separately characterized using already known state equations. However, there is an ongoing discussion in the literature about the nature of the phase transition of liquid expanded/liquid condensed (LE-LC) and the fact that there is no continuous state equation to characterize them. (STEFANIU; BREZESINSKI; MÖHWALD, 2014) (ZUO et al., 2016) (VOLLHARDT; FAINERMANAN ; SIEGEL, 2000).

For example, the liquid expanded/liquid condensed (LE-LC) phase transition is identified as a first-order phase transition if a horizontal plateau is observed in a π-A isotherm. Otherwise, if the plateau of the π-A isotherm is a non-horizontal one, a second-order phase transition it is defined as a second-order phase transition. Many authors have found experimental results and theoretical explanations to support both hypotheses, a first-order (ZUO et al., 2016) and second-order (D. VOLLHARDT, V. FAINERMAN, 1999) (D. VOLLHARDT, V. FAINERMAN, 2006) transitions. This plateau is noticed based on the qualitative observation of the isotherm and through the tangent of the curve.

The authors also claim to have derived complex and simple equations, capable of representing experimental data with acceptable accuracy. However, it is still necessary to use more than one state equation to model all the isotherm phases. Therefore, it is still essential to study state equation models to better describe the phases transition, mainly, the transition liquid expanded/liquid condensed.

The PC-SAFT (Perturbed Chain-Statistical Associating Fluid Theory) is the equation of state that describe chain-type molecules. It is based on a hard-chain reference fluid argument with attraction, association, and hydrogen-bond-free-energy contributions (AVLUND; KONTOGEORGIS; MICHELSEN, 2012). This work proposes an approach to adapt this model to provide the thermodynamic information needed to describe the two-dimensional structure and properties of surfactant molecules.

Another proposal of this work, which makes it different from other works developed on this theme, was the analysis and experiments to obtain Langmuir isotherms in different conditions, considering the parameters that are used by the industry and by the official body that regulates cosmetic products in Brazil. It is still important to deeper study the Langmuir films not only to enter data into a thermodynamic model but to better analyze how isotherms behave with changes in temperature, surfactant concentration, pH, and the presence of electrolytes.

1.2 OBJECTIVES

The main objective of this research was to investigate the surface behavior of surfactants commonly used in the cosmetics industry by obtaining Langmuir compression isotherms. These isotherms were used to enter the data into a thermodynamic model based on PC-SAFT equation, to understand the role of the monolayer films on the stability of oil-in-water emulsions:

Specifically, in this research, the following goals were established:

- Select the parameters to influence the stability and integrity of the monomolecular surfactant film;

- Characterize interfacial films of solutions by obtaining the Langmuir isotherms in different conditions;

- Investigate the relationship between the type of film formed and its correlation with the emulsion stability;

- Correlate experimental data using an adaptation of a 2-D PC-SAFT equation of state in the McMillan-Mayer framework.

1.3 THESIS ORGANIZATION

This thesis is divided into five chapters: Chapter 2 introduces a brief review of the literature on emulsions, emulsion destabilization mechanisms, Langmuir monolayer, surfactant properties, analysis of phases, and phase transitions. Chapter 3 demonstrates the methodology used in this research. The experimental and theorical results as well as its discussions are presented in Chapter IV. The conclusions followed by the suggestions are presented in Chapter V.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

This chapter introduces a bibliographic review on emulsions, the cosmetics industry and the components used in cosmetic emulsions, focusing on the surfactants behavior and the emulsion destabilization mechanisms. The monomolecular films formed will also be explained with their phases and phases transitions. The science behind the surfactants will be briefly demonstrated as well as the stability tests recommended by ANVISA to the cosmetics companies to ensure the safety and integrity of their products.

The emulsions characteristics will be introduced as well as its formation by thermodynamics explanation, the factors that affect the stability of emulsions and how through the Langmuir monolayers we can identify the mechanical stability of the films.

2.2 COSMETICS

Cleopatra is the oldest example of an icon of beauty that fascinates the world. Historically, Egypt has become the hub of a true beauty trade. For example, Hatshepsut, the first pharaoh woman in history whose name means “The First of Noble Ladies” who reigned from 1479 to 1458 b.C was like Cleopatra aware of the importance of fragrances and cosmetics and did not just look at them as instruments of seduction. Beauty was an expression of divinity. (TUNGATE, 2013).

The word cosmetic derives from the Greek expression kosmetike tekhne, which means “the art of clothing and ornaments” whose history coincides with the real history and development of humanity (BIZ; ANTIGUIDADE; GR, 2014).

According to ANVISA, the definition of cosmetics is “substances or preparations that are applied externally on the human body and in the oral cavity, including dentures, for cleaning, care, to influence the appearance or odor of the body, unless if they are interpreted to treat or remove disease, illness, bodily injury or health distress. Exception: products to influence the shape of the body” (“Portal Anvisa”, [s.d.]).

Nowadays, life without cosmetics cannot be imagined; creams, shampoos, for example, are part of the beauty and hygiene routine of the population. Unlike in the past, the complexity behind the development of products that are found on the market involves science and innovation. Over the years, the personal care sector has used well-being, treatment, and science to develop new products to meet consumers’ needs (CONNECT, 2014).

In general, cosmetic products are composed of vehicles (the most used is water), surfactants, emollients, thickeners, actives, and preservatives independent if the product is for skin or hair and its galenical forms (liquid, cream, gel). The choice of the use of the ingredients is made according to the functional properties of the ingredients that are derived from their structures and chemical properties (RACINE, 2016).

The choice of the ingredients is especially important because even within the same surfactant classification, for example, anionic, they are used for different purposes and consequently in different products. This class of surfactants are used mainly in products that provide detergency and cleaning, such as shampoo and facial liquid soap. Despite this, the same surfactant used for skin products is not necessarily used for hair due to many aspects such as allergenic potential and detergent power. An internet search of shampoo products that are already on the market it is possible to observe that the anionic surfactants such as Sodium Laureth Sulfate, Sodium Lauryl Sulfate and Cocamidopropyl Betaine are widely used in shampoo. Also, for shampoo but for baby products a widely used surfactant is Coco glucoside which is non-ionic and is known to be a milder surfactant. Sodium cetyl phosphate, for example, is a recognized anionic O/W emulsifier and widely used for skin care products and sunscreens (RACINE, 2016).

There are many cosmetic ingredients and even though for many types of cosmetic products some ingredients are more used than others it is still an area that has a lot to discover about ingredients behavior. Some examples of ingredients widely used in the industry for cosmetic products at Table 2.1:

Category	Examples of ingredients	Example of cosmetic product
Tensoatifs	**Anionic**	
	Potassium cetyl phosphate	Shampoo
	Sodium lauryl sulfate	Liquid soap
	Sarcosinates	Cleansing lotion
	Coco isethionates	
	Cationic	
	Behentrimonium chloride	Hair conditioner
	Quaternary esters	Deodorants
	Dialkyl dimethyl ammonium chloride	
	Non ionic	
	Sucrose esters	Shampoo
	Sorbitan esters	Sunscreen
	Glyceryl mono and distearate	Liquid soap
	Ethoxylated fatty acids	Deodorants
	Amphoteric	
	Coconut Betaine	Shampoo
	Cocoamidopropyl betaine	Liquid soap
Emollients	Myristyl myristate	W/O and O/W creams and lotions
	Carnauba wax	
	Fatty carboxylic acids	Sunscreen
	Grape oil	
Preservatives	Benzyl acid	Sunscreen
	Capril glycol	Liquid soap
	Pentylene glycol	Shampoo
Thickeners	Xanthan gum	Any formula that needs to increase viscosity
	Hydroethylcellulose	
	Starch	
	Bentonite	

Table 2.1. Example of the most used ingredients in cosmetic products
Source: Adapted from (RACINE, 2016).

2.3 COLLOIDS

Colloid science has been observed for thousands of years. The Bible and other ancient religious writings refer to strange clouds and mists of a colloidal nature (aerosols) (MYERS, 1999). Colloids, from the Greek kólla, glue + eîdos, from the classical definition are heterogeneous mixtures where one of the phases (solid, liquid, or gaseous), is dispersed in another phase (liquid or gaseous solid) called continuous phase and where at least one of the phases has colloidal dimension (1 to 1000 nm). Due to the advancement of many analytical techniques, mainly for measuring force between two surfaces, colloids have advanced and today follow a modern definition associated with properties due to the increase in area. (PERCEBOM, 2020)

The previous colloids classification is still used today and it is done according to the physical state of the matter of the dispersed and dispersing phases, presenting 8 types of colloidal systems, as exemplified in Table 2.2 (TADROS, 2005).

		Dispersed phase		
		Solid	Liquid	Gas
Continous phase	Solid	Solid sols	Gel	Solid foam
	Liquid	Sols	Emulsion	Foam
	Gas	Solid erosol	Aerosol	-

Table 2.2. Colloids classification
Source: Adapted from TADROS, 2005

But why colloids are used for cosmetics products? The colloids due to the variation of the surface area allows the mixing of ingredients that would be immiscible. This new disposition of the ingredients, in addition to influencing new rheological properties of the mixture and which directly impacts the applications and the sensory of the product, also impacts the visual and the possibility of its use for protection from UV radiation, for example, through absorption and scattering of light (PERCEBOM, 2020).

However, the increase of surface area generates a challenge of maintaining the mixture without it returning to its previous phase separation state. This challenge occurs because of the intermolecular forces. The intermolecular forces can be attractive when there are opposite electrostatic charges, and repulsive, when there are equal electrostatic charges or due to steric impediment. In general, molecules attract each other due to polarizability, the ability of an electronic cloud to move. Even though the molecules tend to mix themselves where they do the same interactions, they can also mix themselves where they do different interactions, but the intensities will not be the same (RACINE, 2016).

The intermolecular forces are van der Waals forces (ion-dipole, dipole-dipole, induced dipole-dipole, and induced dipole-induced dipole) and hydrogen interactions. All these forces are attractive but in a different intensity as aforementioned.

In the surface the unbalanced of intermolecular interactions is big, so the surface is a region where few molecules want to be and consequently a high surface tension is generated. This means that if the surface tension is high, the surface area must be small. This directly impacts the existence of the colloid once it needs a high surface area to exist and to be stable over the time. This shows the high importance of the interface in the study of colloids (PERCEBOM, 2020).

Besides the cosmetics products, the colloidal system is important for other different industries such as food, painting, petroleum.... The best-known examples of colloidal systems are milk, whipped cream, fog, mayonnaise, smoke, gelatin, and various cosmetics, including moisturizing creams, sunscreens, shampoo, and conditioners. (SHCHUKIN et al., 2001)

For products exist as we know them today, this surface tension needs to be reduced and this will be possible through a molecule that will be in the surface: the surfactants.

2.4 SURFACTANTS

The difference of products from the time of the pharaohs to the present day is the diversity, complexity, and number of ingredients used in the products. One of the reasons why this was possible was scientific advances in the understanding of interfacial phenomena which contributed, among other issues, the use of surfactants. (TUNGATE, 2013).

Surfactants are surface-active agents, substances that tend to adsorb on surfaces and interfaces (LEE et al., 2013). Structurally, they are amphiphilic substances due their specific chemical structure that has a polar head also called hydrophilic and a nonpolar or hydrophobic tail, shown in Figure 2.1. Surfactants have an affinity for oily and aqueous phases, acting fundamentally to help the formation and stabilization of emulsions. They may act as detergents, emulsifiers, and soap. (LEE et al., 2013).

The hydrophilic, polar, water-soluble head is formed mostly by acidic or basic groups (examples: amines, carboxyls and sulfates). The hydrophobic, nonpolar tail, insoluble in water and soluble in oils, is most often formed by groups of aliphatic, linear, or branched hydrocarbons, for example.

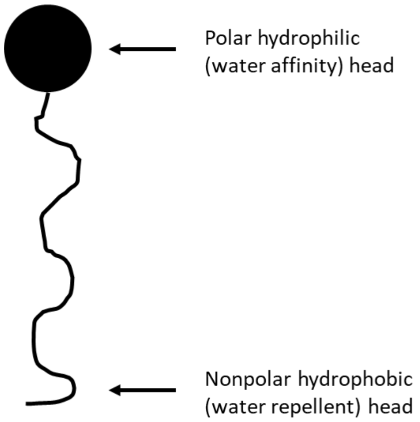


Figure 2.1. Surfactants general structure
Source: Adapted from ("University of Bristol - School of chemistry", 2020)

2.4.1 SURFACTANTS CLASSIFICATION

The different charges of the polar head generate different classifications for the surfactants.

When in aqueous solution, surfactants undergo dissociation. When dissociated and the hydrophilic polar head of the ionic molecule has a negative charge, it is classified as anionic. Generally, their cations are inorganic ions such as calcium and sodium, for example. These surfactants are generally better than the others in terms of detergency and foaming power. On the other hand, when the hydrophilic, polar group of the molecule has a positive charge, it is classified as cationic. They are widely used in hair conditioners, for example. When in aqueous solution, surfactants can ionize to produce anions or cations, depending on the solution pH. In this case, if in basic medium they behave like anionic surfactants and in acidic medium, like cationic surfactants (RACINE, 2016).

Some molecules in aqueous solution do not dissociate and its solubility in water is due to the hydration of hydrophilic groups via hydrogen bonds. The HBL (hydrophilic-lipophilic balance) is an indicator for nonionic surfactants of their emulsification behavior. The predominance of hydrophilic emulsifiers facilitates the formation of the O/W emulsion. The lipophilic fraction of the surfactant molecule is adsorbed in the oil droplets, while the hydrophilic or polar head of the molecule remains hydrated by water. In this way, the oil droplets are as if they were encompassed by the surfactant molecules that form a molecular film, packaged in the O/W interface (RACINE, 2016).

2.4.2 SURFACTANTS PROPERTIES

As previous explained, surfactants have specific characteristics that differ from other substances due to their chemical structures. The presence of a polar head and nonpolar tail results in the interaction of similar ones, consequently allowing surfactants to self-assemble and form structures called micelles. These structures start to be formed above a concentration called a critical micellar concentration - CMC (LOH; BRINATTI; TAM, 2016).

2.4.2.1 SURFACE AND INTERFACIAL TENSION

The surface activity of surfactants is due to the adsorption, concentration, and orientation of their molecules at the interfaces. In a liquid-gas system, for example, the addition of surfactant causes deep changes on its surface. The surface is the border region between two phases where there is an imbalance of forces. It occurs because unlike what occurs inside the medium phase, on the surface of a liquid-gas interface the attractive forces have no intensity, and consequently, the resulting force is not zero (OPAWALE; BURGESS, 1998).

