Fragrance in dermocosmetic emulsions: From microstructure to skin application

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Abstract

Fragrance is added to almost all dermocosmetic emulsions, as it has been found to be a key driver in consumer choice and contributes to the perception of product performance. Fragrance is a complex mixture of odorant chemicals at different concentrations. When incorporated into a formulation, the individual fragrance chemicals partition between the emulsion phases depending on their physicochemical properties, which can impact the structure, stability, texture and odor of the final product. On the other hand, it is well known in the food industry how the composition and structure of food emulsion matrices influence the release of aroma chemicals. Fragranced dermocosmetic emulsions have been studied to a lesser extent but it is interesting to apply findings from the food domain since emulsion structure, composition and aroma compounds share common features. This review aims to give an overview of the literature dealing with the interactions between fragrance and dermocosmetic emulsions. The effects of fragrance on emulsion microstructure, stability and texture are highlighted and discussed. The effects of composition and structure of emulsion on the release of fragrance molecules are also presented. Finally, the interactions between skin and fragranced emulsions are addressed.

Keywords

Fragrance; emulsion; microstructure; texture; formulation/stability, skin barrier

1. Introduction

Fragrance is defined as a complex combination of natural and/or synthetic chemicals added to many consumer products (perfume, household products, cosmetic products) to give them a distinct scent. Fragrance raw materials are characterized by great chemical diversity; synthetic and natural molecules of various natures - alcohols, aldehydes, ketones, esters, lactones - are used, making the total mixture extremely complex. The volatility and polarity of the individual chemicals mainly determine the behavior and performance of the fragrance in diverse media [1]. It can be challenging for the formulation chemist to obtain a formulation performing well with the fragrance of choice at its proper use level. Knowledge of the chemical properties of the individual chemicals in the fragrance composition, often 50 to 100 ingredients, is essential. But unlike other ingredients, fragrance compositions are considered trade secrets and components that make up the fragrance are not revealed on the product label. Fragrance is added to almost all dermocosmetic emulsions. It is one of the most important ingredients of a formulation, as it has been found to be a key driver in consumer choice [2] and contributes to the perception of products performance [3]. The level of fragrance used varies according to the cosmetic product type. Typically, a face cream may contain only 0.01 – 0.1% fragrance by weight, while a soap bar might range from 0.5 - 3.0% fragrance [4]. Depending on their physicochemical properties, fragrance molecules have different affinities with the aqueous and oil phases of the emulsion, and will be located in different parts of the microstructure. Undesirable interactions between fragrance molecules and ingredients of the emulsion matrix can occur, leading to destabilization, discoloration and odor change of the final product [5], [6]. Understanding the interactions between fragrance molecules and dermocosmetic emulsion matrices is crucial, to predict how fragrance can alter the physicochemical properties of emulsions, and to optimize fragrance release. In the past, some authors studied the solubilization and location of fragrance molecules in water surfactant

systems [5]–[23]. These studies were conducted on different model systems, and do not allow for the comprehension and prediction of the behavior of fragrance molecules in complex cosmetic emulsion matrices. Aromas and fragrances are very close in terms of chemical composition; thus, analogies can be made between these two fields. There are many publications about the interactions between aromas and food emulsion matrices, focused on the effect of emulsion composition on aroma release [24]–[34]. However, no similar study was conducted on cosmetic emulsions and a comprehensive review of the interactions between fragrance and dermocosmetic emulsions is still lacking.

The final step of dermocosmetic emulsion usage is the application on the skin. Rubbing the emulsion into the skin induces an external shear, resulting in the quick evaporation of water and other volatiles, and leading to structural changes. As the water evaporates, the surfactant concentration increases and the fragrance can then be re-emulsified [35], retarding its evaporation and thus muting its character and impact [1]. The residual film left on the skin after complete evaporation of water is composed of the oil phase, most of the fragrance and the surfactants. Depending on its structure and surface properties, it can react with skin lipids, causing changes of stratum corneum lipid structure [36]. This can alter the skin sorption of the fragrance, influencing its evaporation rate [37] and thus the fragrance character. Although the understanding of skin – fragrance interactions during and after evaporation is key to minimize allergic reactions and optimize fragrance release, there are few publications regarding this topic. The evaporation of fragrance chemicals from the skin has been measured using analytical measurements by the dynamic headspace technique [38] and then the odor intensity was calculated over time using the odor value (OV) concept [39]. However, the literature is still scarce when dealing with modelling multicomponent mixture release from different types of product matrices.

