

HLB (Balance Hidrofílico-Lipofílico) como novel herramienta para la solubilización de D-limoneno en sistemas de aerosoles

HLB (Hydrophilic-Lipophilic Balance) as a novel tool for the solubilization of D-limonene in aerosol systems

Mata-Zabala, Ericson^{1,2,3}; Pereira, Juan^{1*}

¹ Facultad Experimental de Ciencia y Tecnología,
Laboratorio de Petróleo, Hidrocarburos y Derivados
(PHD), Universidad de Carabobo, Venezuela

² Corporación Creatón, C.A., Carabobo, Venezuela

³ Suramericana de Aerosoles, C.A., Carabobo, Venezuela

*jcpereir@uc.edu.ve

Abstract

The primary objective of this study was to employ the well-known colloidal chemistry tool, the HLB (Hydrophilic-Lipophilic Equilibrium) method, for the solubilization of D-limonene in aerosol systems. This was achieved through formulation scans, first in Surfactant-Oil-Water (SOW) systems with an oil phase of heptane + D-limonene (20% to 40%) with a water-to-oil volume ratio (WOR) of 1:1, and then in SOW systems where the heptane in the oil phase was replaced by GLP (A60), and a portion of this, from 20% to 40%, was replaced by D-limonene. Mixtures of non-ionic surfactants (Span® 20, 80 and Tween® 80, 85) were used, and the optimal formulations at phase equilibrium were determined. D-limonene was solubilized in the aerosol-sol system at HLB values close to the formulation optimum in HLB scans where the oil phase was heptane, to harness the chemical energy of the systems and obtain water-in-oil (O/W) formulations. Thermodynamic stability and micellar aggregate formation were validated by determining the Tyndall effect. The results demonstrate that precise HLB control allows its use as an effective tool for the efficient solubilization of D-limonene in aerosol systems, offering a sustainable technological platform for the potential development of biopesticides, pharmacological agents, other types of products, and delivery systems for molecules that are poorly or insoluble in water.

Keywords: HLB, aerosols, D-limonene, formulation optimum, LPG.

Resumen

Este trabajo tuvo como objetivo central el uso de la muy conocida herramienta de química coloidal, el Método de HLB (Balance Hidrofílico-Lipofílico), para la solubilización de d-limoneno en sistemas de aerosol, mediante barridos de formulación, en primer lugar en sistemas Surfactante-Aceite-Agua (SOW) con fase oleosa heptano+d-limoneno (de 20% al 40% de dicha fase) con una relación volumétrica agua-aceite (WOR) de 1:1 y luego, sistemas SOW donde en la fase oleosa fue sustituido el heptano por GLP (A60) y sustituyó parte de éste, de 20-40% por D-limoneno. Se emplearon mezclas de tensoactivos no iónicos (Span® 20, 80 y Tween® 80, 85), determinando los óptimos de formulación al equilibrio de fases. Luego se realizaron solubilizaciones de d-limoneno en el sistema aerosol, en los valores de HLB parcialmente cercanas al óptimo de formulación en los barridos de HLB donde la fase oleosa era el heptano, para aprovechar la energía química de los sistemas y obtener formulaciones de fase externa agua (O/W). La estabilidad termodinámica y la formación de agregados micelares se validaron mediante la determinación del efecto Tyndall. Los hallazgos demuestran que el control preciso del HLB puede permitir el uso del mismo, como una herramienta efectiva la solubilización eficiente del d-limoneno en sistemas de aerosol, ofreciendo una plataforma tecnológica sostenible, para el posible desarrollo de biopesticidas, agentes farmacológicos, otros tipos de productos y sistemas de liberación de moléculas poco o nada solubles en agua.

Palabras claves: HLB, aerosoles, óptimo de formulación, d-limoneno, GLP.

1 Introduction

The HLB (Hydrophilic-Lipophilic Balance) was proposed by William C. Griffin in 1949 as one of the first methods to quantify the hydrophilic and lipophilic balance of surfactants in a SOW (Surfactant-Oil-Water) system. This method assigns a number to each surfactant. However, one of the main weaknesses of this proposal is that it relies on arbitrary assumptions and does not take into account certain trends and variables such as temperature, salinity, and other system characteristics (Griffin, 1949). This initial theoretical-practical approach provided a first formulation scheme called HLB, related to the balance between the hydrophilic and lipophilic (hydrophobic) portions of the molecule. Over time, HLB values have been assigned to many commercial emulsifying agents. In some cases, the HLB number is calculated from the molecule's structure, and in others, it is based on experimental emulsification data (Rosen, 2004).

Griffin proposed a classification of surfactants based on HLB, as shown in Table 1.

Table 2. HLB ranges and surfactant classification
HLB Surfactant application

4-6	Emulsifier W/O
7-9	Wetting agent
8-18	Emulsifier O/W
13-15	Detergents
15-18	Solubilizer

In developing an understanding of SOW (Surfactant-Oil-Water) systems, in 1954 Winsor proposed the basic concepts for correlating the phase behavior of SOW systems with the relative interactions of surfactant molecules adsorbed at the oil-water interface. Although Winsor's model simply describes how surfactant, oil, and water interactions affect the physicochemical formulation, its application can be complex in practice. According to the Winsor model, SOW systems can be classified into three types of balanced systems: Winsor I ($R = A_{co}/A_{cw} < 1$), Winsor II ($R = A_{co}/A_{cw} > 1$), or Winsor III ($R = A_{co}/A_{cw} = 1$), based on the R ratio of affinities of surfactant molecules (C) for oil (O) and water (W), where A_{co} and A_{cw} are the molecular interactions between the adsorbed surfactant molecule and nearby oil and water molecules (Figure 1). Winsor I systems correspond to an S1-type micellar aggregation of surfactant molecules, possibly with some oil molecules solubilized within, in what is called a swollen micelle. Winsor II systems correspond to S2-type reverse micelles, that is, the opposite structure of surfactant aggregation in the oil phase, eventually with some water solubilization in their core. Winsor III systems, in which the interactions between surfactant and oil and water are equal, exhibit three-phase behavior with an intermediate phase that has been represented as a bi- or tricontinuous system of highly complex struc-

tures containing fluctuating oil and water domains, resembling an arbitrary "sponge" geometry or other unusual models. Although this phase has been commonly called a "microemulsion," it should be noted that no emulsion droplets are present (Marquez et al., 2023).

In 1957, Davies introduced a system for the empirical quantification of HLB, taking into account Cassel's work from 1936 and 1938 on Bancroft's rule (the phase in which the stabilizing agent is most soluble will be the continuous phase), the coalescence rate (as the speed of droplet union in a given interfacial film), and the Gibbs free energy of the system. Davies' development of his quantitative theory of emulsion type led him to establish four main conclusions:

(i) The emulsion type depends solely on the relative coalescence rates of oil-in-water and water-in-oil systems; (ii) the logarithm of the relative coalescence rates should vary directly with the HLB values for different emulsifiers; (iii) Although Bancroft's rule cannot have a thermodynamic basis, a strict theoretical correlation is established between the relative coalescence rates and the preferential solubility of different emulsifiers in one of the phases, under certain conditions and (iv) the empirical HLB values have a fundamental meaning in terms of free energies, i.e., they must be related to the surfactant distribution between oil and water under certain conditions (Davies, 1957).

As an evolution of the HLB concept and considering its physicochemical limitations, between the 1970s and 1980s, Salager and his collaborators (1979a, 1979b) introduced the HLD concept, which measures the deviation of a SOW system from the optimal formulation state, Winsor type III, where the surfactant's affinity for water or oil becomes exactly the same and as a result, minimum interfacial tensions are achieved and $HLD = 0$.

$$HLD = \ln S - kACN - f(CA) + \sigma - \alpha T \Delta T$$

Where, S is the salinity of the aqueous phase in % by weight of NaCl; ACN , is the number of carbons (or equivalent) of the alkane used; $f(CA)$, is a function of the concentration of alcohol used as a cosurfactant; σ is a characteristic parameter of the chemical structure of the surfactant used (which increases linearly with the length of the hydrophilic chain); ΔT is the deviation of the temperature from a reference temperature (25 °C) and k and αT are empirical constants (Rosen & Kunjappu, 2012)

On the other hand, limonene is a cyclic monoterpene with the molecular formula $C_{10}H_{16}$ and is an essential oil found in citrus fruits such as lemons, limes, and oranges. It has two optical isomers, with identical chemical properties but different odors. (+)-limonene, or D-limonene, has an orange aroma, while (-)-limonene, or L-limonene, has a pine aroma. The two isomers of limonene are shown in Figure 1 (Royle, 2023).