Surface tension happens due to the unbalanced attraction of surface molecules, as shown in Figure 2.2. Surface tension is one of the properties that determines the size of the drop itself. The greater the force of attraction, the greater the capacity of the molecules to cluster in a given volume, which is one of the reasons that leads to the increase of the drop. Therefore, liquids (of similar density) with high surface tension form larger drops than liquids of low surface tension (JIAO; RHODES; BURGESS, 2002).

As a result, the surfactant tends to migrate to the air/water interface, accumulate and orient themselves in this region, with the hydrophobic tail oriented to the air. Due to the surfactants ability to adhere to surfaces, they can reduce the surface tension that exists between water and air affecting its intermolecular interactions. That is because the water does not want to be exposed to the air. With surfactants it is easier to increase the surface area since the water does not need to be exposed as much to the air. The hydrophilic group of the surfactant molecules keeps them in contact with the liquid and is one factor that contribute to prevent phase separation (TADROS, 2005).

The longer the hydrophobic chain of the surfactant the higher the ability to reduce the surface tension of O/W emulsions. When the hydrophobic tail is larger, CMC decreases, because there are more parts that have no affinity for water, so the molecules tend to form micelles before. From a chemical perspective, it can be said that it is as if the molecules were less soluble. (TADROS, 2005).

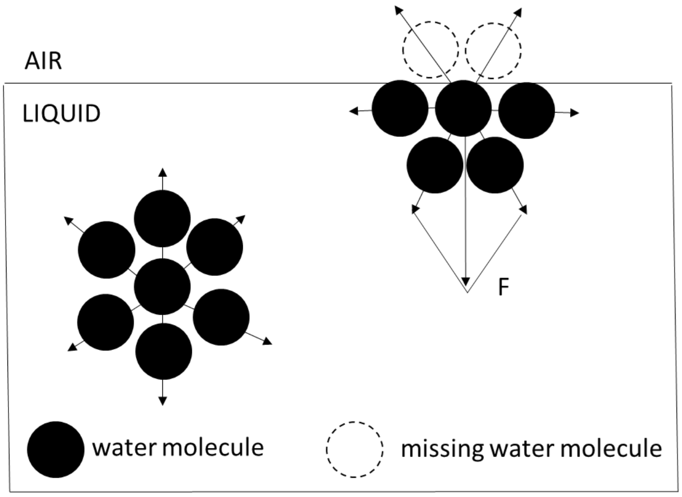


Figure 2.2. Surface tension schema
Source: Adapted from (“SITA - process solutions”, 2020)

2.4.2.2 CRITICAL MICELLAR CONCENTRATION - CMC

The migration of the surfactant to the surface happens until it is saturated, and thus the limit concentration of surfactant molecules on the surface is reached. From this point, there is the formation of molecular aggregates of colloidal dimensions inside the solution called micelles as shown in Figure 2.3. The concentration of the beginning of micelle formation is defined as the critical micellar concentration (CMC), determined by the inflection point in a curve of surface tension curve versus solution concentration (MARTINS, 2011).

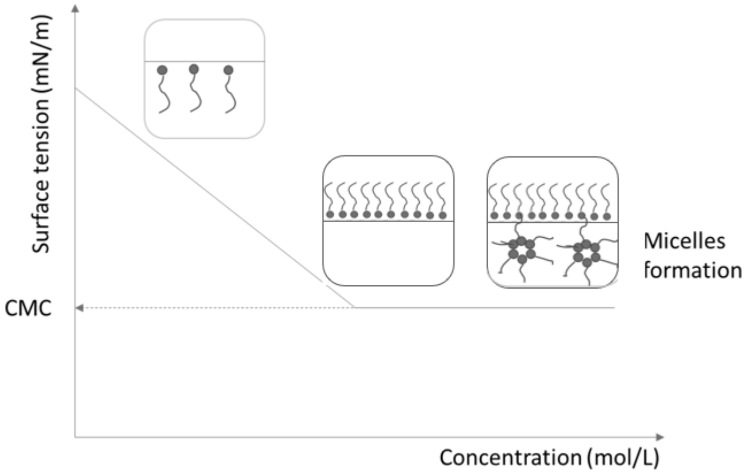


Figure 2.3. Obtaining critical micellar concentration (CMC)
Source: Adapted from (FAYET, 2018)

When the CMC is passed, from this moment on, most part of the added surfactants will form micelles. The micelles can present different structures, some of them are shown in Figure 2.4. However, there will also be free surfactants in the medium that had been dissolved before. The sooner micelles form (lower CMC) the less surfactants will be free in the medium. This impact, among other aspects, irritability when using a product, for example (PERCEBOM, 2020).

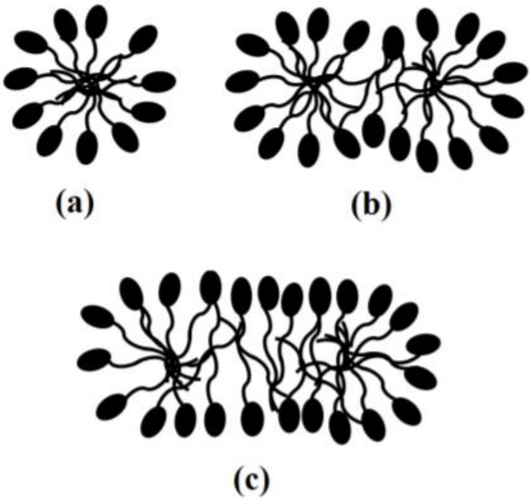


Figure 2.4. Micelle geometry- a. spherical, b.globular, c.spherocylindrical
Source: (SANTOS, 2014)

2.5 EMULSIONS

Emulsions are metastable that are systems out of their most stable equilibrium state, formed by two immiscible liquids, one dispersed in the other (GOIBIER et al., 2017). Usually, one of the liquids is the water (aqueous phase), and the other is an oil or other fatty derivative that is insoluble in water (oily phase). (GANLEY; RYAN; VAN DUIJNEVELDT, 2017). Depending on which liquid is in the dispersed and dispersing phase, emulsions can be represented as O/W (oil-in-water emulsion, where the dispersed phase is oil and the continuous one is aqueous) or W/O (water-in-oil emulsion, where the dispersed phase is water and the continuous phase is oil) as shown in Figure 2.5 (GILBERT et al., 2013).

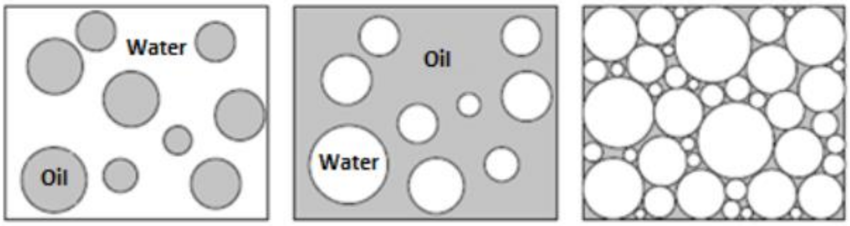


Figure 2.5. Emulsions O / W and W / O
Source: Adapted from BUTT, H., GRAF, K., & KAPPL, 2003

The huge use of emulsions in different industries as mentioned in Table 2.3 confirms the importance to best understanding of various emulsion issues, such as their stability. (TADROS, 2009). Among the industries that use emulsions a lot, the cosmetics industry is present. Despite considerable available literature about emulsions, there is not much data regarding the mechanical stability through the Langmuir isotherm characterization technique, taking the idea of this research unique.

INDUSTRIAL APPLICATIONS OF EMULSIONS	
Food industry	Mayonnaise, drinks and sauces
Pharmaceutical industry	Emulsion
Paint industry	Latex emulsions
Agroindustry	Self-emulsions in the oil
Emulsions in the oil industry	Crude oils removed from oil ell containing drops of water.

Table 2.3. Industrial applications of emulsions
Source: Adapted from TADROS, 2009

2.5.1 EMULSIONS FORMATION

Emulsification implies the creation of interfaces, and consequently, a high interfacial area between the two immiscible liquids is necessary. (BECHER, 1985). The interface is the transition region of the properties from one phase to another (RAHBAR; AYATOLLAHI; GHATEE, 2010).

To bring a given molecule from the bulk to the surface, work must be done. The minimum work required to increase the interfacial area follows the Equation 2.1 (PHILIP C. MYINT ABBAS FIROOZABADI, 2015) :

$$W = \sigma_i \Delta \mathrm{A}$$

Equation 2.1: work need to bring a molecule from the bulk to the interface

where W is the minimum work to increase the interfacial area, σ_i is the interfacial tension and $\Delta \mathrm{A}$ is the change in the interfacial area.

The formation of the interface between the continuous and dispersed phases causes an increase in the free energy of the system. Therefore, from the thermodynamic point of view, emulsions are unstable systems; they do not form spontaneously. Consequently, the formation of emulsions needs adding energy to occur. There is a natural tendency of the liquid-liquid system to segregate, with a reduction in the interfacial area and, consequently, interfacial energy (ERBIL, 2006).

2.5.2 EMULSIONS STABILITY

The interactions between particles manage various phenomena of colloidal systems, and for the system to remain stable for a specific time, substances such as surfactants and thickeners are added to keep the systems stable (GANLEY; RYAN; VAN DUIJNEVELDT, 2017).

The first successful description of colloidal stability interactions was made in Russia (Derjaguin & Landau 1941) and Netherlands (Verwey & Overbeek 1948), resulting in the DLVO theory (Derjaguin-Landau-Verwey-Overbeek). However, this theory has limitations as it does not consider other forces such as steric forces and hydrophobic interactions. Today, the industry continues mainly with empirical tests to analyze emulsions stability (IN, 1999).

2.5.2.1 FACTORS THAT AFFECTS THE EMULSIONS STABILTY

The most mentioned factors related to affecting stability are:

- Physical nature of the interfacial film: the characteristic of the interfacial film created at the interface of the liquid-liquid and gas-liquid surfaces by surfactants affects the stability of the emulsion. The created film generates a mechanical barrier between the phases, which depending on its characteristics such as rigidity and flexibility, impact its short and long-term break (OPAWALE; BURGESS, 1998).

- The existence of electrical and steric barriers against the coalescence of drops: the steric impediment contributes to the bigger or smaller exposure of particles in the medium. The higher the steric impediment, the less the possibility of particle organization. Besides, the bridge effect (low coverage) between the molecules is reduced. The electrical barriers act in the double electrical layer of the particles that through repulsion repel aggregation (BECHER, [s.d.]).

- Formation of liquid crystals in the interfacial film: When the concentration of surfactants increases a lot, there is a moment when the micelles no longer fit in the system. With the increase of the volumetric fraction occupied by the micelles, a self-organization is necessary. Consequently, liquid crystalline structures with the capacity to flow are formed. Crystals have small bonds and therefore they are super hard. These structures maintain characteristic properties of movement attributed to liquids and interaction between molecules attributed to solids. Its presence impacts on the stiffness of the interfacial films (GOIBIER et al., 2017).

- The viscosity of the continuous phase: high viscosities act as barriers for phase mobility and consequent impediment for aggregation of the particles (CUI, 2005).

- The droplet’s size distribution: The size of the droplets is directly associated with the shear intensity used to produce the emulsion. The higher the number of drops, the greater the area of the system, and consequently, the higher is energy the system has (FRELICHOWSKA; BOLZINGER; CHEVALIER, 2010). However, for bigger drops, the speed, either of sedimentation or flotation, increases. Besides, the droplet size distribution also influences the stability of the system. A uniform distribution of droplets decreases the possibility of flocculation (HUANG; KAKUDA; CUI, 2001)

- The relative volume fraction of the phases: Depending on the prepared emulsion system, the volume between the aqueous and oily phases changes. For sunscreen type formulations, for example due to the presence of a high concentration of organic filters the oil phase can reach 50% of the system, generating high complexity and requiring emulsifiers that stabilize the emulsion.
- Temperature: the increase of temperature reduces the viscosity of an emulsion system because the kinetic energy of the particles rises and consequently increases the frequency of shocks between the particles and conducts to system instability. Besides, this parameter can increase or decrease the solubility of the surfactant in the medium impacting on the emulsion stability (FIROOZ; CHEN, 2012).

The physical-chemical mechanisms are shown in Figure 2.6. The phase separation described in the literature are coalescence, Ostwald ripening, flocculation, sedimentation, and creaming.

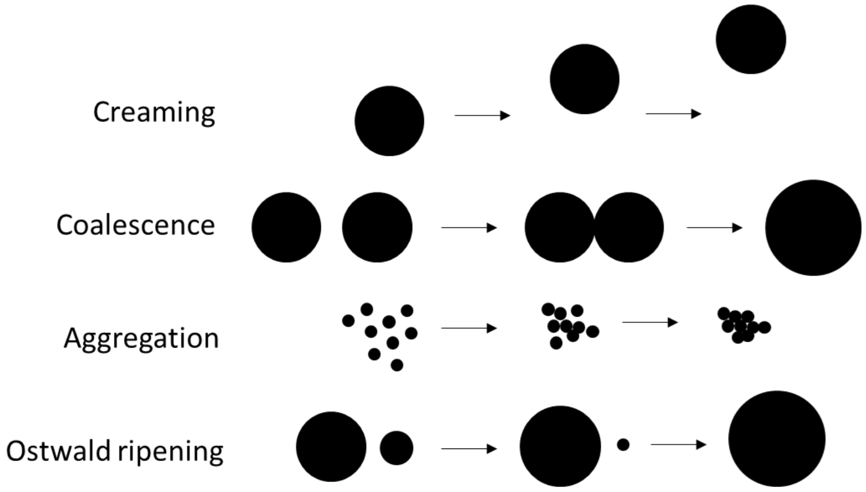


Figure 2.6. Mechanisms of emulsions nonstable
Source: Adapted from (FEDRICK; WALSTRA; DEWETTINCK, 2010)

2.5.2.1.1 COASLESCENCE

Coalescence happens when two or more drops form bigger drops with a smaller total interfacial area. There is an increase in the average particle size by breaking smaller drops to become bigger drops (S.S DAVIS, H.P ROUND, 1981) (A.S.KABAL’NOV, A.V.PERTZOV, 1987).

An example of this phenomenon is called Gibbs-Marangoni effect. The rupture of the film is generated by thinning it, which generates an increase in local surface tension because the concentration of surfactants is reduced. With these surfactant imbalances a surface tension gradient is generated and consequently, they migrate from more concentrated regions (with less surface tension) to less concentrated regions (with higher surface tension). The diffusion of compounds at the interfacial film due to the interfacial-tension gradient. An example of this phenomenon is seen in wine glasses being called wine tears and in the stability of soap bubbles too (FRANZOL; REZENDE, 2015).