This review aims to give a comprehensive overview of the existing literature about the interactions between fragrance molecules and dermocosmetic emulsion matrices, from microstructure to skin application. One the one hand, the effect of fragrance on dermocosmetic emulsion structure, stability and texture is presented and discussed. One the other hand, the highlights of the effect of emulsion composition and structure on fragrance release are addressed.

2. Dermocosmetic emulsions and fragrance

2.1 Dermocosmetic emulsions

2.1.1 Emulsion composition

Emulsions are the underlying basis of personal care formulations for skin [1]. An emulsion is a colloidal dispersion of two (or more) immiscible liquids. The discontinuous phase is dispersed as discrete droplets in another liquid, the continuous phase. The majority of cosmetic emulsions are oil-in-water (O/W) emulsions. Dermocosmetic emulsions form a distinctive group among emulsions, as they must meet a whole series of exacting demands. Primarily, they must offer a pleasing appearance to the original formulations, retain this appeal during storage, give an agreeable feeling during application and, most importantly, provide long-term beneficial effects to the skin [40]. The sensory and textural properties of emulsions play a decisive role in the consumer acceptance of a formulation. Typical sensory properties are odor, consistency, spreadability, glossiness and stickiness. Thus, cosmetic emulsions are complex matrices containing specific ingredients, providing the desired physicochemical properties and esthetic standards mentioned above. As an example, the continuous phase of an O/W emulsion typically contains water as the solvent, humectants (glycerin, propylene glycol), thickeners (gums), chelating agents and salt. The oil phase of an O/W emulsion typically contains emollients (oils, butters, fatty esters…), consistency agents (waxes) and surfactants. Due to their amphiphilic structure, surfactants spontaneously adsorb

at interfaces, lowering the surface tension between the aqueous and the oil phases. There are different classes of surfactants depending on their nature, namely ionic (anionic, cationic), non-ionic and zwitterionic. Other ingredients are found in cosmetic emulsions, such as pH adjusters, antioxidants, active ingredients, preservatives, colorants, and fragrances. The formulation of a typical O/W cosmetic emulsion can be found in **Table 1** (from [41]). Formulation chemists must follow strict regulations, and all raw materials composing the formulation must be approved by competent authorities in the country where the product will be sold.

Table 1. Typical formulation of an O/W cosmetic emulsion, inspired from Salka [41]

Ingredient	Typical use level (%)	Role
WATER PHASE		
Water	60 – 85	Solvent
Humectant	2 – 5	Moisturizer
Thickener (gums)	0.1 – 2	Thickening agent
Chelating agent	0.05 – 0.2	Stability
Salt	As needed	Stability
OIL PHASE		
Emollients	5 – 30	Lubricant
Surfactant	0.5 – 5	Stability
Waxes	0.1 – 0.5	Consistency agent
MISCELLANEOUS PHASE		
Preservative	0.05 – 1	
Actives	0 – 10	
Pigments	As needed	
Fragrance	0,01 – 0.1	

2.1.2 Emulsion formation

Tadros [42] described the science of emulsion formation and stability, which is governed by interfacial tension γ. Interfacial tension refers to the energy needed to increase the size of the interface between two immiscible phases and is expressed in Newtons per meter ($N.m^{-1}$). For a stable interface, γ is positive. For a curved interface, such as the oil droplet-water interface

in an emulsion, one should consider the effect of the radius of curvature. Curved interfaces produce some important physical phenomena which affect emulsion properties, such as the Laplace pressure Δp (**equation 1**) which is determined by the radii of curvature of the droplets:

$$\Delta p = \gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \qquad \textbf{equation 1}$$

where r_1 and r_2 are the two principal radii of curvature.

To prepare an emulsion, oil, water, a surfactant and energy are required. Indeed, one must consider the energy needed to expand the interface, $\Delta A\gamma$ (where ΔA is the increase in interfacial area and γ is the interfacial tension). Since γ is positive, the energy needed to expand the interface is large and positive. Thus, the formation of emulsions is nonspontaneous, and the system is thermodynamically unstable. As the surface free energy for a solid/gas interface or surface tension for a liquid/gas interface, interfacial tension is the result of the unbalanced intermolecular interactions between both phases. Surface tension of a liquid can be decomposed according to the different intermolecular forces and gathered as: Lifshitz–van der Waals component, the non-polar one, and the acid-base component (electron donor and electron acceptor), the polar one. Knowledge of these parameters is a benefit as it helps to understand and explain the interactions at the surface and interface between each component. Surfactants play a major role in the formation of emulsions. As they accumulate at the interface, following a mechanism of adsorption, the interfacial tension is reduced. By lowering the interfacial tension, p is reduced and hence the stress required to break up a drop is reduced. Furthermore, in the presence of surfactants, an energy barrier is created between the droplets, and the system becomes kinetically stable.