It is important to highlight that the structural characteristics of D-limonene give it its lipophilic, nonpolar, yet polarizable character due to its double bonds (Figure 2). It has a cyclohexene ring, a chiral center represented by a carbon

atom bonded to four different groups, resulting in the d-(R) and l-(S) enantiomers, represented in Figure 1. Also noteworthy are the two cyclohexene substituents: a methyl group ($-\text{CH}_3$) and an isopropenyl group ($-\text{C}(\text{CH}_3)=\text{CH}_2$) attached to the ring. Regarding its conformation, the ring is generally shown in a non-planar, chair-like or boat-shaped conformation, making it bent and three-dimensional (IA Gemini, 2025).

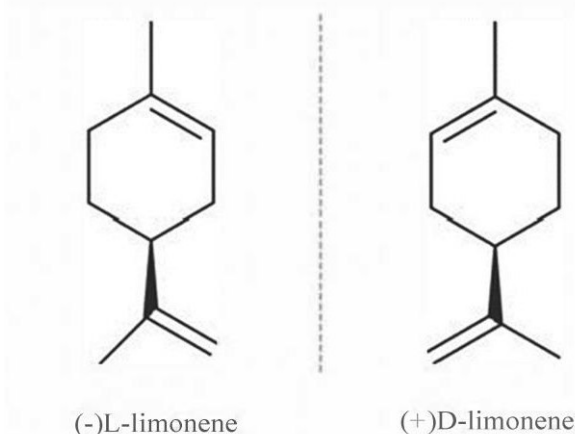


Figure 1.- Optical isomers of Limonene (Royle, 2023)

On the other hand, among the numerous natural compounds, limonene, due to its wide presence in the essential oils of various plants, such as *Citrus bergamia*, *Citrus deliciosa*, *Montanoa quadrangularis*, *Juniperus oxycedrus*, *Citrus unshiu* and *Bursera graveolens* and its excellent bioactivity, has been considered by researchers as a versatile sustainable natural active compound (Lin et al, 2024).

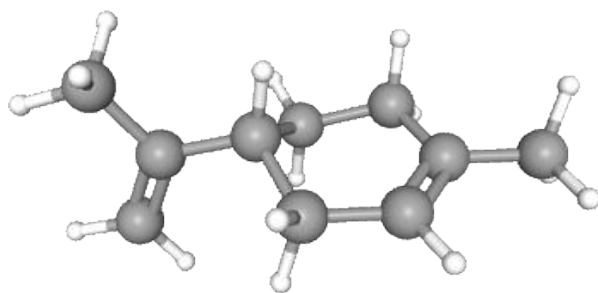


Figure 2. 3D representation of D-limonene.39 CC BY 4.0 License. National Center for Biotechnology Information (2026)

General Applications of D-limonene

While studies on the antibacterial⁷ and antifungal¹³ activity of D-limonene have been described, a body of knowledge on its mechanisms of action is still being built. Its bioactivity, related to its anthelmintic and pharmacological activity, potential uses, and, of course, the elucidation of its mechanisms of action and the enhancement of its biological activity through techniques such as nano- or microencapsulation are also being investigated. There is extensive literature on the antibacterial and antifungal power of

D-limonene, as well as its anthelmintic, insecticidal, pharmacological, and antiviral activity (Lin et al., 2024).

Pharmacological Applications

Limonene demonstrates remarkable anti-inflammatory effects by modulating pro-inflammatory cytokines and oxidative stress pathways, leading to its inclusion in formulations targeting chronic inflammatory diseases. In oncology, preclinical studies have shown that monoterpenes such as D-limonene have demonstrated the potential to induce apoptosis and inhibit tumor proliferation in combination with metformin (Salim et al., 2024). Furthermore, D-limonene nanoemulsions have been reported to exhibit a strong anti-oral cancer effect by reducing cell viability and cell cycle arrest, making these nanoemulsions a promising alternative therapeutic strategy for the treatment of oral cancer (Manmuan et al., 2025).

In neuropharmacology, components of essential oils such as linalool, borneol, and α -pinene have been found to modulate the central nervous system, exhibiting sedative, anxiolytic, and neuroprotective effects, which has implications for the treatment of disorders such as anxiety, depression, and neurodegeneration (Kaspute et al, 2025).

Applications as a biopesticide

D-limonene, in addition to being an effective insect repellent for direct application to skin and textiles,²⁸ could inhibit the growth of various fungal pathogens, including *Pyricularia oryzae* (rice blight), *Rhizoctonia solani* (rice sheath blight), *Colletotrichum gloeosporioides* (pepper anthracnose), and *Phomopsis amygdali* (peach bud blight). Notably, the formulation of stable and effective nanoemulsions containing D-limonene offers a practical solution for controlling agricultural crop diseases, complying with FAO regulations, and providing sustainable and environmentally friendly formulations (Ebru et al., 2025).

Applications in electronics.

D-limonene has been used as a non-aromatic, non-chlorinated solvent in the electronics industry, specifically for the solution processing of polymers (polyfluorene and copolymers) and conjugated molecules for applications in optoelectronic devices (Zhu et al., 2015).

Micro- and Nano-emulsification of D-limonene

To improve the stability and bioavailability of essential oils, and especially those containing D-limonene, various innovative delivery/release systems have been developed. Micro- and nano-emulsification involves solubilizing/encapsulating essential oils or their derived components in protective matrices, preserving their aromatic profiles and therapeutic properties while allowing for controlled release. For example, liposome technology improves the bioavailability of essential oils by encapsulating hydrophilic and hydrophobic compounds, ensuring targeted delivery and sustained release in cosmetic formulations. Self-emulsifying systems further enhance the solubility and ab-

sorption of essential oils, enabling their incorporation into diverse formulations. Overall, essential oils represent a promising and underutilized class of bioactive natural products with considerable potential in modern pharmacotherapy. Their versatility and biocompatibility make them attractive candidates for the development of new therapeutic agents and delivery systems (Kaspute et al., 2025). Based on nanoemulsions, insect repellents have been developed that have demonstrated great potential for controlled release in malaria control, in light of the very worrying reality of insect resistance to pyrethroids (Mapossa et al., 2023). D- limonene microemulsions have also been used for improved crude oil recovery, with promising results (Royle, 2023).

Currently, numerous studies focus on the use of essential oils and their micro- or nano-emulsified components as drug delivery systems for oral, parenteral, ocular, pulmonary, and topical administration. New herbal formulations based on nanoemulsions and microemulsions can significantly contribute to the economic growth of the cosmetic, nutraceutical, and pharmaceutical industries. In the future, to overcome the application limitations of essential oils, research could focus on combining different nanocarriers, such as gel systems based on nanoemulsions and nanoemulsions loaded with nanoparticles. Likewise, essential oils and their micro- or nano-emulsified components have promising prospects in the food industry, as they offer effective methods for improving food safety, performance, and preservation by inhibiting microbial growth. In other words, these micro- and nano-emulsified formulations can serve as natural preservatives, extending the shelf life of food while maintaining its nutritional value and sensory appeal. Furthermore, they can improve the absorption of vital nutrients and antioxidants by encapsulating bioactive substances, thus increasing the value of functional foods. However, alongside these potential advantages and benefits (Figure 3), the optimization of large-scale production techniques, ensuring the stability of the formulations under diverse storage conditions, and regulatory issues are some of the drawbacks that must be addressed for their widespread use (Bolgen et al., 2025).