2.5.2.1.2 OSTWALD RIPENING

As previous mentioned, in the modern colloid classification the particle size scale is not so used. However, when we discuss about the destabilization phenomena, some uses of this concept is still common. The coalescence that occurs most by breaking the film that separates two drops forming a larger film is different from Oswald's ripening. Basically, because Oswald ripening is associated with a disproportionate size of particles in the medium, considering as the smaller ones even being on a nanoscale. We can also explain it by Laplace's law, Equation 2.2:

$$\Delta P = \frac{2\gamma}{a'}$$

Equation 2.2: Laplace’s equation

where P is pressure, γ is the surface tension and a' is the bubble radius. With a non-uniform drop distribution, the system presents small and large drops disproportionately. In this case, smaller droplets have a higher pressure due to their larger curvature. This produces a net flow of oil from small towards big droplets. In this way, the larger particles will grow due to this solubility of the smaller particles, until complete disappearance, by mass transfer (A.S.KABAL’NOV, A.V.PERTZOV, 1987) (S.S DAVIS, H.P ROUND, 1981).

2.5.2.1.3 FLOCCULATION

The particles present in the emulsion can be electrically charged positively or negatively depending on their chemical nature and the mechanical phenomena to which they were subjected. When the charges are totally or partially neutralized, the drops approach to form aggregates without compromising the individual integrity of the drops. Despite being reversible if the interfacial film is not strong enough it can evolve into a coalescence, an irreversible phenomenon. (A.S.KABAL’NOV, A.V.PERTZOV, 1987) (S.S DAVIS, H.P ROUND, 1981)

2.5.2.1.4 SEDIMENTATION AND CREAMING

The driving force for sedimentation and creaming is the difference in density between the two phases. The drops aggregate without breaking the interfacial film that separates the drops. The aggregation moves to the top of the emulsion (creaming), or to the bottom (sedimentation) depending on the substance density.

2.6 STABILITY OF COSMETIC PRODUCTS – ANVISA

As mentioned at the beginning of this work, the National Health Surveillance Agency, ANVISA prepared a guide for the stability of cosmetic products to help companies to carry out their stability studies compliance with the law requirements (ANVISA, 2004).

Stability tests should be conducted under conditions that allow the information on product stability to be provided in the shortest possible time. Samples must be conducted in a study under conditions that simulate any change that could happen during the life cycle of the product. The sequence of studies (preliminary, accelerated, and off-the-shelf) showed in the guide from ANVISA aims to evaluate the formulation in stages, looking for evidence that leads to decisions about its stability (ANVISA, 2004).

Each component of the formula can affect the stability of a product. The manufacturing process, the packaging material, and the environmental as well as transport conditions can influence the stability of the product. The most common storage conditions for the samples are temperature (ambient, high, low), exposure to light, and freezing-thawing cycles during a specific time (ANVISA, 2004).

- Temperatures

For the analysis of the impact of temperature on product stability, the guide recommends that the following high temperatures be used in an accelerated laboratory oven study in different times are:

Laboratory oven: T = 37 ± 2°C
Laboratory oven: T = 40 ± 2°C
Laboratory oven: T = 45 ± 2°C
Laboratory oven: T = 50 ± 2°C

Under these conditions, the occurrence of physical-chemical changes is frequent and even expected, so the results obtained must be carefully evaluated.

Evaluation at low temperature should be also evaluated. The recommended low temperatures to be used in an accelerated laboratory oven study in different times are:

Refrigerator: T = 5 ± 2°C
Freezer: T = –5 ± 2°C or T = –10 ± 2°C

The formula must present the same analytical results after the accelerated study. In general, the following analytical analysis are done:

- Organoleptic parameters: appearance, color, odor, and taste, when applicable.

- Physical-chemical parameters: pH value, viscosity, density, and in some cases, dosage of some ingredients in the formulation.

- Microbiological parameters: count microbial and challenge test.

Before starting the stability studies for a pre-analysis of product is behavior it is recommended to submit the product to the centrifugation test (suggested to centrifuge a sample at 3,000 rpm for 30 minutes). After this, the product must remain stable and any sign of instability indicates the need for reformulation. Otherwise, it is possible to move further with other tests (ANVISA, 2004).

A reference sample, also called standard, should be keep at room temperature and protected from light. The samples are evaluated by the analytical analysis previous mentioned and compared to the standard sample and products considered “reference”, submitted to the same test conditions. Generally, acceptance limits are defined for the evaluated parameters, and the standard sample should remain unchanged throughout the product's usefulness (ANVISA, 2004).

The correspondence between the data and its interpretation must be relative, considering that in practice the objectives and characteristics of each product (or category) are quite different. The shelf life period can be estimated through the stability studies, and its confirmation must be carried out through the shelf test (ANVISA, 2004).

2.7 MONOMOLECULAR FILMS

Amphiphilic molecules can orient themselves at the interface of an aqueous subphase with a gas phase or a liquid phase to minimize its Gibbs energy. The resulting interfacial film is the thickness of a molecule and is commonly called a "monomolecular layer" or simply "monolayer" which schema is shown in Figure 2.7. The name “Langmuir monolayer” was given in honor of scientist Irving Langmuir, whose work in this area was pioneering. (LEE, 2008)

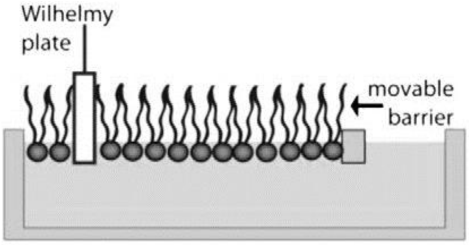


Figure 2.7. Representation of aqueous dispersions with amphiphilic molecules monolayers on an aqueous subphase
Source: (STEFANIU; BREZESINSKI; MÖHWALD, 2014)

2.8 PROPERTIES OF MONOMOLECULAR FILMS

A wide variety of experimental techniques have been employed in the study of Langmuir films. The most common properties: surface tension, surface pressure and surface potential.

2.8.1 SURFACE PRESSURE

The surface pressure (π) is defined as the difference between the surface tension between a sub-phase in the absence of a substance (the sub-phase is usually water, γ_0, which is equal to 72.8 mN m^{-1} at 25ºC) and the surface tension of the sub-phase with the substance (γ), (ZHAO; EISENTHAL, 1995) as shown in Equation 2.3:

$$\pi = \gamma_0 - \gamma$$

Equation 2.3: surface pressure equation

where γ_0 is the surface tension of the subphase in the absence of surfactant, and γ is the surface tension with the surfactant.

This spreading pressure can be obtained by measuring the force per unit length on the energy per area on a barrier kept fixed by means of an electrobalance with the Wilhelmy plate method shown in Figure 2.8, among other methods.

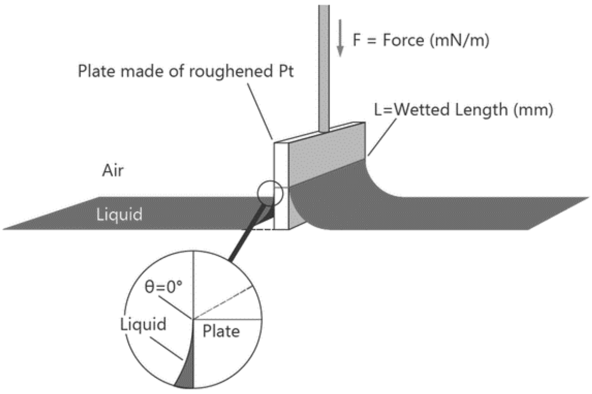


Figure 2.8. Representation of Wilhelmy plate method
Source: (KRUSS, [s.d.])

The minimum pressure measured is zero, and the maximum - for very stable monolayers - approaches the surface tension of the sub-phase. A surface pressure vs. area curve per molecule is the two-dimensional analog of a pressure-volume isotherm (MYERS, 1999b).

2.8.2 SURFACE POTENTIAL (ΔV)

This potential is defined as the difference in electrical potential between an aqueous surface covered with Langmuir film and a surface without a monolayer. The potential difference (ΔV) arises due to the presence of permanent electrical dipoles of the material that makes up the film or the double layer formed at the film / water interface (MYERS, 1999b).

2.9 COMPRESSION ISOTHERMS

Langmuir films can be generated using the Langmuir trough, where a solution is applied to the surface of the aqueous subphase with a micropipette. An example of this isotherm is presented in Figure 2.9. The phases of a monolayer in the generated isotherms vary from substance to substance. The distribution of molecules on the surface is correlated with the thermodynamic behavior of the physical, solid, liquid, and gas states (PICHOT; WATSON; NORTON, 2013).

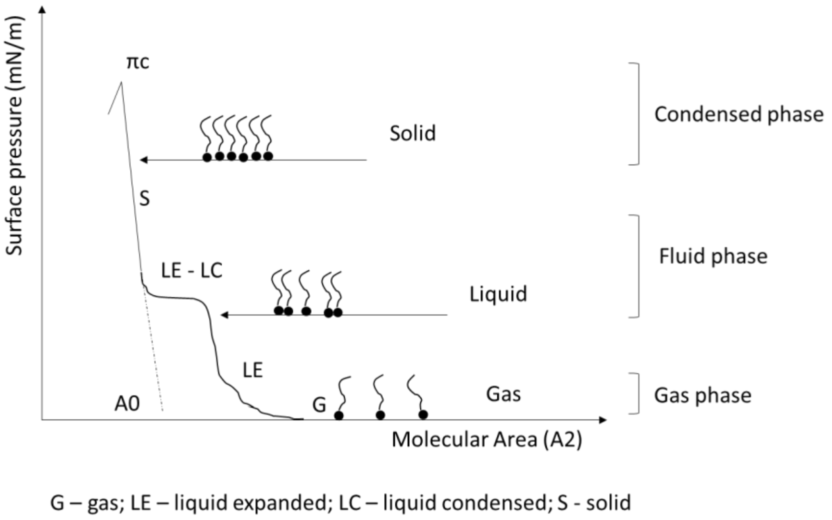


Figure 2.9. Example of the isotherm of a stearic acid in pure water and its respective physical phase transition states.

Source: Adapted from (ALMEIDA, 2012)

When a film is compressed, the molecules can behave like a two-dimensional fluid. At low spreading pressure, the fluid behaves like a two-dimensional gas. As the compression continues, the molecular area decreases, the surface pressure increases, generating orders, and the fluid behavior approaches a liquid-like phase. The molecules then move closer, creating structures, until they behave as a solid-state. At some point, the film is already so densely packed that the compression leads to a collapse pressure, π_c. In this collapse, the monolayer molecules begin to overlap, and the film is no longer monolayer once disordered multilayers are generated (FIROOZ; CHEN, 2012).

Thus, the π - A isotherms provide information on the orientation and conformational transformations of molecules in the two-dimensional system on the existence of phases and their transitions (gaseous, liquid-expanded, liquid-condensed, solid), and with these data it is possible infer the mechanical behavior of the obtained monomolecular film. (GIRARD-EGROT et al., 2005). The shape of the isotherm depends on the temperature and the substances that are part of the film. The main types of isotherms will be discussed in the next topics.

2.9.1 Ideal gas (G)

Thermodynamically, ideal gases are defined by Equation 2.4. This equation is defined in the Lewis-Randall framework, where the vacuum is the medium.

$$PV = NK_B T$$

Equation 2.4: State equation of perfect gases (Clapeyron equation)
Source: PETTY, 1996

where P is the pressure, V the total volume, N is the number of molecules, K_B is the Boltzmann constant, and T is the absolute temperature.

The ideal gas equation-of-state can be expressed by the McMillan-Mayer framework, where the interface is the interface without surfactant in the medium as shown in Equation 2.5:

$$\pi \bar{A} = K_B T$$

Equation 2.5: Ideal gas equation adapted to Langmuir isotherms
Source: PETTY, 1996

where $\bar{A}$ is the area occupied by a molecule, K_B is the Boltzmann constant and T is the absolute temperature.

Once the molecules are far from each other in the gas phase, the interaction force between them is small, and consequently, this phase has a low surface pressure for a high molecular area.

2.9.2 Liquid films (L)

The molecules in the film come together in such and show a phase transition from gas-like to liquid-like due to significant attractive interactions (PICHOT; WATSON; NORTON, 2013).

Two types of liquid phases are described in the literature and shown in Figure 2.10:

- Expanded liquid (LE or L1): the molecules are close to each other, but there is no defined order.

- Condensed liquid (LC or L2): the expanded liquid begins to condense, and this transition can be or first or second-order. There is an ongoing discussion in the literature about the nature of the LE-LC phase transition. The group defend first-order phase transition when a horizontal plateau would be observed in an π-Ā isotherm. The other group defend second-order phase transition when non-horizontal slope on the π-A curve is observed.

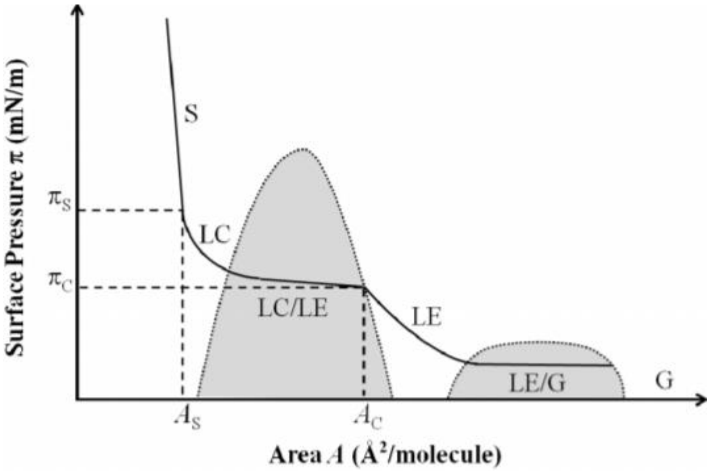


Figure 2.10. Representation of phospholipid surface pressure (π) vs. area per molecule (A) isotherm where S is solid phase, LC is condensed liquid phase, LC/LE is condensed liquid/expanded liquid phase transition, LE is expanded liquid phase, LE /G is expanded liquid/gas phase transition and G is gas phase

Source: (PICHOT; WATSON; NORTON, 2013)

In classical thermodynamics, the equation of state used to describe the properties of fluids (vapor and liquid) are cubic equations, such as van der Waals, Peng-Robinson, Soave-Redlich-Kwong (SRK), among others. Using the van der Waals equation of state, for example, we would have Equation 2.6:

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

Equation 2.6: The van der Waals Equation, in Lewis-Randall framework

Where P is the pressure, $\bar{V}$ the molar total volume, R is the universal gas constant, a is the measure of the attraction between the particles and b represents the volume excluded by the particles. a and b are the constants that are defined as: a = (27 (RT_c)) / ($64P_c$) and b = (RT_c) / (8 P_c), where T_c and P_c are the critical temperature and pressure.