It is necessary to consider that aerosols, in this work, are understood, beyond their classic definition, not as a suspension of minute particles (from nanometric to micrometric in scale) of solids or liquids dispersed in air or another gas, but as all products packaged under pressure in a metallic or non-metallic container, from which various contents are dispensed like a spray by activating a simple valve with the tip of a finger (Yule, 2003). As shown in Figure 4, a typical aerosol container (normally pressurized to 4 or 5 bar, using a liquefied gas), that is, the propellant gas, is a low-boiling-point fluid such as mixtures of hydrocarbons, fluorocarbons, and inert gases like N₂, CO₂, and even dehydrated compressed air.

It is important to note that the term aerosol also describes the industry that manufactures such products, which generates considerable confusion, especially given the rigor

required by scientific definitions. As a relevant fact, in the early days of the industry, most products were indeed aerosols—liquid insecticides with nanometric particle sizes. Later, products such as shaving foams, which strictly speaking are not aerosols, entered the market. Currently, only some products are aerosols, but most are not (Reed, 1968).

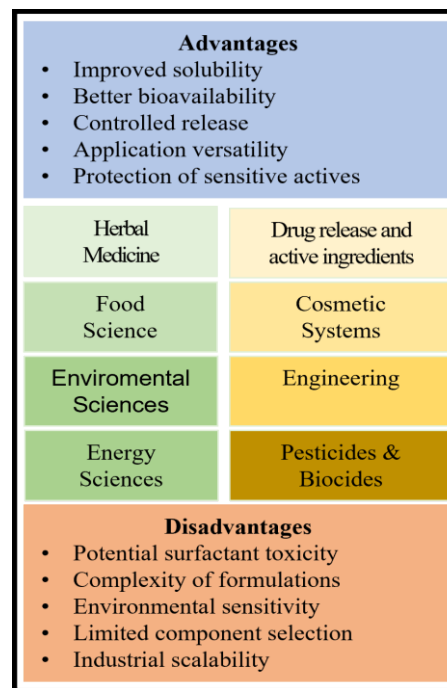


Figure 3. Summary of Microemulsion and Nanoemulsion Applications

It is also necessary to clarify that in English, "spray" is used interchangeably with "aerosol," which always causes confusion. In contrast, in Spanish, "espray" or "spray" is distinct from "aerosol," since "spray" refers to a mechanical pumping system (spraying) and "aerosol" to an application or dispensing system containing a gaseous propellant.

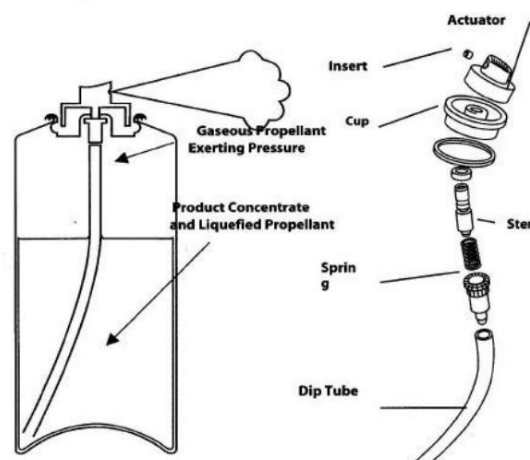


Figure 4. Basic diagram of an aerosol (BAMA, 2022).

Having made the above clarification, it can be said, according to historical records, that the development of aerosol tech-

nology began with U.S. patent 34894, granted on April 8, 1862, to John D. Lynde, a technologist from Philadelphia, USA. He called it a "bottle faucet," and the patent referred to it as an "Improved Bottle for Aerated Liquids" (Lynde, 1862).

In 1899, inventors Heinrich Helbing and Gustave Pertsch received patent US628463A for the development of a system for preparing and applying insulating and coating materials using a propellant such as alkyl chlorides (primarily ethyl and methyl) with or without the addition of alcohol (Helbing & Pertsch, 1899).

However, it wasn't until 1931, in terms of technical and, above all, commercial feasibility, that Erik Rotheim (a Norwegian chemical engineer) received patent US1800156A, entitled "PROCEDURE AND MEANS FOR THE ATOMIZATION OR DISTRIBUTION OF LIQUID OR SEMI-LIQUID MATERIALS," which he had introduced in 1927. According to the patent, the material to be dispensed is packaged in a pressure-resistant (metallic) container along with dimethyl ether, under sufficient pressure to cause the dimethyl ether propellant to liquefy through condensation. The patent description adds that when an outlet is opened in the container holding the material and the condensed dimethyl ether, the material will be expelled under the pressure prevailing in the container. The propellant, which is discharged simultaneously, will evaporate immediately. This patent expands the use of aerosols to atomize or distribute liquids, semi-liquids, or solid substances of any kind (Rotheim, 1931).

Continuing in the vein of evolution and innovation, Julian Kahn received patent US2170531A in 1939 for his APPARATUS FOR MIXING A LIQUID WITH A GAS. This invention is a household appliance for mixing a liquid with a gas, and more specifically, for whipping cream—that is, the mixture of cream and propellant gas—to be dispensed through the appliance's orifice. This appliance was refillable, possessed a protective device or safety valve to prevent excess pressure inside the appliance, and also simplified filling and dispensing, since the valve serves to charge the container with gas and then, by its design, facilitates the formation of cream and gas foam when the contents are dispensed. Another objective of the invention was to greatly simplify the apparatus by using a single valve for two purposes: first, as an inlet valve when filling the container with gas, and second, as a narrow, somewhat labyrinthine passage to induce foaming of the cream and gas mixture (Kahn, 1939).

However, it wasn't until 1941, motivated by military reasons (the need for a product to reduce malaria infections among U.S. military personnel in Southeast Asia), that the research of American inventor and entomologist Lyle Goodhue and entomologist and military officer William Sullivan gave a definitive boost to the development of aerosol technology. Goodhue was a research chemist of lacquer formulations at DuPont Chemical laboratories in 1929, but it was at the U.S. Agricultural Research Center in Maryland, where he developed with Sullivan, his research on an insecticide called "bug bomb", where they used a mixture of pyrethrum, sesame oil and freon 12 (dichlorodifluoromethane). Goodhue and Sullivan applied for the patent in 1941, receiving it in 1943, with the number US2331117A and in whose description it is reported that the invention relates to a

dispensing apparatus, and one of the objectives thereof is the provision, in combination with a container adapted to hold a pressurized liquid and a spray device for dispensing the liquid, of means for dosing a predetermined amount of liquid into the container and expelling with the aid of the spray device a predetermined amount or dose, in such a way that each dose dispensed is exactly the same (Goodhue & Sullivan, 1943).

The portability of the Goodhue and Sullivan container, along with its refillable nature, definitively opened up a whole new horizon for aerosols after the end of World War II. But one link remained in the chain of aerosol innovations, and that was, paradoxically, a valve to prevent or facilitate their release. The solution to this technological crux is owed to Robert H. Abplanalp, an American inventor and mechanical engineer, who developed the modern aerosol valve, as it's known today. His patent, filed in 1949, was granted in 1953 under number US2631814A, VALVE MECHANISM FOR DOSING GASES AND LIQUIDS UNDER PRESSURE³¹. The facsimile of this patent describes the invention as improvements in valve mechanisms, highlighting that the design is particularly adapted for use with aerosol dispensers, which utilize the principle of mixing a liquefied gas with an active liquid in a container under sufficient pressure to dispense minute particles that can be directed onto an object to form a film, as in the case of paints, waxes, lotions, and others, or for insecticide applications. Germicides, nasal solutions, and other products where the dispensed active ingredient needs to remain airborne. The Abplanalp design was also adapted for use with either of the two known types of aerosol cans/containers prevalent in the 1950s. One of the many advantages of the Abplanalp design was ensuring the airtightness of the can-valve assembly with a mechanical sealing procedure called "crimping," which prevents propellant leakage and eliminates the need for welding. Another notable advantage was the inclusion of sealing gaskets compatible with the formulations. The design also conformed to the consensus among most container manufacturers of having a neck with a one-inch diameter (Abplanalp, 1953).

In 1974, a globally significant scientific event occurred when Mexican chemical engineer and postdoctoral student José Mario Molina Pasquel y Henríquez and his advisor, American chemist Frank Sherwood Rowland, presented to the United States Congress the results of their research, "Stratospheric Sink of Chlorofluoromethanes-Atomic Chlorine-Catalyzed Ozone Destruction" (Contreras Nuño et al., 2015). These results, previously published in the scientific journal *Nature*, revealed that the use of chlorofluorocarbons (CFCs) from the manufacture and operation of refrigeration equipment, and to a lesser extent, from their use as propellants in the aerosol industry (Reed, 1968), contributed to the destruction of the planet's ozone layer. This work earned them both the 1985 Nobel Prize in Chemistry and also triggered a technological leap in the industry. Aerosols, based on scientific evidence and negative opinions about aerosol products, initially slowed their development. However, the industry then replaced freons (CFCs - Chlorofluorocarbons) with fluorocarbons, and from 1989 onwards, the aerosol industry voluntarily eliminated CFCs from its products, except for specific applications such as medical inhalers. Despite this change, flammable

liquefied gases with high VOCs persist as propellants. However, they are often replaced by compressed gases such as nitrogen, carbon dioxide, or even compressed air, which are inert gases that not only have a lower environmental impact but are also more stable (Niemiec et al., 2021). Unlike petroleum gases, however, they experience a pressure drop in the container during dispensing, since they are in a gaseous state.

However, the development of aerosols is a multifaceted one, given the complexity of the system in terms of container type, propellants, valves, and other aspects. This technology faces immense challenges because, according to data from the European Commission report "Evaluation of Directive 75/324/EC on Aerosol Dispensers," demand for aerosol products was expected to exceed 18 billion units by 2020. This visible quantitative increase in the aerosol products market simultaneously indicates the need for innovation in this industry segment. The main driver of innovation in this technology is the environment and the requirements of regional and global environmental bodies. Manufacturers of metal containers (tinplate and aluminum), as well as those of plastic containers, are focused on finding innovative solutions in their respective fields. Aluminum and stainless-steel containers have limitations related to the specific properties of the material. The advantages of using plastic as a packaging material include: elimination of corrosion and oxidation, reduced container weight, more flexible delivery times, and, importantly, the lower carbon footprint of modern plastics compared to metals. Ongoing developments in Bag-on-Valve (BOV) technology should also be noted. This technology not only has a less negative environmental impact by using air and nitrogen as propellants, but also offers consumer benefits by reducing the use of preservatives, extending product shelf life, and simplifying formula application (Niemiec et al., 2018).

The aim of this research work was to apply the HLB technique for the solubilization of different percentages of D-limonene in the aerosol system.

2. Experimental Procedure

2.1 Surfactants

The surfactants used are commercial surfactants, purchased from suppliers that provide the corresponding Certificates of Analysis for the batches purchased, as shown in Table 1.

2.2 Reagents

The reagents used were reagent grade and USP grade, except where otherwise indicated, and were purchased from various suppliers. The only salt used in the different HLB scans was sodium chloride. In the HLB scans, heptane was used as the oil phase; this heptane was distilled at the PHD Laboratory, and D-limonene was used as a substitute in different percentages (20, 25, 30, and 40). In the aerosols, deodorized liquefied petroleum gas (LPG-A60), supplied by UNI-GAS, C.A., was used as the oil phase, along with D-limonene in the same substitution proportions.

For all tests, deionized water with low conductivity (2-

3 $\mu\text{S}/\text{cm}$) and pH between 6.8-7 was used, obtained by ion exchange or distillation.

Table 1. Surfactants used for HLB scans

Surfactant Type	Common surfactant names	Scan type
Noónico	- Span20-Sorbitan Monolaurate [2-[(2R,3R,4S)-3,4-dihydroxyoxolan-2-yl]-2-hydroxyethyl] dodecanoate	HLB
	- Span80-Mono-sorbitanoleate (2R)-2-[(2R,3R,4S)-3,4-dihydroxyoxolan-2-yl]-2-hydroxyethyl (9Z)-Octadec-9-enoate	
	- Tween80-Polysorbate80. - Polyoxyethylene(20)sorbitanmonooleate	
	- Tween85-Polysorbate85. - Polyoxyethylene(20)sorbitantrioleate	

2.3 Equipment and materials

HLB scans: graduated 15 mL test tubes, burettes, volumetric pipettes, volumetric flasks, and test tube racks were used. An analytical balance with ± 0.0001 g precision was used to prepare surfactant stock solutions and salt.

Solubilization of D-limonene in the aerosol-sol system: Safety aerosol test tubes with an average volume of 110 mL, ungraduated, were used with an average pressure of 8.17 atmospheres and aerosol filling machine, fabricated by AILED.

To verify the presence of surfactants and determine the Tyndall effect, both in HLB scans and in the solubilization of aerosol systems, a 640-680 nm laser with a power of 3 mW was used in each phase of the formulated tubes after reaching equilibrium. For photographic documentation of the initial and equilibrium states of each formulated system, natural light was used against a non-glare black background, and an iPhone 8 was used, recording at 4K resolution at 60 fps.

2.4 Experimental Methodologies

HLB scans: Formulation scans were performed, oil-water-surfactant scans where the formulation variable is the HLB (Hydrophilic-Lipophilic Balance) of a mixture of non-ionic surfactants, in our case Span 80, Span 20, Tween 85 and Tween 80, whose individual HLB values are respectively: 4.3; 8.6; 11 and 15, with the minimum HLB being 4.3 and the maximum 15. Mixtures of the surfactants are made in different proportions to obtain an HLB scale and the solubility (1%), the hydrocarbon (heptane) and D-limonene (its substitute part in the percentages 20, 25, 30 and 40% of the oil phase) and the 2:1 mixture of sec-butanol/pentanol are kept constant. The objective was to evaluate for each percentage of substitution of D-limonene, in what proportion of surfactants or HLB, the optimal formulation is obtained, whose characteristics are indicated above.

In each formulation tube, the SOW (surfactant-water-oil) systems contained a water:oil volume ratio of 1:1, i.e.,

WOR=1. Each phase contained a volume of 5 mL, to obtain a total volume of 10 mL in each analyzed tube.

The tubes were prepared by adding the components in the following order: a) low HLB surfactant, Span 80, and then the mixtures for each previously calculated HLB, b) water and sodium chloride solution, c) high HLB surfactant, d) oil (heptane), and e) the alcohol mixture. The tubes were gently shaken by hand three times.

The tubes were left to stand to allow the systems to reach phase equilibrium, defined as the state where no changes occur in the visible configuration of the system. Once in equilibrium, the presence of surfactants in each phase of the formulated tubes was verified using a laser to determine the existence of micellar formations or micro-emulsions. Photographic records were made of the systems at the beginning and when they reached equilibrium.

The tube with the optimal formulation was designated as the tube where a three-phase system is formed, with similar volumes (Pereira, 2009; Salager et al, 1979b). In cases where the optimum is not obtained, the changes in HLB values are refined, usually by 0.1. This scale refinement is called the HLB scan zoom.

D-limonene solubilization by HLB: The previous formulation scans performed with the heptane oil phase, formulated according to the HLB criteria of a mixture of non-ionic surfactants, in our case Tween 85 and Tween 80, whose individual HLB values are 11 and 15 respectively, served as the basis for this part of the experimentation. In each formulation tube, the surfactant/water/oil systems contained a water:oil volume ratio of 1:1, i.e., WOR=1. Each phase contained a volume of 20 mL, to obtain a total volume of 40 mL in each analyzed tube.

Four D-limonene solubilization systems were studied, at 20%, 25%, 30%, and 40% of the oil phase. The selected HLB values are listed in Table 2.