This equation can describe first-order phase transition, such as vapor-liquid. This equation can be applied to describe first-order transition in the film, using the McMillan-Mayer framework such as in Equation 2.7:

$$\pi = \frac{K_B T}{\bar{A} - b} - \frac{a}{\bar{A}^2}$$

Equation 2.7: The van der Waals Equation in McMillen-Mayer framework

2.9.3 Solid films (S)

As the film is compressed, the molecular area is reduced. The interaction between surfactants reaches a point just to collapse as shown in Figure 2.11 and the packing of monolayer molecules is maximum the phase is correspondent to a solid film. From this point on, the graphs of the π-A isotherm are linear. Extrapolation to zero pressure of the film results in a surface that corresponds to a specific molecular area.

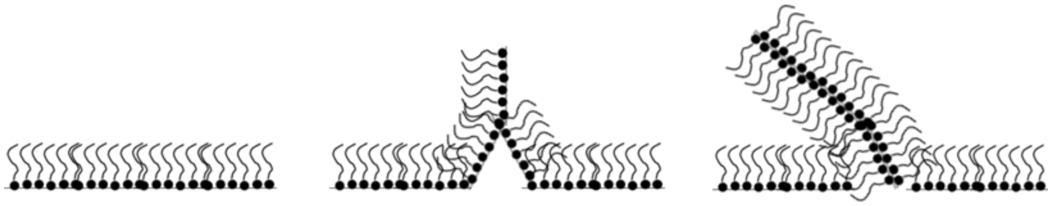


Figure 2.11. Collapsed monolayers
Source: Adapted from (PHAN; LEE; SHIN, 2016)

There are not many studies in the literature that do experimental tests to obtain Langmuir monolayers and correlate the obtained isotherms with emulsion stability.

The impact of interfacial strength in O/W emulsions associated with its stability has been studied in the literature. In these investigations, several techniques such as microscopy and FTIR, for example, were used to evaluate the interfacial area (OPAWALE; BURGESS, 1998) (JIAO;

RHODES; BURGESS, 2002) (LAD et al., 2003).

WEI et al., 2018 used molecular dynamics simulation to analyze sodium dodecyl sulfate (SDS) phase transitions. Based on the results obtained, they were able to relate the different 2D phases of the isotherm and the surfactant alignment in the interfacial film.

MARCZAK et al., 2016 modeled experimental results of π-A isotherms to better understand the mechanism of the interfacial film formation. The results obtained show that the model proposed can be used as a tool for an increasing number of applications, identifying the construction of particle films.

STHOER and TYRODE, 2019 analyzed the theoretical and experimental models in different conditions such as temperature, presence of electrolytes, and pH. Compared to theoretical models, the experimental results were consistent only with the Gouy-Chapman predictions at low charge densities. They used the most recent model Boltzmann-Poisson modified (MPB) that predicted the correct surface potential dependence, partial deprotonation of the monolayer due to condensation of hydronium ions as well as the pH dependence.

2.10. THERMODYNAMIC MODELS

As mentioned earlier in the π-A isotherms, the phase transitions are represented by the behavior of the phases separately. There is no thermodynamic model that describes the phase transition accurately. Another constraint today, regarding the thermodynamic equations that exist, is that if there is more than one liquid-liquid transition in the system, the cubic equations cannot predict them. Besides, it is necessary to improve the methodology to generate second-order transition using equations of state.

There is a discussion in the literature about the order of the LE-LC transition, which can be first-order, in which horizontal area an π-A isotherm would be observed or if it would be a second-order phase transition, leading to a non-horizontal slope in the curve π-A (ZUO et al., 2016) (VOLLHARDT; FAINERMAN; SIEGEL, 2000).

The most recent thermodynamic models propose to add the hydrogen bonds contribution. These models are called “association models” and they are divided chemical theories, network theories (quasi-chemical), and perturbation theories. They are used to describe phase equilibrium mainly to mixtures with polar compounds or other compounds with a strong chemical association.

One way to explain “association models” is to use mechanical statistical methods, such as the theory of perturbations. In 1984 Wertheim presented a theory of perturbation that accounted for hydrogen bonds based on statistical mechanics. In 1989, CHAPMAN, et al. presented the theory and form of state Equation that was called Statistical Associating Fluid Theory - SAFT. In this theory, the effects of hydrogen bonds were presented as additives in the Helmholtz free energy. Over the years, several other models were developed from SAFT. The one that stood out the most was PC-SAFT (GROSS and SADOWSKI, 2001).

A proposal to analyze the phase transition is to describe the phase behavior at the air / water interface of the Langmuir monolayer. Our approach is an adaptation of the PC-SAFT state equation to a two-dimensional model.

The PC-SAFT Equation is based on a hard-sphere chain fluid as a reference fluid. For a two-dimensional structure, this reference fluid can be considered composed of chains of hard spheres that interact through attraction and repulsion. The second-order perturbation theory of Barker and Henderson was extended to chain molecules (“TU - technische universitat dortmund”, [s.d.]).

As the potential of the pair in the structure of the Barker and Henderson perturbation theory can be considered as having a reference and a perturbation contribution, in addition to the ideal, as in Equation 2.8:

$$\frac{A}{NK_B\,T} = \frac{A^{id}}{NK_B\,T} + \frac{A^{ref}}{NK_B\,T} + \frac{A^{pert}}{NK_B\,T} + \frac{A^{assoc}}{NK_B\,T}$$

Equation 2.8: Helmholtz association energy

where A is the Helmholtz energy, with A^{id} being the ideal contribution, A^{ref} is the reference contribution, and A^{pert} is the perturbation contribution. The ideal gas contribution, in Equation 2.9, is a direct adaptation of a two-dimensional structure:

$$\frac{A^{id}}{NK_B\,T} = \ln(\rho\Lambda^2)$$

Equation 2.9: Ideal contribution

where ρ is the numerical density (in this case, the number of surfactants per unit area) and Λ is the d'Broglie thermal wavelength.

The reference contribution is that of a hard chain fluid, composed of m hard drives segments. Based on the first-order approximation of the Wertheim perturbation theory, Equation 2.10:

$$\frac{A^{ref}}{NK_B T} = mA^{HD} - \sum_{i}^{NC} x_i(m_i - 1) lng_{ii}^{HD}(\sigma_i)$$

Equation 2.10: Reference contribution

$$m = \sum_{i}^{NC} x_i \; m_i$$

Equation 2.11: mass contribution

where A^{HD} is the Helmholtz energy of the contribution of hard drives, g_{ii}^{HD} is the radial distribution function for hard drives, x_i is the molar fraction and NC is the number of components in each mix in Equation 2.11. Following the Henderson Equation of state for hard-chain contribution, in Equation 2.12:

$$\frac{A^{HD}}{NK_B T} = \frac{9}{8} \frac{\eta}{1-\eta} - \frac{7}{8} \ln{(1-\eta)}$$

Equation 2.12: The hard-chain contribution

where η is the packaging fraction of hard chain, given by Equation 2.13:

$$\eta = \frac{\pi}{4} \rho \sum_{i}^{NC} x_i \; m_i \, d_i^2$$

Equation 2.13: Packaging fraction

For the radial distribution function at the contact value, according to Henderson's Equation of state, we use the expression of Barrio et al., Equation 2.14:

$$g_{ij}^{HD}(\sigma_{ij}) = \frac{1}{1-\zeta_2} + \frac{9}{8}\frac{d_i d_j}{d_i + d_j}\frac{\zeta_1}{(1-\zeta_2)^2}$$

Equation 2.14: Radial pair distribution function for segments of component i in the hard sphere system

where in Equation 2.15:

$$\zeta_2 = \frac{\pi}{4}\rho \sum_i^{NC} x_i m_i d_i^m \qquad \mathrm{n} \in (0,1,2)$$

Equation 2.15: Zeta function

For the perturbation contribution, the original expression from the work of Barker and Henderson shows as Equation 2.16:

$$\frac{A^{pert}}{NK_B T} = \frac{1}{2}\rho\beta \int u_1(r) g_0(r) dr - \frac{1}{2}\rho\beta^2\pi \int [u_1(r)]^2 K_B T \left(\frac{\partial\rho}{\partial P}\right) g_0(r)\, dr$$

Equation 2.16: Perturbation contribution

where u_1 is the perturbation part the pair potential, g_0 is the radial distribution function for the reference fluid, dr is the derivative overall dimensions with respect to the distance r. If we consider the pair potential to be circularly symmetric, we can reduce the integrals to only one coordinate, then, in Equation 2.17:

$$\frac{A - A_0}{NK_B T} = \rho\beta\pi \int u_1(r) g_0(r) dr - \frac{1}{2}\rho\beta^2\pi \int [u_1(r)]^2 K_B T \left(\frac{\partial\rho}{\partial P}\right) g_0(r)\, dr$$

Equation 2.17: Considerations in the perturbation contribution

The most of the substances to be studied here are amphiphile molecules with a polar head comprised of hydrogen bonding structures (e.g. alcohols, esters), it is crucial to add the free energy of association to the residual Helmholtz energy of the system, which can be described, for a two-dimensional McMillan-Mayer framework, as given by Equation 2.18:

$$\frac{A^{assoc}}{NK_B T} = \sum_{A}^{ns} [\ln X_A - \frac{X_A}{2}] + \frac{1}{2} M$$

Equation 2.18: Association contribution

where ns is the number of sites, X_A is the fraction of non-bonded sites of type A, which can be calculated as Equation 2.19:

$$X_A = \left[1 + N_{Av} \sum_{B}^{ns} \rho X^B \, \Delta^{AB}\right]^{-1}$$

Equation 2.19: Fraction of non-bonded sites of type A

where N_{Av} is the Avogadro number, ρ is the number density, and Δ^{AB} is the interaction energy between sites A and B, calculated via Equation 2.20:

$$\Delta^{AB} = 2\pi g^{HD} \left[\exp \frac{\in_{AB}^{HB}}{K_B T}\right] K_{AB}$$

Equation 2.20: Interaction energy between sites A and B

where $\in_{AB}^{HB}$ is the association energy between sites A and B, and K_{AB} is the association volume between sites A and B.

CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

This chapter describes the entire methodology used in this work, from designing the experiments, through the preparation of different solutions with the chosen surfactants in different conditions, formation, and characterization of monomolecular films at the air-water interfaces.

The experiments were carried out at the Laboratory of Interfacial Phenomena Engineering (LABEFIT) and the Applied Thermodynamics and Molecular Simulation Laboratory (ATOMS) of PEQ / COPPE / UFRJ.

3.2 METHODOLOGY

As the objective of this work was to evaluate different conditions of solutions for cosmetics, six variables were selected to be tested in the planning: type of surfactant, pH, volume of the sub-phase of the surfactant, surfactant concentrations, sub-phase temperatures and in the presence of electrolyte at 25 °C.

The aqueous sub-phase was prepared with ultra-pure water (Milli-Q, Millipore) and the electrolyte used was NaCl purchased from Sigma Aldrich.

Potassium cetyl phosphate developed and kindly provided by raw material supplier, DSM. It is an oil-in-anionic water emulsifier that meets the needs for high stability of challenging and complex formulations, such as sunscreens or liquid bases. It is an emulsifier considered by the market as the gold standard for challenging formulations due to its versatility of application, being able to go in the aqueous and oily phase. It offers high flexibility to formulate various types of products, from creams to sprays and mousses. This emulsifier has proven thermal and long-term stability and is stable over a wide pH range. In addition, it can be used to increase the SPF and water resistance of formulations. The commercial name of the reference used is Amphisol K. ("DSM website", [s.d.]) Its structure is shown below by Figure 3.1:

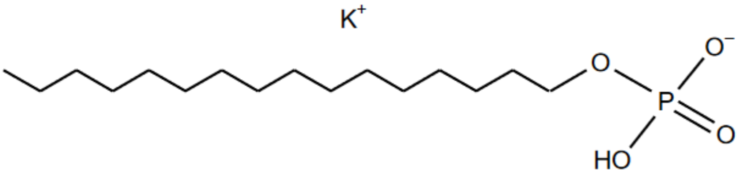


Figure 3.1: Potassium cetyl phosphate – molecule structure
Source: ("DSM website", [s.d.])

DSS (Dioctyl sulfosuccinate sodium) was purchased from Sigma Aldrich. It is an anionic surfactant used in cosmetic emulsions whose chemical structure is shown in Figure 3.2. It is obtained from the reaction of octane with malic acid anhydride, followed by the reaction with sodium bisulfite ("Sigma-Aldrich Website", 2020).

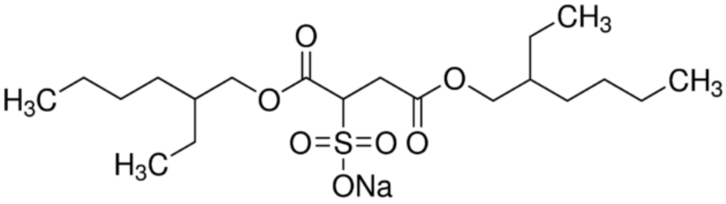
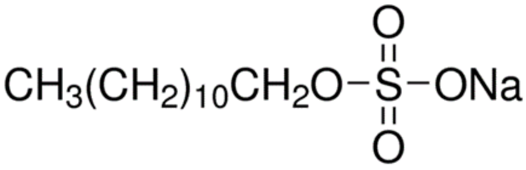


Figure 3.2: DSS (Dioctyl sulfosuccinate sodium) – molecule structure
Source: ("Sigma-Aldrich Website", 2020)

SLS (sodium lauryl sulfate), also called SDS (sodium dodecyl sulfate), was purchased from Sigma Aldrich. It is an anionic surfactant widely used in cosmetic emulsions whose chemical structure is shown in Figure 3.3. It is used in products such as shampoos, detergents, among others, due to its good detergent and foam characteristics ("Sigma-Aldrich - SLS", 2020).



$$CH_3(CH_2)_{10}CH_2O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-ONa$$

Figure 3.3: SLS (sodium lauryl sulfate) – molecule structure
Source: (“Sigma-Aldrich - SLS”, 2020)

Summary of characteristics such as molecular weight, molecular formula and CMC are presented in the table 3.1 below:

Chemical name	Molecular Formula	Molecular Weight	CMC
Sodium Lauryl Sulfate	$C_{12}H_{25}SO_4Na$	288.38 u	8.2 x 10^{-3} M at 25 °C
Sodium dioctyl sulfosuccinate	$C_{20}H_{37}SO_7Na$	444.56 u	6.8 x 10^{-4} M at 25 °C
Potassium cetyl phosphate	$C_{16}H_{34}O_4P.K$	360.40 u	-

Table 3.1: Summary of the properties of the surfactants.
Source: (“Sigma-Aldrich - SLS”, 2020), (“Sigma-Aldrich Website”, 2020), (“DSM website”, [s.d.]) (PAUL M. MUCHINSKY, 2012)

3.2.1. LANGMUIR ISOTHERMS

The Langmuir balance, also called the Langmuir trough, is a device where it is possible to change the average area occupied by a molecule through compression and decompression of the film, thereby obtaining the surface pressure of the film. It is obtained by the difference between the surface stresses of the pure solvent, Υ_0, and the surface tension of the solution, Υ (Equation 2.2).