Table 2. HLB for the solubilization of different % of D-limonene

Sistema	%de D-limoneno de la fase oleosa	HLB óptimo	HLB, región hidrofílica (>opt)			
			T1	T2	T3	T4
1	20	10,7	11,1	11,6	12,1	12,6
2	25	11,2	11,6	12,1	12,6	13,1
3	30	10,9	11,3	11,8	12,3	12,8
4	40	11,1	11,5	11,9	12,4	12,9

The premises for selecting the solubilization HLB values were as follows:

1. Heptane, in the reference HLB scans, was replaced with liquefied petroleum gas (LPG) A60 as the oil phase.
2. For all systems, HLB values close to the optimum were chosen, excluding those where three-phase systems (pseudo-optimums) formed, starting at the first point with an HLB value 0.4 points above the optimum.
3. Aerosol packaging was developed only in the hydrophilic region (>opt) with HLB values increasing by

0.5 points after the initial tube (T1). This criterion is linked to the general objective of this doctoral thesis, which refers to the study of SOW systems with an external water phase in aerosol applications, that is, O/W emulsification systems.

4.-The lowest HLB value is 11.1 and the highest HLB value is 13.1

The tubes were left to stand to allow the systems to reach phase equilibrium, defined as the state where no changes occur in the visible configuration of the system. Once in equilibrium, the presence of surfactants in each phase of the formulated tubes was verified using a laser to determine the existence of micellar formations or microemulsions. Photographic records were made of the systems at the beginning and when they reached equilibrium. Two tubes were selected from each system, resulting in a total of eight. These were selected based on the criteria of greatest solubilization of D-limonene and microemulsion formation. The contents of these tubes were collected in glass bottles, allowing them to degas (the oily phase of LPG—liquefied petroleum gas) and were then identified.

3.1 HLB scans with heptane and D-limonene.

As initially stated, the process of examining the phase behavior of SOW systems was carried out using commercially available surfactants widely used in industry, such as Span 20, Span 80, Tween 80, and Tween 85. It is worth mentioning that the scan technique and the preferred surfactants were chosen based on two technical criteria: first, these surfactants tend to have low foamability in aerosol formulations, and second, the widespread acceptance of the SPAN and TWEEN series (CRODA trademarks) as additives in food, cosmetics, pharmaceuticals, and other industries. The HLB scan, unlike the salinity scan, leaves the salinity fixed and

through mixtures of non-ionic surfactants in different proportions, it is possible to obtain a scale of HLB values which, in the case of this project, was from 4.3 to 15.

Initial scan 0% D-limonene (System 1)

As shown in Figure 5 (System 1), the HLB formulation for the Surfactant-Heptane-Water system, with 0% D-limonene, resulted in its triphasic HLB being 11.5. This HLB point is important because, in subsequent systems, It can be observed how the incorporation of a lipophile such as D-limonene affects/shifts the optimum.

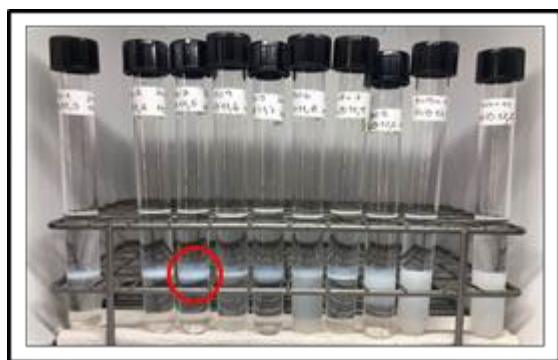


Figure 5. Reference HLB scan with fixed concentration of 1% w/v NaCl.

Scan with 20% replacement of the oil phase with D-limonene (System 2)

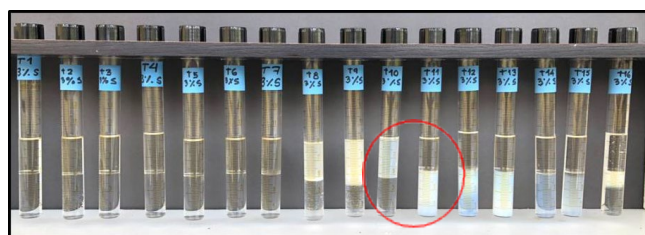


Figure 6. HLB scan (4.3 to 15) with fixed concentration of 1% w/v NaCl.

As can be seen in this scan (Figure 6), a change in the surfactant's location is observed between tubes 10 and 11. That is, in tube 10 the system was a 2 up system (surfactant located in the oil phase or Winsor II) and in tube 11 it was a 2 down system (surfactant located in the aqueous phase, Winsor I), which means that the optimum formulation (Winsor III) is between HLB values of 10.5 and 11. Therefore, a zoom of 10 tubes was performed, with HLB=0.1 graduation, which is described below.

Zoom of the scan with 20% replacement of the oil phase with D-limonene (System 2)

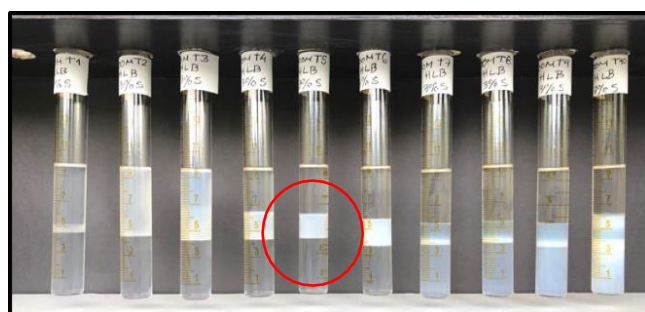


Figure 7. Zoom scan of HLB (T1=10.3 to T10=11.5) with fixed concentration of 1% w/v NaCl. 20% D-limonene in the oil phase

As can be seen in the HLB zoom of system 2 (Figure 7), the formulation optimum (Winsor III) was formed in tube 5 correspondig to HLB=10.7.

Scan with 25% replacement of the oil phase with D-limonene (System 3)

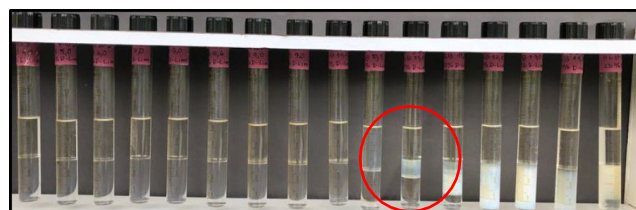


Figura 8. Barridode HLB (4,3 a 15) con concentración fija de NaCl 1% p/v.

In this scan, the amount of D-limonene was increased to 25% (Figure 8) of the oil phase, and the formulation optimum was formed in tube 11 with an HLB value of 11. To determine if this was the true optimum (Winsor III), a zoomed HLB scan was performed between HLB=10.5 and HLB=11.5 with a graduation of 0.1. The results are described in Figure 9.

Zoom of the scan with 25% replacement of the oil phase with D-limonene (System 3)

In the zoom of system 3 (Figure 9) it can be observed that in the formulation optimum (Winsor III) it was formed in tube 8 which corresponds to the value of HLB=11.2.

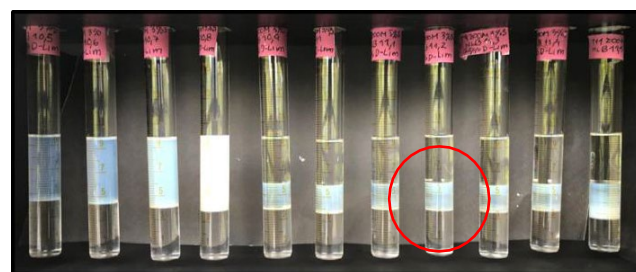


Figure 9. Zoom scan of HLB (10.5 to 11.5) with a fixed concentration of 1% w/v NaCl.

Scan with 30% replacement of the oil phase with D-limonene (System 4)

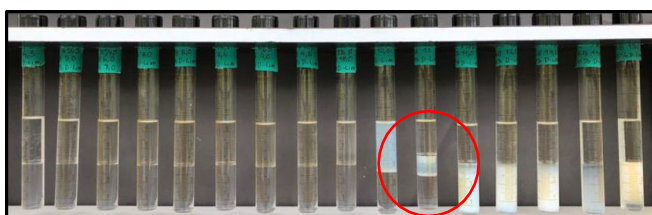


Figure 10. HLB scan (4.3 to 15) with fixed concentration of 1% w/v NaCl.