With the compression of the film (smaller area per molecule), the surface tension decreases, and with that the surface pressure increases. The trough has a shallow compartment, with hydrophobic material, where the aqueous sub-phase is located, a surface tension sensor, of the Wilhelmy plate type, and movable barriers used to compress the monolayer formed on the surface as show in Figure 3.4 (ROBERTS, 1990).

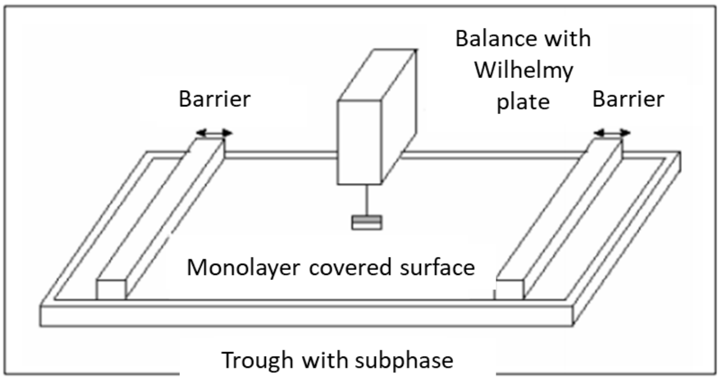


Figure 3.4: Langmuir balance model with Wilhelmy plate, which measures surface pressure while moving barriers reduce surface area
Source: (“Langmuir Films”, 2020)

The barrier can move over the surface of the liquid, and the surface pressure and molecular area are continuously monitored during compression. The Wilhelmy sensor measures surface pressure.

The experiments were carried out on a Langmuir scale model MicroTrough - S, Kibron Inc., (Figure 3.5). This equipment was equipped with movable Teflon (poly (tetrafluoroethylene)) trays, barriers, and a Wilhelmy plate type pressure measurement system. The software used to generate the isotherms was Filmware version 2.5. It was possible to adjust the initial parameters and record the values obtained during the experiments.

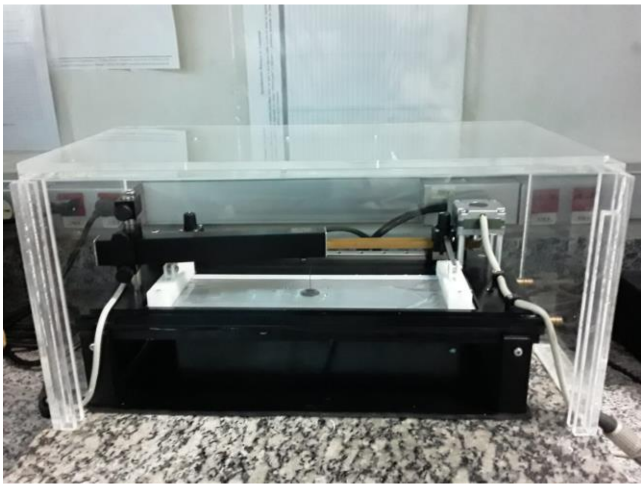


Figure 3.5: Langmuir balance model MicroTrough - S, Kibron Inc from LABEFIT

Langmuir trough is an extremely sensitive equipment, and the presence of any impurity or residue of solutions on the plate impacts the obtained isotherms. Therefore, a fundamental step for proper data collection is cleansing the plate. It is done by immersing the plates and barriers in a 70% ethanol bath every day that no readings are done on the equipment. Besides, the bath was changed once a day. On the day of the experiment, the tray and barriers are removed from this bath, and they are washed with ultrapure water Milli-Q (Millipore) at room temperature. It was necessary to work on a bench isolated to avoid interference, and then, obtain adequate and consistent data. In each analysis, the Langmuir balance was maintained with the acrylic box to avoid impurities from the external environment.

To guarantee that the cleaning was efficient, we obtained the water compression isotherm before each experiment.

The primary purpose of this work is to obtain and characterize Langmuir's films. Obtaining the films requires that they be stable on the water sub-phase, which is not trivial. The compression speed of the barriers cannot be high either, so 10 mm min^{-1} was fixed for all experiments. The software calculated the number of molecules present on the surface from the input data (volume, concentration, and molar mass of the analyzed molecule). Thus, as the movable barriers of the Langmuir vat approached each other, decreasing the area between them, the average area occupied by a molecule was reduced, and the Wilhelmy-type sensor detected the surface pressure.

Compression-decompression cycles of the monolayer were performed to study the reversibility of Langmuir films. The surfactant solution was placed on the surface, and, after 10 minutes, the film was initially compressed.

3.2.2. PREPARATION OF THE SOLUTIONS

Solutions with the 3 selected surfactants were prepared, to evaluate their action in the stability of the emulsions. These were prepared and stored at room temperature, around 24°C. Besides, it was determined that the evaluations would be made only at the instant zero, right after the production of the emulsion, to determine its initial stability.

The aqueous solutions containing the surfactants were prepared using a glass stick and a heating plate as the solubilization of potassium cetyl phosphate needs heat above 80°C.

3.2.3. EXPERIMENT PLAN

Several works in the literature study the factors that affect the stability of cosmetic emulsions to pass the empiricism that is still the industry's direction today. In this work for exploratory analysis of the significant main effects on the system's response (the shape of the compression isotherm), the following parameters were varied and evaluated:

- Surfactant: SDS, DSS, and potassium cetyl phosphate.
- pH of the aqueous sub-phase: from 4 to 7.
- Volume of potassium cetyl phosphate surfactant: from 50 µL to 100 µL in the aqueous sub-phase.
- The concentration of potassium cetyl phosphate surfactant: from 0.5 mg/L to 3.0 mg/L in relation to water, according to the suggested concentrations for formulation when it is used as a single emulsifier and as a co-emulsifier.
- Presence of an electrolyte, NaCl at 0.2% (W/V) in the subphase solution. For these tests, the surfactant was potassium cetyl phosphate at a concentration of 0.5% in 100 µL of the subphase.
- The temperature: from 4 to 55 ° C. These temperatures are in accordance with are placed in the stability study according to the ANVISA stability guide. The temperature was controlled with a circulation bath coupled to the Langmuir trough.

Not all these parameters were analyzed for all surfactant's solutions. The tests that were done for each surfactant solution were:

- Potassium cetyl phosphate: temperature, concentration, volume, pH of aqueous subphase, presence of electrolyte
- DSS: pH of aqueous subphase
- SDS: pH of aqueous subphase

The experimental error includes, among other factors, the influence of the equipment error, the residue present on equipment surface, the temperature variation, the experiment operator, the stabilization of the laboratory's electrical system.

3.2.4. SURFACE ELASTICITY – STATIC ANALYSIS

The mechanical properties of Langmuir films can be evaluated through the elasticity measurements performed in the static and dynamic regimes. In the static regime, compressibility is given by C_s. This is related to the ability of a material to change its physical state by applying a force date on the material. The inverse of compressibility, C_s^{-1}, is the compression module, known as elasticity (PAVINATTO, 2010). The formulas of C_s and C_s^{-1} are given by Equations 3.1 and 3.2 respectively:

$$C_s = -\frac{1}{A}\left(\frac{\partial A}{\partial \pi}\right)$$

Equation 3.1: Compressibility in static regime

$$C_s^{-1} = -A\left(\frac{\partial \pi}{\partial A}\right)$$

Equation 3.2: Elasticity in static regime

where A is the area per molecule and π is the surface pressure. Both, the compressibility, and the elasticity, are calculated directly from the angular coefficient of the Langmuir isotherms π-A.

In theory, the higher the compressibility module, C_s, the lower the interfacial elasticity will be. C_s^{-1} will depend on the state of the monolayer, being lower for more condensed monolayers indicating high interfacial elasticity. (GONG et al., 2002).

Graphs of C_s or C_s^{-1} can be obtained depending on the area per molecule and surface pressure. These help in determining the isotherm phases and the phase transition regions (SABATINI; MATTILA; KINNUNEN, 2008).

The elasticity measurements performed in a dynamic regime are given by the drop method. In this alternative method to measure surface rheology, experiments of oscillating the size / area of a drop suspended on the tip of a microsyringe on the surface where the Langmuir film is obtained (PAVINATTO, 2010).

Both methods can be used but, in this work, only analyzes were performed in static regimes.

3.2.5. PARAMETER ESTIMATION – THERMODYNAMIC MODEL

An adaptation of the PC-SAFT model used in this work was one developed by the Applied Thermodynamics and Molecular Simulation Laboratory (ATOMS) team of PEQ / COPPE / UFRJ.

The parameters for each substance were estimated by the ATOMS laboratory with a Particle Swarm Algorithm (WEN; MA; ZHANG, 2016) for global search, coupled with a Nelder-Mead algorithm for local search (ROWAN, 1991).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 INTRODUCTION

This chapter introduces and discusses the main results obtained in this study. The results regarding the isotherms of the films obtained in the Langmuir trough are presented below.

The variables of the experiment plan are also evaluated in this chapter. The main objective is to analyze the responses obtained in the experiments plan and correlate some of them with the theoretical results by using the thermodynamic model.

4.2 LANGMUIR ISOTHERMS

The first characterization performed was the compression isotherm on the Langmuir trough to determine the mechanical stability of the films formed by the different surfactants. All the characterizations were done with 20 mL of Milli-Q (Millipore) water as aqueous sub-phase.

4.2.1. THE EFFECT OF TEMPERATURE

The effect of temperatures was analyzed at 4 ºC, 25 ºC, 45 ºC and 55 ºC for the potassium cetyl phosphate and shown in Figures 4.1, 4.2, 4.3, 4.4.

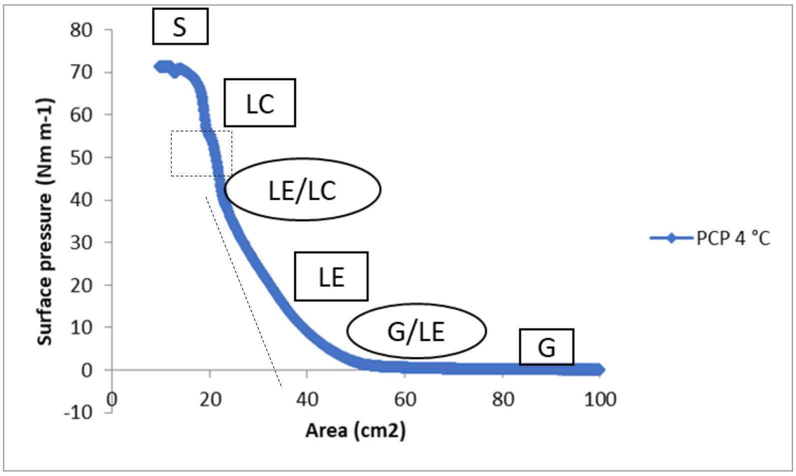


Figure 4.1. Langmuir compression isotherm of potassium cetyl phosphate at 0.05% temperature of 4 ºC. The value obtained by the intersection of the dashed line with the abscissa axis represents the average area occupied by a molecule in the Langmuir film.

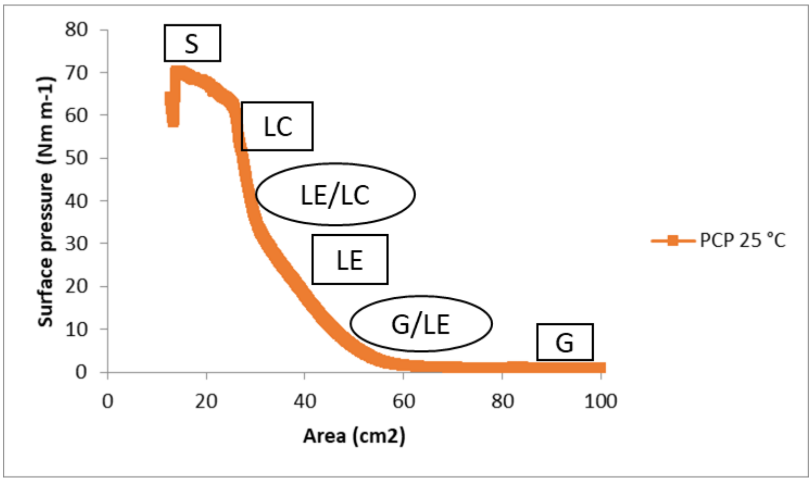


Figure 4.2. Langmuir compression isotherm of potassium cetyl phosphate at 0.05% temperature of 25 ºC.

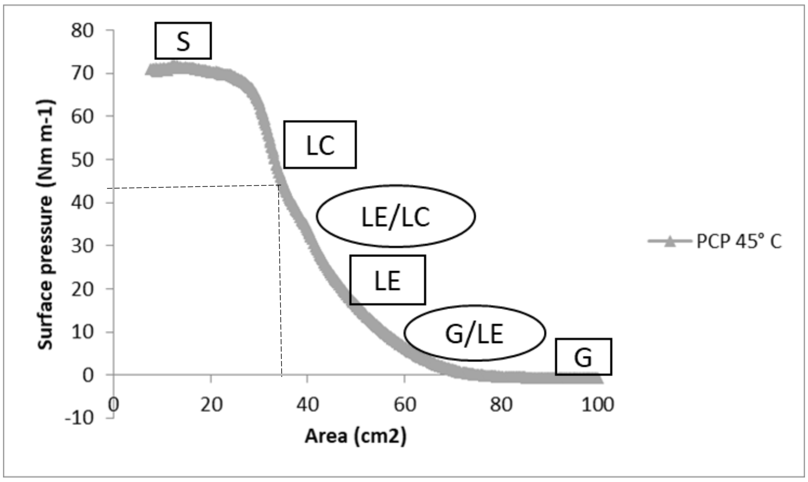


Figure 4.3. Langmuir compression isotherm of potassium cetyl phosphate at 0.05% temperature of 45 ºC. The intersection of the dotted line representing the same point at temperatures of 45 ºC and 55 ºC.