In this scan, the amount of D-limonene was increased to 30% (Figure 10) of the oil phase, and the formulation optimum (Winsor III) was formed in tube 11 with an HLB value of 11. To determine if this was the true optimum, a zoomed HLB scan was performed between HLB=10.5 and HLB=11 with a graduation of 0.1. The results are described in Figure 11.

Zoom of the scan with 30% replacement of the oil phase with D-limonene (System)

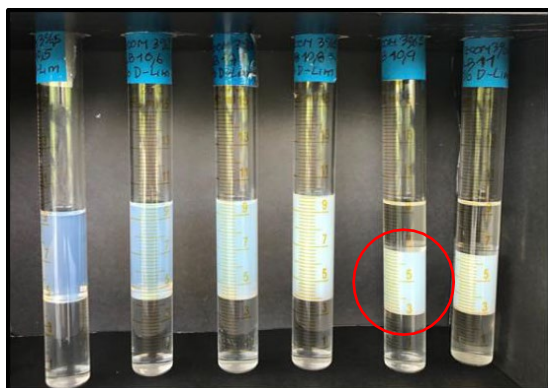


Figure 11. Zoom Scan of HLB (10.5 to 11.0) with fixed concentration of 1% w/v NaCl.

In this zoom it can be observed that the formulation optimum (Winsor III) was formed in the tube 5 which corresponds to the value of HLB=10.9.

Scan with 40% replacement of the oil phase with D-limonene (System 5)

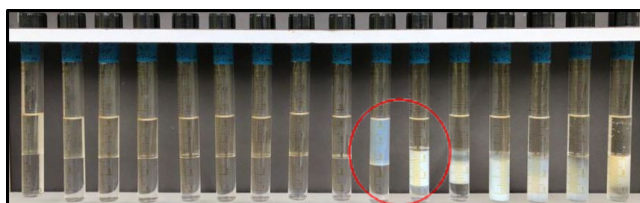


Figure 12. HLB scan (4.3 to 15) with fixed concentration of NaCl 1% w/v.

As can be seen in Figure 12, between tubes 10 and 11 there is a change in the surfactant's location (from Winsor II to Winsor I). That is, in tube 10 the system was a 2 up system (surfactant located in the oil phase, Winsor II) and in tube 11 it was a 2 down system (surfactant located in the aqueous phase, Winsor I), which means that the optimum formulation (Winsor III) is between HLB values of 10.5 and 11. Therefore, a zoom of 10 tubes was performed, with HLB graduation of 0.1, which is described in Figure 13.

Zoom of the scan with 40% replacement of the oil phase with D-limonene (System 5)

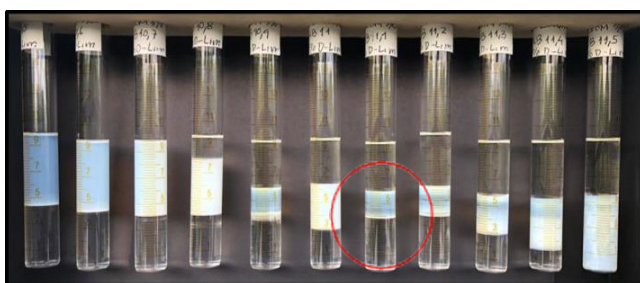


Figure 13. Zoom Scan of HLB (10.5 to 11.5) with a fixed concentration of 1% w/v NaCl.

In the zoom of system 5 (Figure 13) it can be observed that the formulation optimum (Winsor III) was formed in tube 7, which corresponds to the value of HLB=11.1.

Table 3 consolidates the data of the optimal HLB values, corresponding to the 5 systems studied, with D-limonene concentrations from 0 to 40% of the oil phase.

The slight reduction in the HLB value could be due to increased segregation of limonene at the interface and a possible change in the surfactant conformation at the interface, considering that heptane, the solvent used in the experiments, is a linear alkyl hydrocarbon and D-limonene is a lipophilic solvent. It has been reported that the dynamic structure of the surfactant monolayer is strongly affected if the packing of the surfactant or its system decreases, causing the system as a whole to incorporate less water and affecting, as in this case, the HLB and therefore the hydrophilicity of the system (Papadimitriou et al., 2008).

Table 3. HLB optims for the solubilization of D-limonene from 0 to 40% of the oil phase.

System	% D-limonene oil phase	HLB opt
1	0	11,5
2	20	10,7
3	25	11,2
4	30	10,9
5	40	11,1

3.2 Solubilization of D-limonene in the aerosol System

In this experiment, the heptane in the initial HLB scans was replaced with liquefied petroleum gas (LPG) A60, which represents a technological and scientific novelty, since most of the scientific literature refers to formulation scans at atmospheric pressure (Márquez et al., 2023; Salager et al., 1979a; Salager et al., 1979b) and not at 8.16 atmospheres, as is the average of the systems presented below.

As initially stated, the solubilization process was carried out using the formation of SOW systems with the HLB technique. Commercial surfactants, Tween 80 and Tween 85, widely used in industry, were employed. This was chosen because it aligns with the overall objective about to analyze SOW systems with an aqueous continuous phase in order to reduce VOC. Therefore, solubilization was performed in the hydrophilic region, to which these two surfactants belong. It is worth mentioning that, in the solubilization technique, the surfactants were selected based on two technical criteria: first, these surfactants tend to have low foamability in aerosol formulations; and second, the Tween series is widely accepted as a food, cosmetic, and pharmaceutical additive. Furthermore, the figures shown represent the equilibrium state of all the solubilization systems performed, thus omitting the initial states.

As can be seen in Figure 14, tubes 2 (HLB: 11.6) and 3 (HLB: 12.1) exhibit the highest amount of solubilized D-limonene. These tubes present two-phase systems, with the lower phase being isotropic and bluish, where the D-limonene is solubilized. It is important to mention that a

three-phase system, which could be called "pseudo-optimal," formed in tube 1. This system was discarded because it violates premise 2 of the solubilization criteria using the HLB scan technique.

Final State FO System 2-20% D-limonene

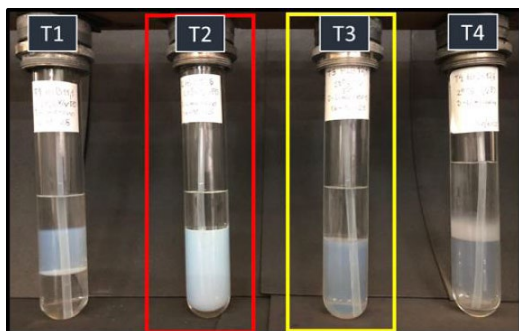


Figura 14. Estado final Sistema 1 solubilización D-limoneno 20% de la fase oleosa. HLB: T1-11.6 / T2-11.6 / T3-12.1 / T4-12.6, concentración fija de NaCl 1% p/v.

Tyndall Effect Verification System 2. Selected Tubes (T2 and T3)

As can be seen in Figure 15, when the red laser is applied to the solubilized phase, the Tyndall effect is confirmed, which is an indication of the formation of ordered solubilization structures, of nanometric order, since they do not cause scattering of the coherent light beam.

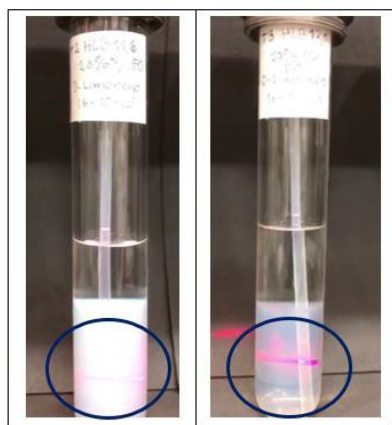


Figure 15. Verification of Tyndall effect, in the selected tubes T2 HLB 11.6 (left) and T3 HLB 12.1 (right) 640 nm red laser.

Final State FO System 3-25% D-limonene

As can be seen in Figure 16, tubes 1 (HLB: 11.6) and 2 (HLB: 12.1) exhibit the highest amounts of solubilized D-limonene. As detailed, these tubes present three-phase systems with the solubilized D-limonene in the lower portion, but with two distinct solubilization patterns: one pattern with the formation of a macroemulsion, characterized by its white color, and an aqueous phase in the lower portion, characterized by its isotropic and bluish appearance. It is important to note that in tube 2, the amount of emulsified

D-limonene is greater than the amount of D-limonene in the aqueous phase.

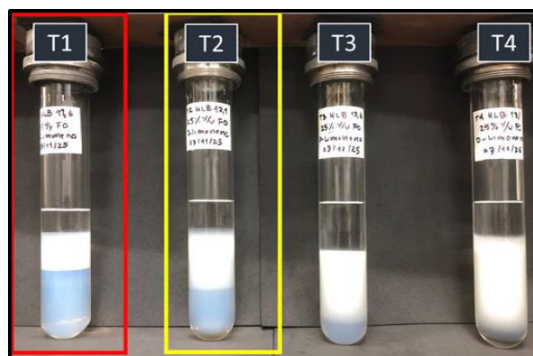


Figure 16. Final state System 2 solubilization D-limonene 25% of the oil phase. HLB: T1-11.6 / T2-12.1 / T3-12.6 / T4-13.1 fixed concentration of NaCl 1% w/v.

It is important to mention that, in tube 4 of figure 16, D-limonene is completely solubilized in an emulsion (white appearance and high light scattering).

Tyndall Effect Verification System 3. Selected Tubes (T1 and T2)

As can be seen in Figure 17, when the red laser is applied to the solubilized phase, the Tyndall effect is confirmed, which is an indication of the formation of ordered solubilization structures, of nanometric order, since they do not cause scattering of the coherent light beam.

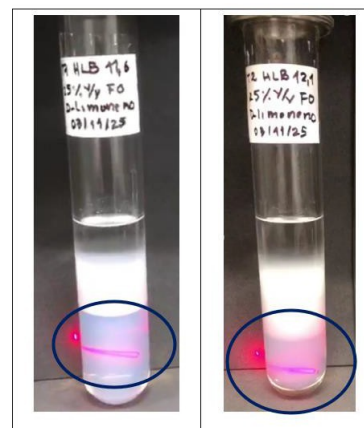


Figure 17. Verification of the Tyndall effect in the selected tubes T1 HLB 11.6 (left) and T2 HLB 12.1 (right) 640 nm red laser

Final State FO System 4-30% D-limonene

As can be seen in Figure 18, tubes 1 (HLB: 11.3) and 2 (HLB: 11.8) show the highest amount of solubilized D-limonene. As detailed, the tubes exhibit biphasic systems, with the lower phase being isotropic and bluish, where the D-limonene is solubilized.

It is important to note that, although in tubes 3 and 4

D-limonene is solubilized via aqueous phase, it is done in a smaller quantity, with the presence of a higher phase of solubilization in emulsion (tube 3).

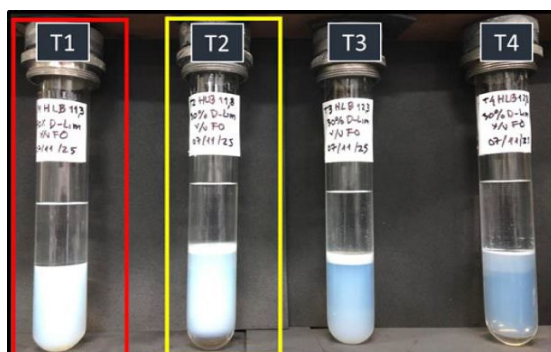


Figure 18. Final state System 3 solubilization D-limonene 30% of the oil phase. HLB: T1- 11.3 / T2-11.8 / T3-12.3 / T4-12.8, fixed concentration of NaCl 1% w/v.

Verification of the Tyndall Effect in System 4. Selected Tubes (T1 and T2).

As can be seen in Figure 19, applying the red laser to the solubilized phase of both tubes (1 and 2) confirms the Tyndall effect, which indicates the formation of ordered solubilization structures of nanometric order, since they do not cause scattering of the coherent light beam.

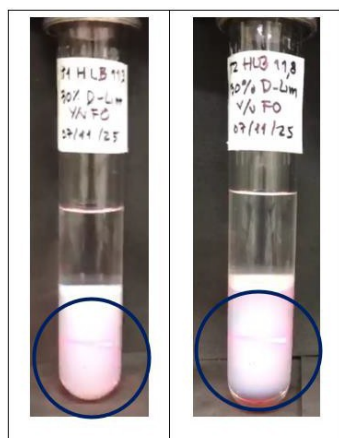


Figure 19. Verification of the Tyndall effect in the Selected tubes T1 HLB 11.3 (left) and T2 HLB 11.8 (right) 640 nm red laser

Final State FO System 5-40% D-limonene

As can be seen in Figure 20, tubes 2 (HLB: 11.9) and 3 (HLB: 12.4) exhibit the highest amounts of solubilized D-limonene. As detailed, these tubes exhibit biphasic systems, with the lower phase being isotropic and bluish, where the D-limonene is solubilized.

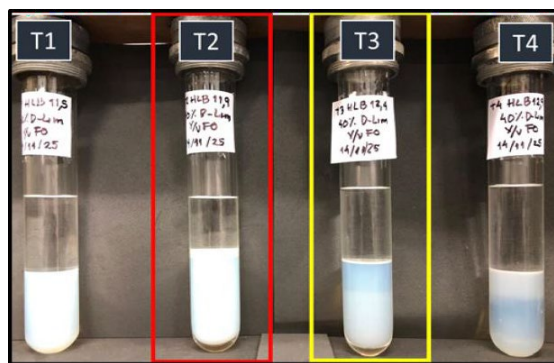


Figure 20. Final state System 4 solubilization D-limonene 40% of the oil phase. HLB: T1-11.5 / T2-11.9 / T3-12.4 / T4-12.9, fixed concentration of NaCl 1% w/v.

Verification of Tyndall Effect in System 5. Selected Tubes (T2 and T3).

Como se puede observar en la Figura 21, al aplicar el láser rojo en la fase del solubilizado ambos tubos (2 y 3) se corrobora el efecto Tyndall, lo cual es indicio de la formación de estructuras ordenadas de solubilización, de orden nanométrico, puesto que no causan esparcimiento del haz de luz coherente.

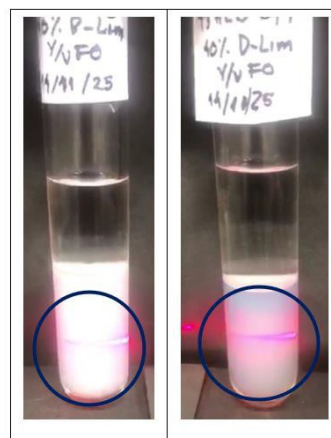


Figure 21. Verification of the Tyndall effect in the selected tubes T2 HLB 11.9 (left) and T2 HLB 12.4 (right) 640 nm red laser

However, the solubilization of D-limonene in SOW systems containing non-ionic surfactants, such as those described above, cannot be explained solely by the chemical affinity of the species. Intermolecular forces also play a role in these systems, and therefore the following premises will be considered to explain them: structural analysis and structural affinity of the components; lipophilic (hydrophobic) phase interactions; hydrophilic phase interactions and the stabilization mechanism by steric effect (Rosen, 2004; Salager et al., 1979b; McClements, 2004; Israelachvili, 2011).

Let's begin with the structural analysis and structural affinity of the components, to understand the forces, based first on the molecular geometries, namely: The Dispersed Phase is made up of D-limonene (from 20% to 40% of the oil phase) and this, as already mentioned, is a cyclic monoterpene (C₁₀H₁₆), with lipophilic, non-polar character, but polarizable due to its double bonds (π electrons) and the aerosol propellant, which is a mixture of low

molecular weight alkanes, such as propane (C_3H_8), butane and isobutane (C_4H_{10}), which are lipophilic and non-polar.