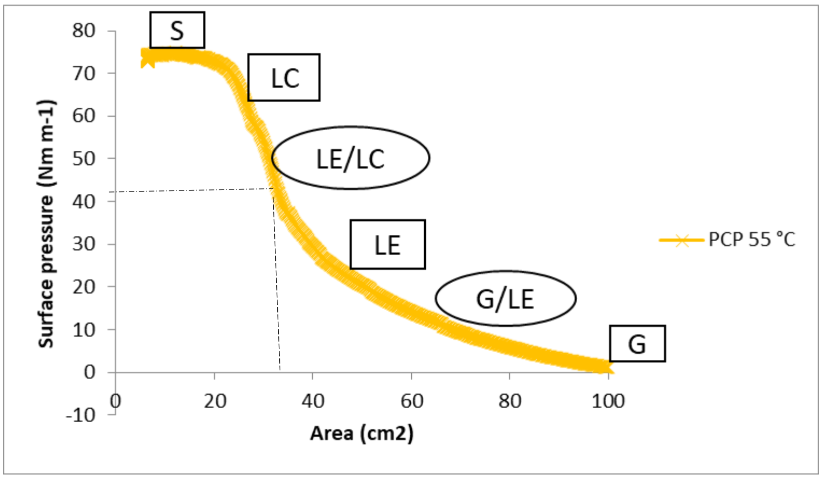


Figure 4.4. Langmuir compression isotherm of potassium cetyl phosphate at 0.05% temperature of 55 ºC. The intersection of the dotted line representing the same point at temperatures of 45 ºC and 55 ºC.

This test was done to evaluate the influence of temperature on Langmuir isotherms. When the temperature increases, the intensity of the intermolecular forces decreases. Hence, the interaction between two surfactant molecules at the film will be weaker, leading to more expanded films, as observed. Thus, it is expected that the isotherms obtained for the same substance and in the same concentration, at higher temperatures, present a more extended phase behavior, whereas, for lower temperatures, the behavior is of a more condensed phase. Thus, identifying that in the same instant the comparison between temperatures leads to a higher surface pressure the higher the temperature.

Such behavior expected in theory was observed in the experiment. The temperature of 55ºC presented the highest surface pressures compared to the temperatures of 4 ºC, 25 ºC, and 45 ºC in a same point. At a certain point, the isotherms of 55 ºC and 45 ºC overlapped, and the surface pressures for both temperatures did not diverge. Such situation is plausible for low temperature. The theoretical values of water surface tension at 10 ºC and 25 ºC, are 74.2 mN / m and 72.0 mN / m, respectively, for example. The surface tension values had little difference for a difference of 15 ºC.

Regarding the phases and phase transitions present in this isotherm, we identified the presence of distinct phases: gaseous, liquid-expanded, liquid-condensed, and solid phase. The identification of the phases and the phase transition is done by observing the isotherm π-A format.

For temperatures of 4 ºC, 25 ºC, and 45 ºC we were able to identify the gas-liquid transition. At a temperature of 55 ºC, we also observed a gas-liquid expanded transition, however more subtle and in a larger molecular area than when it occurred at other temperatures.

As the molecular area decreases and the surface pressure increases, we see that the isotherms are well inclined, practically vertical, the gas transition to an expanded or condensed liquid is observed. With continuous compression of the area, more transitions are observed as the slopes of the curves change. The non-continuity in the isotherm profile represents the phase transitions. This leads us to assume that the first transition is gas-expanded liquid and 2 more gas-condensed liquid transitions are identified.

In the 55 ºC isotherm, the slope of the curve presents a different behavior from the other isotherms, being more horizontal than the others. At the same pressure, represented in the Figure 4.3 and 4.4 by the dotted line, there are two different phases at 45 ºC and 55 ºC. There is probably an expanded liquid-gas transition at 55 ºC and condensed liquid–gas at 45 ºC. Thus, the film's properties change considerably from expanded liquid to condensed liquid upon cooling, both in the rigidity of the film and in the transfer of mass that can occur through the formed film when it breaks. As previously mentioned, the interfacial film's mechanical strength is one of the factors that prevents coalescence of the W/O emulsion drops. Therefore, from this data, we can see that the 45 ºC film would be more rigid than the 55 ºC film, reducing mass diffusion and preventing more drops from coalescing.

However, comparing the highest temperatures, 45ºC and 55ºC with 25ºC and 4ºC, we observe that 25ºC and 4ºC have more condensed phases, being 4ºC, the one with the most condensed phase this is because the curve is more inclined and is the expected behavior for the condensed phases. Thus, the temperature of 4ºC has more rigid and consequently more stable films.

The most pronounced difference in inclination is seen between 45 ºC and 55 ºC. It could indicate the presence of a triple point between these temperatures. In thermodynamics, the triple point is a state of a substance defined by the coexistence of the three phases - solid, liquid, and gas - determined by the values of temperature and pressure. It is an essential property of a substance, as it represents the limit for the occurrence of the liquid phase, that is, it marks the minimum pressure under which a liquid can exist.

At a pressure less than that of the triple point, no pure substance can stably exist in the liquid phase, with only the balance between the solid and gaseous states.

The theoretical value of the triple point of potassium cetyl phosphate has not been found in the literature. For the assumption of a triple point between 45 ºC and 55 ºC to be better evaluated, we must create the phase diagram and assess where the triple point is. The phase diagrams relate temperature, chemical composition, and quantity of phases in equilibrium.

For the isotherm at 4ºC isotherm, we observed several condensed phases that it was not identified in the other isotherms. The slopes changes are very subtle; in Figure 4.1 they are marked as a square. By the type of transitions, they may be second-order since the plateau is non-horizontal. Besides, these transitions occur at a critical point, and the higher the temperature, the more challenging to see these transitions.

In the literature we do not find many studies that vary the temperature to obtain different isotherms. One of the reasons these studies are few is that it is difficult to control the temperature using the Langmuir though. However, Zuo et al. studied compression isotherms of the DPPC (dipalmitoylphosphatidylcholine) monolayer at different temperatures of 10, 20, 30, 40, and 45 °C obtained by using a new method called CDS (constrained drop surfactometry). They observed that for temperatures between 20 and 40 °C, the isotherms indicate a LE-LC phase transition. The plateau of this transition was not observed for the other temperatures that is outside this range. They concluded that LE-LC phase transition happens only for molecules considerable flexibles and at low temperature, due the molecular rigidity the gas passed directly to condensed phases without passing though expanded phases. In our case, even if we identify the film at temperatures below 10 °C it has a more condensed and rigid profile, in our isotherm profile we still identify the transition from gas to expanded liquid.

4.2.2. THE EFFECT OF CONCENTRATION

The effect-of-concentration test was proposed to evaluate the influence of the concentration of the surfactant solution deposited on the aqueous sub-phase (Figure 4.5). Monolayers are formed by amphiphilic molecules that are at the interface. The higher the concentration of the solution, the lower the surface pressure is. In this case the solution would be closer to reach the critical micellar concentration, CMC.

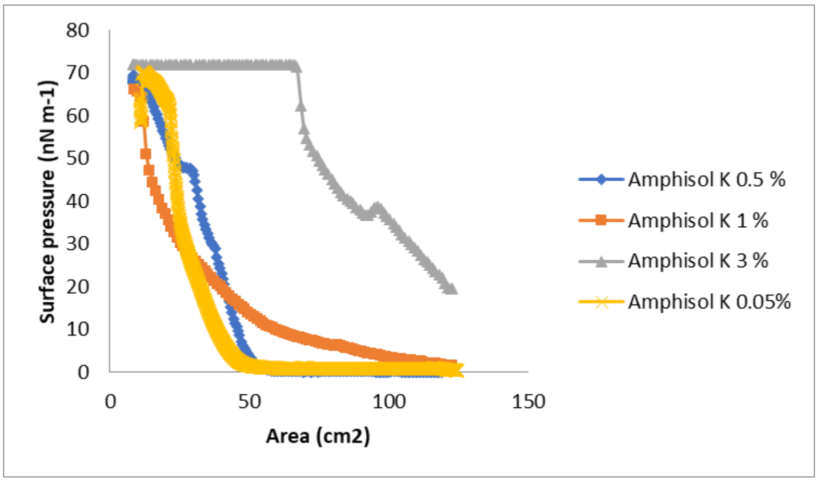


Figure 4.5: Compression isotherm of potassium cetyl phosphate in concentrations of 0.05%, 0.5%, 1% and 3%.

Comparing the isotherms obtained for 0.5% and 1%, the higher concentrations, the closer the surfactant molecules are and, consequently, there is more lateral interaction. It implies that the film may be more condensed even for larger areas. Thus, it is reasonable to imagine that the gas phase does not appear in higher concentrations, which was observed. The gas-phase appeared in the isotherm at a concentration of 0.05% as it was explained and shown in the previous Figure 4.2, at 0.5% and even at 1%.

In the concentration of 0.5% we also observe the presence of different phases and phase transitions: gaseous, liquid-condensed, and solid-like. The slope of the isotherm is too vertical to have expanded liquid. In point 1 of the graph, we see a transition in the condensed liquid phase, which may represent a condensed liquid - condensed liquid transition. The transition condensed liquid-solid is present at the end of the isotherm showing the film's collapse.

At 1%, even though a gas phase is observed for high areas, the isotherm slope is even higher, and it could be a representation of only liquid phases, an expanded liquid to condensed liquid transition. At 3%, however, due to the lower slope of the isotherm, the hypothesis is that everything will be condensed liquid. For those higher concentrations, the behavior of isotherms is quite different. One hypothesis is that there is no monomolecular region in these concentrations but rather a region containing multiple layers, as shown in Figure 4.5.

Another way to analyze the effect of the surfactant concentration is by varying the volume of solution applied to the aqueous sub-phase, as shown in Figure 4.6.

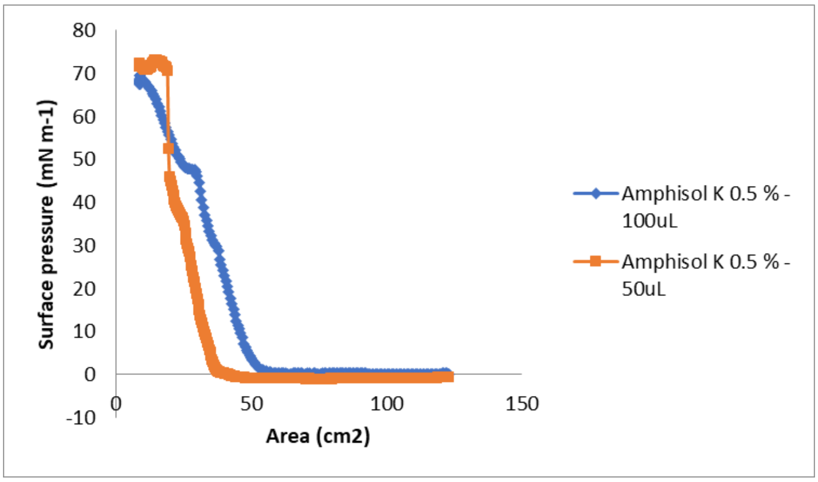


Figure 4.6: Compression isotherm of potassium cetyl phosphate at 0.5% in different volumes, 50 µL and 100 µL in the aqueous sub-phase

This test was done to evaluate the influence of the solution volume on Langmuir isotherms. As it was expected same concentrations, for different volumes, for the same area, the higher the volume of the aliquot of the same concentration is put into the surface, the larger molecules will be presented on the surface. It was already expected and verified in the evaluation of the different concentrations and at 25 ºC temperature conditions.

In the volume of 50 µL the number of molecules is half the number of molecules in the volume of 100 µL. Then, it is expected that for smaller aliquots volumes, the gas phase will be larger and that the film will be more rigid. Even though the perceived difference was not extremely high, the experiments under other conditions were decided to be performed at 100 µL.

4.2.3. THE EFFECT OF pH OF AQUEOUS SUBPHASE

This test was proposed to evaluate the influence of pH on Langmuir isotherms, shown in Figure 4.7. The pH of the sub-phase directly affects the charge balance in the surfactant molecules. Depending on pH value, an ionization process occurs, and the molecules acquire a net electrical charge. In the case of the anionic surfactants, in aqueous solutions, they will already have negative charges that will interact with the pH of the medium.

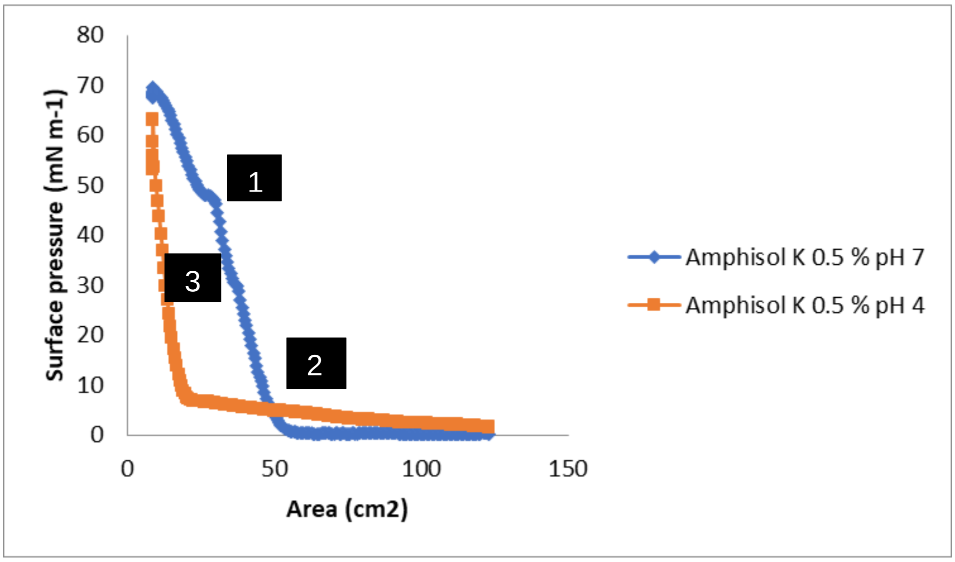


Figure 4.7: Compression isotherm of potassium cetyl phosphate in pH of aqueous subphase, 4 and 7. Point 1 and 3 are condensed liquid phases, point 2 is a LE-LC phase transition

When the molecule is charged, there is a greater electrostatic repulsion between the polar heads, and this implies that the film formed is more expanded, since the side interactions are reduced.