Among the surfactants are Tween 80 and 85, both non-ionic surfactants of low molecular weight, but with remarkably different characteristics. Tween 80 has a lipophilic tail (oleic acid residue, C18:1) and in this tail, it has a cis unsaturation that creates a "knee" or bend in the chain. The head of Tween 80 is a highly hydrophilic head, due to the polyoxyethylene (POE) groups attached to a sorbitan ring; it is therefore a bulky and highly hydratable head, hence the HLB of Tween 80 is 15. In contrast, Tween 85 has three lipophilic tails, two of which have a cis unsaturation that creates "knees" or bends in the chain, and a shorter tail than the previous ones, which also has an unsaturation, but does not cause the tail to bend. The head of Tween 85 is a less hydrophilic head than that of Tween 80, due to the insertion of the tails in the OH groups, attached to a sorbitan ring, although the head is bulky and is less hydratable and hence Tween 85 has an HLB of 11, that is, less hydrophilic than its counterpart, Tween 80.

Secondly, there are interactions in the oily (lipophilic) phase, which occur in the tails of Tween 80 and 85 and D-limonene. At the internal interface of the droplet, the surfactant tails anchor to limonene, with greater power for Tween 85 and less for Tween 80. Furthermore, quantitatively in the solubilization experiments, for the lowest chosen HLB (11.3), the composition and percentage mixing ratio Tween85:Tween80 is 93:7, and for the highest chosen HLB (12.4), the composition and percentage mixing ratio Tween85:Tween80 is 52:48. Given these characteristics, the following forces govern these systems:

London Dispersion Forces (Van der Waals), as the primary interaction, since D-limonene lacks strong polar functional groups, the attraction is based on fluctuating induced instantaneous dipoles. The long alkyl chains of Tween 80 and 85 maximize the contact points with the terpene ring.

π - π interactions ("weak stacking"): D-limonene has a cyclohexene ring and a vinyl group (double bonds), and the tails of Tween 80 and Tween 85 also have double bonds. According to the principles of supramolecular chemistry, there is a weak, stabilizing interaction in the orbitals between these unsaturated systems (D-limonene-surfactant tails), which improves solubilization compared to saturated-chain surfactants (such as Tween 40 or 60).

Steric Affinity (Geometry): The "curved" structure of the Tween 80 tail and the two Tween 85 tails (due to cis bonds) prevents the formation of rigid crystalline structures at the interface. This favors mixing with D-limonene, which is a spatially bulky and nonlinear molecule (Figure 3).

Thirdly, there are interactions in the aqueous phase, occurring in the head region of Tween 80 and 85 with water. The hydrophilic parts of surfactants extend into the continuous medium through the following intermolecular forces, namely:

Hydrogen bonds occur due to the polyoxyethylene ($-OCH_2CH_2-$) head groups of both surfactants, which contain oxygen ether atoms with lone pairs of electrons. These electron pairs act as hydrogen bond acceptors with water molecules in the medium. Additionally, a fixed amount of electrolyte (NaCl) has been added to the solubilization systems, reducing the repulsion between the head groups.

Dipolar Hydration: A robust "hydration sphere" forms

around the surfactant heads, as the water in the systems becomes strongly bound to the Tween polymer network, creating a structured physical water barrier.

Likewise, there is a stabilization mechanism, via steric repulsion, that occurs in the "drop-to-drop" zone. Unlike ionic surfactants such as SDS (sodium dodecylsulfonate), where electrostatic repulsion forces governed by Coulomb's Law act, in the D-limonene/Tween 80 and 85 solubilization system, these systems are stabilized by steric repulsion. In effect, when two emulsion drops approach each other due to Brownian motion, the following physical phenomena occur:

1. Osmotic compression, where the polyoxyethylene heads of both drops begin to overlap, locally increasing the polymer concentration in the contact zone.

2. Thermodynamic Response, where the solvent (water) tends to diffuse toward the high-concentration area to dilute the polymer (Osmotic Pressure), thus separating the droplets again.

3. Entropic Constraint (Excluded Volume Effect), which occurs when the Tween 80 and 85 chains are compressed. These chains lose conformational degrees of freedom (entropy decreases, $\Delta S < 0$), and since thermodynamics favors disorder, the system resists this compression, generating an elastic repulsive force.

It is crucial to highlight that, in the case of D-limonene, the hydrophobic effect plays a significant role. This effect is not, in itself, an attractive force for lipophilic molecules, but rather a consequence of the entropy caused by water's ability to form hydrogen bonds. From a classical perspective, this means that when D-limonene is introduced into the system, water is forced to organize itself into clathrate-like structures around the oil phase, resulting in a reduction of entropy. To minimize this entropy loss, the D-limonene molecules and the alkanes in the liquefied petroleum gas aggregate, reducing the surface contact area with water. This aggregation is achieved through the Brownian motion of the solute and solvent: once the hydrophobic molecules aggregate, it is unfavorable for them to redissolve (Google, 2025; González et al., 2011). This theory was formulated by Frank and Evans and is called the "iceberg theory" due to the hypothetical layer of constricted, ice-like water molecules surrounding the hydrophobic molecule. Whether the surface area of the hydrophobic solute is the best measure of the hydrophobic effect is still debated (Norvaišas et al., 2012). Furthermore, the hydrophobic tails of surfactants enhance the solubilizing effect of D-limonene and alkanes. The latter modify the curvature of the interface and thus the solubilizing capacity, because alkanes behave as co-solvents by penetrating these tails, unlike D-limonene, which is a bulky cyclic molecule. In most cases, one of the synergistic effects of this SOW system is a reduction in the viscosity and flexibility of the interface via a decrease in the radius of curvature (Google, 2025; González et al., 2011).

Based on the above description, the SOW systems studied are a promising method for aerosol design, where D-limonene can be a nanoencapsulator or nanocarrier of poorly or not at all soluble molecules, in O/W type micro-emulsification systems.

4 Conclusions

It is possible to solubilize D-limonene in the studied range (0-40%) and obtain in all cases, systems where formulation optima (triphasic) are observed, that is, with ultra-low interfacial tensions.

The formulation optima obtained are useful for developing formulations using the HLB technique partially outside of these optimal values, in the hydrophilic zone (tentatively at HLB > 11.3), in aerosol systems.

The D-limonene solubilization experiments do not drastically change the HLB and could be used in future work for the solubilization of molecules or active ingredients similar to D-limonene, with the aim of encapsulation and controlled release of these molecules from the oil phase.

Under the given conditions, heptane from the atmospheric HLB scans was successfully replaced by GLP-A60 in the aerosol system solubilizations (pressure of 8.16 atmospheres).

For an HLB value of 11.1 in system 1 (20% D-limonene solubilization), a three-phase Winsor III reaction was obtained, with a Tyndall effect in its middle phase. It is possible to solubilize D-limonene (20 to 40%) using the HLB methodology, taking advantage of the system's chemical energy, within the HLB range of 11.3 to 12.4. This results in systems where microemulsions form, and when subjected to laser beam testing, the Tyndall effect is observed.

The presence of the Tween 85 and 80 combination is significant for D-limonene solubilization due to the complex and complex interactions between the surfactants, D-limonene, the electrolyte, water, and the propellant gas (the oil phase of aerosol systems).

It remains to evaluate the qualities of the structures of the solubilized materials. For this purpose, 2 solubilizations were chosen for each system, for a total of 8, which will be packaged in aerosol, and their performance will be evaluated under different conditions (different valves and actuators).

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Mata-Zabala, Ericson L.: MSc in Engineering and Specialist in Higher Education. Executive Director of the Technology Consulting Firm Corporación CREATON, C.A. and Project Director of Suramericana de Aerosoles, C.A. Email: emata1@uc.edu.ve
 <https://orcid.org/0009-0002-7811-8765>

Pereira Antique, Juan Carlos: PhD in Applied Sciences (ULA). Director at Laboratory of Petroleum, Hydrocarbons and Derivatives (PHD). Full Professor, Department of Chemistry at Faculty of Experimental Sciences and Technology, University of Carabobo, Carabobo, Venezuela. Industrial Consultant in Interfacial Phenomena. Email: jcpereir@uc.edu.ve
 <https://orcid.org/0000-0003-4600-726X>