At pH 7, a gas phase and the transition gas-expanded liquid is identified. Then, the transition from the expanded liquid to condensed liquid phase is confirmed due to the inclination of the line. Besides, it is possible to observe another transition of condensed liquid, as shown in point 1 of Figure 4.7. However, the transition gas-condensed liquid to pH 4, is not identified. Due the line inclination, it seems that the transition that appears as point 2 has more a profile of an expanded liquid to condensed liquid transition, and then we identified the condensed liquid in point 3.

It is also observed that the transition from expanded liquid to condensed liquid at pH 7 is much more discrete. We would call it a 2nd order transition because it is not horizontal. In the second-order transition, the exchanges between the phases become much larger and are more continuous. The phases are very well defined separately; they only coexist. Microscopically it is expected to visualize islands of condensed liquid, but most of the film has no surfactant because the gas phase is characterized due the surfactant molecules are distant from each other.

It shows that the film at pH 7 is more expanded than that observed before. Even though the isotherm obtained shows a condensed gas-liquid transition, their pressure is extremely low. So, there may be a region where diffusion is higher. In the liquid condensed phase even by the agglomeration and formation of the film, diffusion is impeded, making it more difficult.

At pH 4 the film is much more condensed and with higher mechanical resistance. It is observed that the change in pH considerably changed the rigidity of the formed film.

Although monolayers' characterization can be found in the literature, information with pH variation is more limited. STHOER; TYRODE, 2019 investigated the interaction of Na^+ cations with a carboxylic acid chain. In the investigation, the conditions of different temperatures and pH> 10 were evaluated. They argue that upon increasing pH of the aqueous subphase, the alkyl chains' cohesive forces are affected by the further deprotonating of the monolayer. One of the isotherms obtained at the same temperature (20 ºC) and at different pH, 12 and 5.8, showed different behaviors. At pH 5.8, it does not present the G-LE transition while it is slightly observed at pH 12. Furthermore, the transition to the liquid phase is more vertical at pH 5.8, showing that the film is more densely packaged at low pH at the same temperature.

4.2.4. THE EFFECT OF THE PRESENCE OF ELECTROLYTE

This test was proposed to evaluate the influence of the ionic strength on Langmuir isotherms (Figure 4.8). As with pH, the presence of electrolytes affects the double electrical layer of the molecules, compressing the surfactant's diffuse layer and, thus, shielding their charges. This effect helps to reduce the repulsion between the polar heads and, consequently, makes the film more condensed.

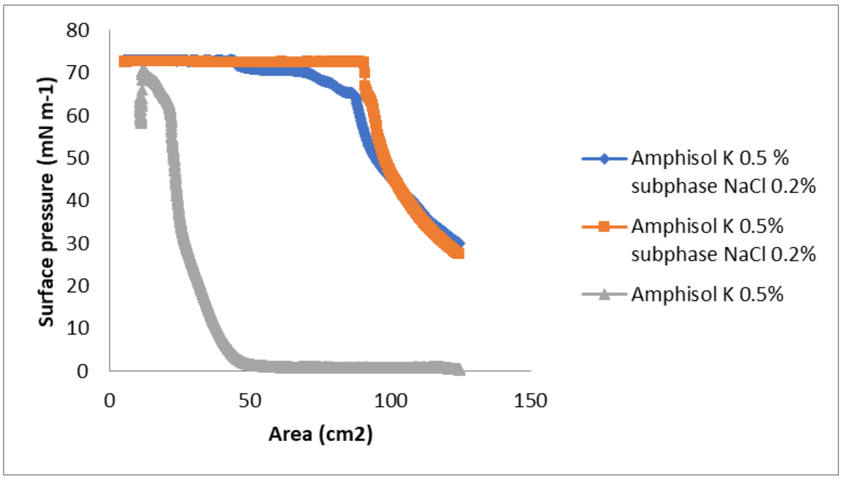


Figure 4.8: Compression isotherm of potassium cetyl phosphate 0.5% in a subphase containing electrolyte at 0.2%

In the isotherm in an aqueous subphase with electrolyte at 0.2%, it was observed that the film already started in a more condensed phase besides high value of total area. They have higher values of surface pressure when compared to an aqueous subphase without the presence of electrolytes. The obtained isotherm shows that the isotherm of potassium cetyl phosphate at 0.5% in a subphase containing sodium chloride at 0.2% does not present a monolayer behavior. It seems that the monolayer film has already collapsed into a much larger area of molecules, forming a multilayer region. The film became more tense and rigid with higher surface pressures because it has more condensed phases in many regions.

STHOER; TYRODE, 2019, observed low pH, such as 6, but high ionic concentration, such as > 0.292%, before concluding that an impact caused by the size of Na^+ cations in the surface, a specific charge needs to be reached. They also suggest that depending on the counterion, different impacts can be observed on the phase transition. They also showed a higher value of molecules per area, even in the low concentration of NaCl. Moreover, even with this scenario, the distance from the surface is shorter than it would be for smaller values of molecules per area. The distance from the surface is smaller than if the molecules per area would be smaller. Therefore, due to steric effects, the salt also has a limited concentration on the surface.

4.2.5. DIFFERENT SURFACTANTS IN DIFFERENT pH

In addition to the tests done previously, an analysis of other anionic surfactants normally used in the industry was conducted, aiming to evaluate the effect of their structure on the surface properties.

DSS compression isotherm is shown in Figure 4.9. In this experimentally profile, at pH 7, a gas phase film seems to be presented due to the slope of the isotherm found. The film is not rigid and therefore not considered stable. Even though we do not know the isoelectric point of this molecule, we can affirm that in the aqueous subphase, the pH 4 is more charged than in pH 7. Therefore, it is expected that the repulsion between the molecules would be more significant in pH 4 than in pH 7, and consequently, the film would be more expanded at pH 4 since the side interactions are reduced.

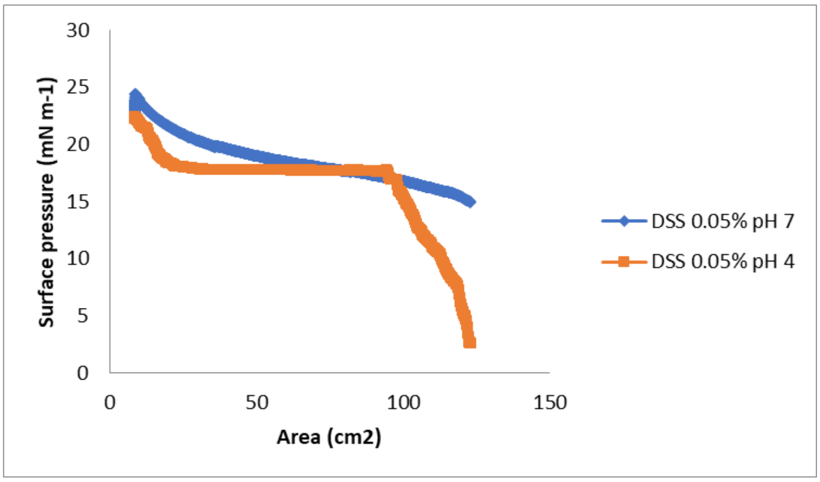


Figure 4.9: Compression isotherm of DSS in different pH of aqueous subphase, 4 and 7

As previously mentioned, the number of researches that analyzes the impact of pH on the isotherm is limited, however for ambient temperature and pH 7 condition, we verify that ALMEIDA, 2012 obtained an isotherm with a similar profile. She noted that DSS isotherm is a typical isotherm of a less condensed state than xanthan gum.

SLS isotherm is seen in Figure 4.10. As pH changed from 4 to 7, the film changed its characteristics. At pH 4 it is present a gas phase and its transition to expanded liquid. No condensed phase is identified. So, at pH 4 the film is not rigid. At pH 7 the film has no gas phase but a larger region of expanded liquid than when compared to pH 4. For both pH conditions, the film is not considered to be rigid.

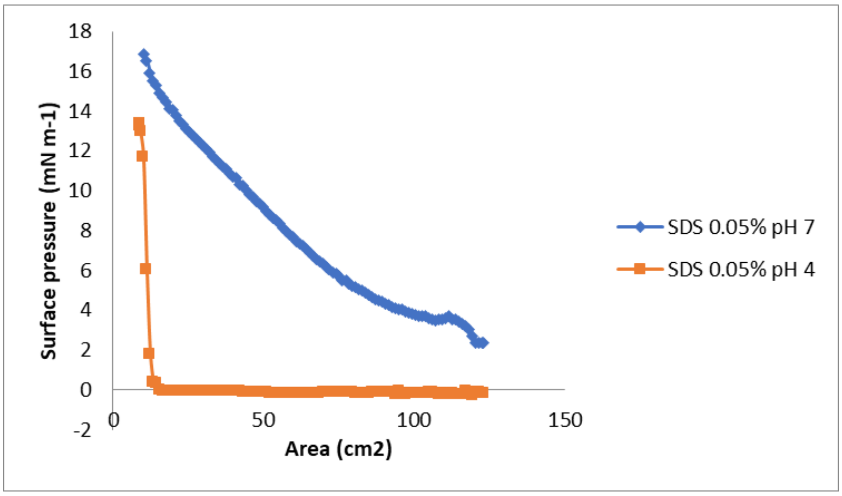


Figure 4.10: Compression isotherm of SLS in different pH of aqueous subphase, 4 and 7

AH-FAT; CRAIG; TAYLOR, 1994 studied the interactions between phospholipid and SDLS monolayer using a surfactant concentration before its CMC. In this study, another molecule, cosurfactant, was used in association. However, they observed a qualitatively similar behavior obtained here. They observed that on increasing the surfactant concentration, the surface pressure was higher at any compression due to the surfactant presence.

Comparing the three surfactants used in this research, potassium cetyl phosphate, SLS, and DSS, it was observed that they have a different monolayer behavior under the same conditions once its chemical structure influences it.

Potassium cetyl phosphate has the largest hydrophobic chain among the selected surfactants. It leads to a lower water solubility and a higher compacted film, resulting in a significant reduction in surface tension and high surface pressures. A more rigid film is observed with this surfactant, which confers a suitable stabilization property to this surfactant.

On the other hand, SDS has a structure like that of cetyl phosphate, but the hydrophobic chain is smaller than others. At pH 4, both molecules are near electrically neutral. This way, SDS should be more soluble than cetyl phosphate, reaching lower surface pressures, as observed. A phase transition to expanded to condensed liquid, observed for cetyl phosphate, is not present for SDS.

DSS is structurally different. Its structure is symmetrical and has ramifications that impact the film packaging, resulting in a more expanded film in high areas. Transition to a more condensed state is only seen in low areas.

The potassium cetyl phosphate film seems to be quite condensed; that is, the surface pressure only begins to increase significantly to the small areas per molecule. It means that there are no great interactions from the bulk contributing to the pressure on the surface, which only increases when approaching the minimum (maximum packing) area occupied by each molecule.

The results presented above are expressed in the total area of molecules. In a graph surface pressure versus area per molecule, the area occupied by an amphiphilic molecule can be calculated by tracing a tangent of the isotherm, which corresponds to the most condensed phase. This intersection is known as the limited area of molecular dispersion. In the above cases, the area estimate occupied by a molecule of potassium cetyl phosphate presented low values (less than 5 A^2). This value may be associated with the formation of multilayers and not of a monolayer on the surface. Lower concentrations of this surfactant should be tested for this verification.

4.3. LE-LC PHASE TRANSITION ORDER

As previously mentioned, the scientific community's discussion of whether the LE-LC phase transition would be a first-order phase transition (whose horizontal plateau would be observed in an π-A isotherm) or if it would be a second-order phase transition (a non-horizontal slope on the π-A curve) still exists.

Analyzing the experimental data obtained in this work and observing the angle of the phase transition between expanded liquid and condensed liquid, we observe that the transition is not a horizontal plateau, thus showing us that these are second order transitions.

However, as our model and other authors (Vollhardt and Fainerman, 2006; Motschmann and Lunkenheimer, 2002) suggests, we can capture this transition as a second-order or first-order transition depending on the critical point at a specified temperature and pressure. Thus, for the observed isotherm at Figure 4.11, the temperature of 55ºC would be above the critical temperature for this substance as a second-order transition was observed. Isotherms at lower temperatures would have a first order transition behavior.

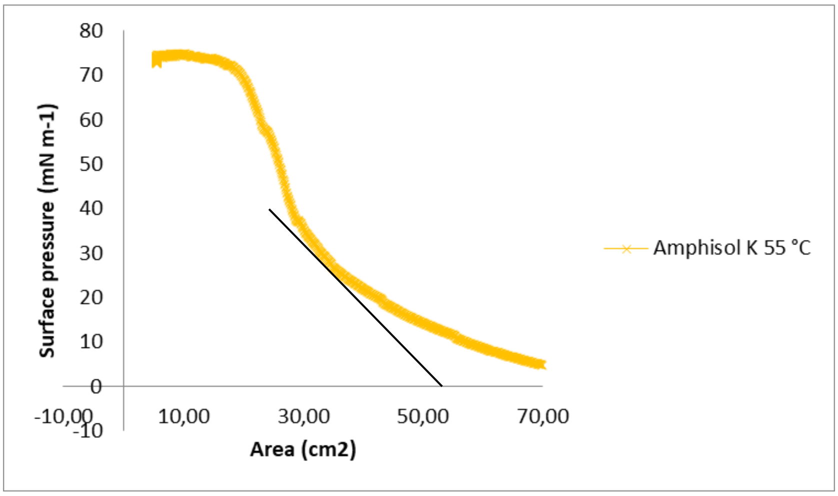


Figure 4.11: Example of experimental isotherm obtained of potassium cetyl phosphate at 55°C. The tangent curve identifies the transition between expanded liquid and condensed liquid.

4.4. ELASTICITY AND COMPRESSIBILITY

To obtain the compressibility graphs, the experimental data of the isotherms of different temperatures were interpolated using a cubic spline. From this interpolation, derivatives were obtained for calculations of elasticity and compressibility. This was done for each isotherm at different levels of smoothing.

The molecular area where the phase transitions occur is indicated by the film compressibility peaks as shown in Figure 4.12.

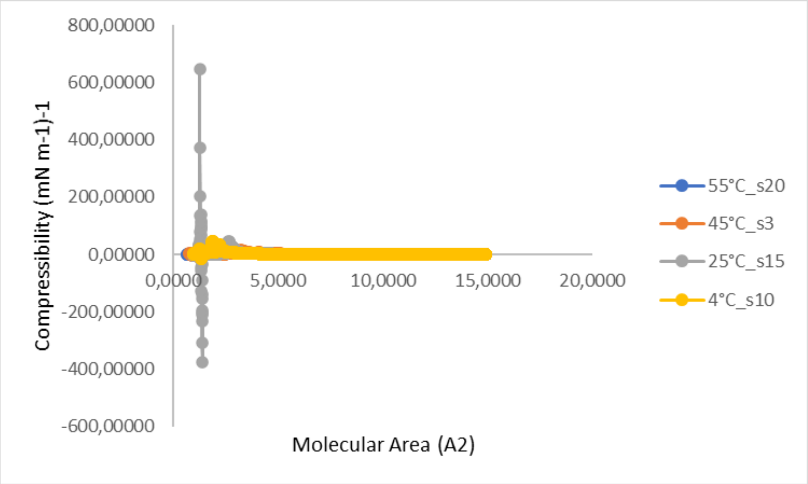


Figure 4.12: Film compressibility of potassium cetyl phosphate at 4°C, 25 °C, 45 °C and 55°C.

We expect high compressibility values to represent less condensed regions and phase transitions like gas and expanded liquid. In smaller molecular areas, we have the highest compressibility values of the film.

The highest compressibility values were identified for temperatures of 25°C and 4°C. The lowest compressibility values were observed for temperatures 45°C and 55°C. Theoretically, it is expected that the lower the temperature, the more condensed the monolayer is, then the lower the compressibility of the films and the greater its elasticity. Even though this behavior was observed at temperatures of 4°C, 45°C and 55°C, the temperature of 25°C showed the highest compressibility values diverging from what was theoretically expected.

Furthermore, at 4 °C there are 3 peaks of elasticity showing 3 phase transitions, while 45 and 55 °C have similar profiles presenting 3 peaks but occurring at lower compressibility values and occurring at higher values of molecular areas.

4.5. THERMODYNAMIC MODELING – PC-SAFT

Thermodynamic modeling was used to verify if an adapted model developed by the ATOMS group could describe the experimental data with all the transition phases. The Langmuir trough is not a quick and easy (considering the equipment's sensitivity) test, several errors can be associated with its manipulation, so the use of a model is essential to use this type of analysis in the stability investigations. Therefore, having a theoretical model that can simulate what is seen in the experimental is scientifically helpful.

The measurement of surface pressure (π) as a function of the molecular area (A) is the most commonly used technique to characterize the behavior of amphiphilic molecules at the air/water - and oil/water (o/w) - interface, due to ease of implementation. In Figure 4.13, an example of experiment isotherm to better explain the phases transitions by thermodynamic side:

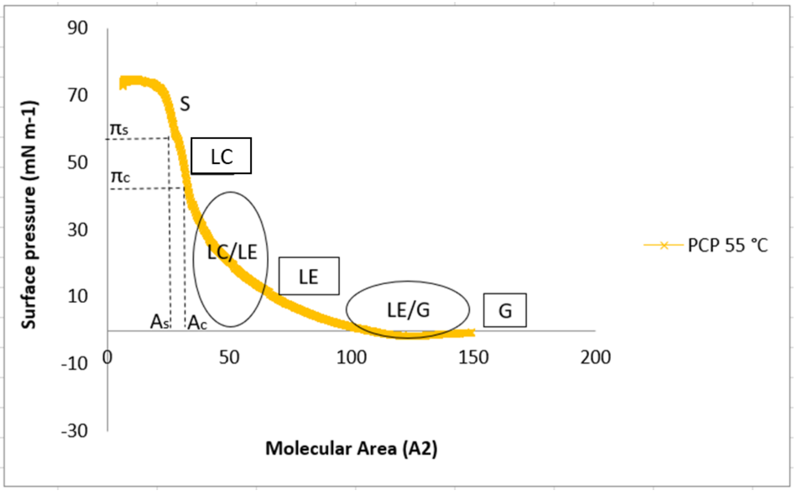


Figure 4.13: Experimental isotherm of potassium cetyl phosphate surface pressure (π) versus molecular area (A^2) at 55°C. Circles correspond to the coexistence regions (LE/G and LC/LE). G is the gaseous region; LE: liquid expanded region; LC is the liquid-condensed region; S is the solid-like region; πs and As are the transition pressure and area between LC and S phases, while πc and Ac are the critical pressure and area between LE and LC/LE coexistence regions.

For now, the model does not yet have support for electrolytes, and to make the modeling of different volumes is a little more complicated because it is necessary a model for 3D phase (the bulk) and a 2D phase (the interface) at the same time. As the focus of the modeling in this work relies on the 2D phase, this development will be left to future works. That was the reason why the only conditions that were modeled in this work were the different temperatures for potassium cetyl phosphate at 0.05% and DSS at pH 4 and 7 at 0.05%.

The theorical data representing the experimental data well, as shown in Figure 4.14 by the curve’s similarity. Its associated modeling total error was 0.985. Besides that, we were able to identify the phases and phase transitions in the theoretical model result. It shows that the model was able to describe both the gas-liquid condensed transition, as well as the liquid condensed phase, and a second liquid condensed phase. Moreover, as mentioned in the experimental data discussion, as we have a condensed gas-liquid transition hinted by the transition at a very low surface pressure with equilibrium between a high and a low area, without going through the expanded liquid, we understand that we are below the triple point. If this conclusion holds true, isotherms at higher temperatures than those present here, would show the presence of liquid expanded phase and the phase transition between this phase and a liquid condensed phase.

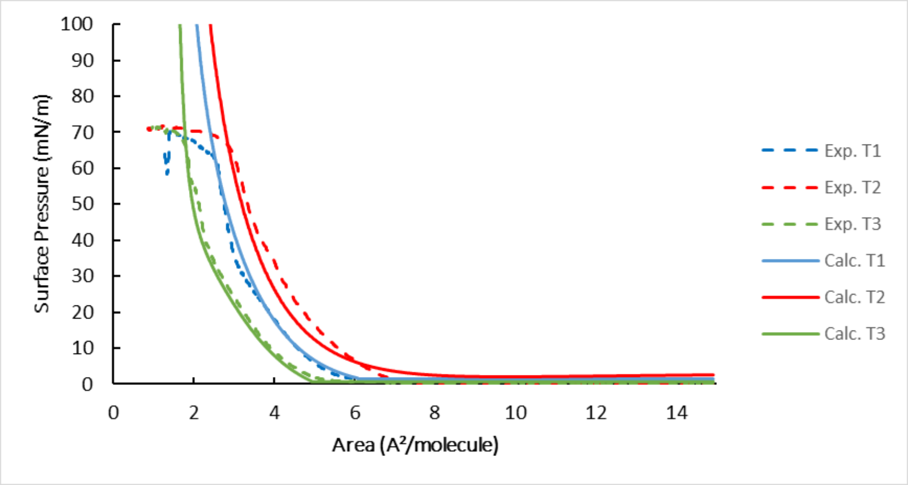


Figure 4.14: Thermodynamic modeling of compression isotherm of potassium cetyl phosphate 0.5% at temperatures of 4 ºC (T3), 25 ºC (T1) and 45 ºC (T2)

In the theoretical isotherm of the DSS we identified a liquid expanded phase, followed by a transition from a liquid expanded to a liquid condensed phase. The beginning of the phase transition observed for the theorical model is not exactly the same observed for the experimental start, this may be caused both by a lack of adjustment of the model and the inherent experimental difficulty of this measure. The comparison of the experimental data with the modeled data shown in Figure 4.15, shows a good correlation between them. The associated modeling total error was 0.985. In these results, we verified that the theoretical data were unable to predict the collapse of the films.

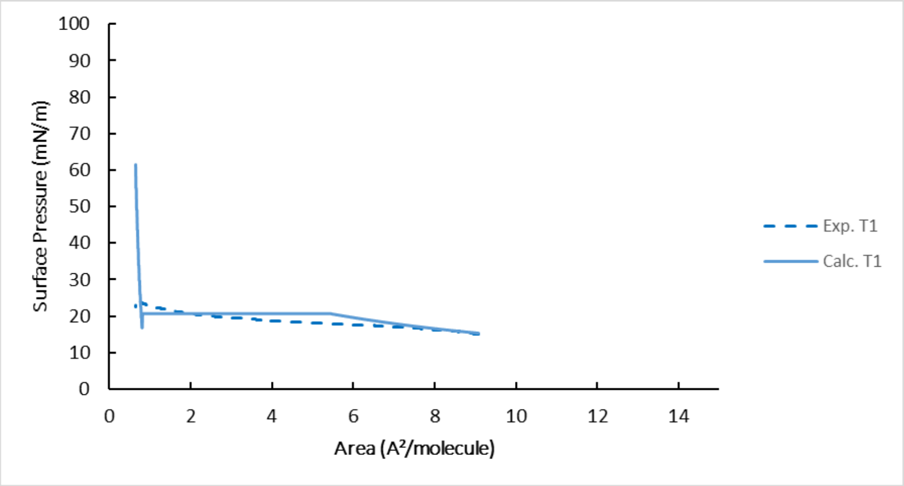


Figure 4.15: Thermodynamic modeling of compression isotherm of DSS in pH 7 of aqueous subphase

Considering the thermodynamic model used in this word as it is, we can adjust the parameters so that a phase transition occurs just in the collapse, but that would not necessarily be the collapse. As mentioned above, the areas per molecule found out were low in the experimental results and one of the possibilities would be to estimate the area per molecule using the thermodynamic model. Once the minimum area for the monolayer is adjusted with the values of "m" and "s" in the model, then one possibility would be to identify when the collapse occurs by identifying a fraction of the area density (the inverse of the area), then we would know at which packing fraction the collapse is occurring.

Working this last possibility, for potassium cetyl phosphate, for example, calculating for each temperature the packing fraction in which the collapse occurred it would be possible to check if the packing fractions in which a collapse may occur are high or low, and thus, this is something to be discussed and evaluated in more detail in future studies.

Despite this, the model was developed based on the PC-SAFT equation of state, which is has a hard chain reference fluid comprised of hard spheres. In this case, the pressure tends to infinity when we approach the maximum packing fraction, which is not the physical reality of the facts but is what we see in the theoretical results. Therefore, another possibility and suggestion for future work is the development of another model that does not consider rigid spheres, but rather, soft spheres, like the Soft-SAFT equation of state.

Therefore, for the model to predict the monolayer collapse, it is essential to better understand how it occurs microscopically and see how it would be possible to introduce this into the theorical model, as this would imply if we need a high packing fraction, or if other mechanism is important to the collapse.

Despite these points, as mentioned at the beginning of the work, what it missed most in the literature are theoretical models that identify and have phase transitions.

DA SILVA ROBAZZI, 2002 in his work applied different equations of state, including equations of polymeric fluids like the Simha-Somcynsky equation and equations for solids like the Mie-Gruneisen equation to characterize Langmuir monolayers with mathematical models. However, what he observed is that even though the different equations of state achieved a qualitative adjustment of the experimental data, it was not possible to obtain a quantitative adjustment that included the phase transitions observed experimentally.

This work and the model used is of great advancement for the scientific community on this subject, since here we identify not only the observed fluid phases but also its phase transitions in the same model. Another advantage of the model is the easy extension to mixtures, which is imperative in the study of these systems and represents a huge advantage of it.

Even if we do not yet achieve a perfect fit between the model and the experimental data, the qualitative representation is important at the level that we are approaching to understand what the microscopic reality of this type of system is like, since the model can reflect at least qualitatively all experimental features.

Thus, having a model with a strong physical background, we can think of new experiments capable of elucidating other issues of this type of system, besides, of course, evolving in the modeling of the systems, which has not only theoretical impact, but also practical in the economic sense for account of modeling.

CHAPTER 5

CONCLUSIONS AND SUGGESTIONS

5.1 CONCLUSIONS

The study of emulsion stability (O/W) in cosmetic formulations is critical since it is the most challenging part of development. The tests today are guided by empirical studies under extreme stress conditions for an answer as to whether the formulation is stable or not to meet the regulatory agencies standards in the registration of products and essential to ensure the safety and quality of consumer use.

The isotherms study makes possible to identify the phases that the monomolecular films present. Through these films, we have an idea if the film is densely impacted, more rigid, or even if it would increase the possibility of mass diffusion. By studying the difference in the surfactant monolayer isotherms, it was possible to understand the behavior of the films and their correlation with emulsions' film mechanical properties.

In the analysis of the parameters that impact the structure of the film, we observed that the temperature, pH, concentration, and presence of electrolytes influence the film's characteristics. The increase in temperature, for example, decreases the packaging of the formed film and, consequently, its stiffness. It has been shown that it is highly necessary to analyze the behavior at different temperatures because mainly at temperatures of 4 °C, 25 °C and 55 °C, isotherms with quite different behavior were detected. The lowest temperature, 4°C presented the film with more stable characteristics and more condensed phases. Among the surfactants used, potassium cetyl phosphate has more condensed phases showing more characteristics to have a more stable interfacial film. However, it is important to understand why the results of potassium cetyl phosphate did not decrease the surface pressure. The presence of the electrolyte, in turn, dramatically contributes to the increase of film stiffness.

The thermodynamic model proposed to model the Langmuir film monolayer showed a good correlation with the experimental data of the isotherms of different temperatures of potassium cetyl phosphate and at pH 7 for DSS. Hence, it becomes a useful tool for these characterizations since the experiment has technical challenges and demands time to do the analysis.

Besides, the LE-LC transition was verified in both, the experimental and proposed model for potassium cetyl phosphate. From observing the π-A isotherms obtained, LE-LC phase transition was second-order, for high and low temperatures because the transition plateaus are not horizontal and have a slight slope on the π-A curve.

5.2 SUGESTIONS

The tests were done only with solutions, a reality far from the emulsions that currently exist in the market. Therefore, a suggestion would be to obtain isotherms with emulsions or solutions containing more than one molecule. Besides, the obtained isotherms are for analysis of the air/water interface. Knowing that most of the products are an emulsion of water/oil, the proposal is to make isotherms from the liquid/liquid interface.

Another proposal would be to study the same solutions and emulsions in an accelerated methodology, according to ANVISA norm, and to evaluate initial and final conditions.

The equation of state (PC-SAFT) with the obtained parameters from surface-pressure data, can be used to predict the monolayer film mechanical behavior.

Regarding the thermodynamic model, one suggestion is the development of another model that does not consider rigid spheres, but rather, soft-spheres, like the Soft-SAFT equation of state. This approach can provide more realistic behavior of these complex systems.

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