The addition of surfactant molecules above a specific concentration results in the formation of aggregates of surfactants, called micelles (**Fig. 1** from [43]). This concentration is called

critical micelle concentration (CMC). Just after CMC and for most of the surfactant molecules, these aggregates are spherical. At higher concentrations, a larger scale order appears, and liquid crystal phases are formed. As the concentration of surfactant is increased, several different types of liquid crystal structures occur in solution, namely hexagonal, cubic and lamellar structures. Lamellar phases are composed of planar surfactant bilayers, separated by interlamellar water layers. If the oil volume fraction is increased, reverse phases are formed, with water encapsulated within the structures formed by the amphiphilic molecules.

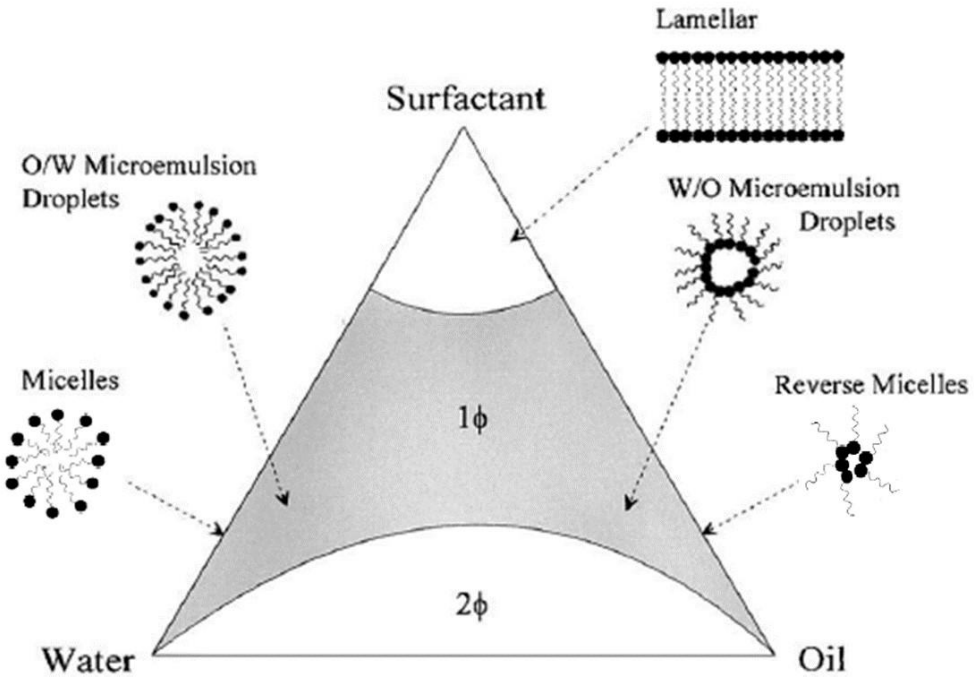


Figure 1. A hypothetical pseudo-ternary phase diagram of a water/oil/surfactant system. Φ for phase; from Lawrence [43]

2.1.3 Emulsion texture

Textural properties of dermocosmetic emulsions are also known to be of great importance, as they are closely related to consumer assessment of product performance [44]. Texture refers to "the sensory and functional manifestation of the structural, mechanical, and surface properties […] detected by vision, hearing, touch, and kinesthesia" [45]. Texture is a complex and multidimensional organoleptic attribute involving all the senses, which makes it complex

to characterize instrumentally. Moreover, the texture evaluation of cosmetic emulsions is complex, as texture must be apprehended at different levels. When evaluating a product, one must consider the product feel on the fingertips when being taken from the container, while being rubbed into the skin and after application, and the feel on the skin itself after application (*i.e* one can sense if the skin feels dry or oily, irritated or soothed, etc.). Thus, texture evaluation of cosmetic products can be divided into three stages, corresponding to the set of sensations perceived as they appear during the evaluation of the product [46]. These three main stages are:

1) *Pick up*: the removal of the product from the container;
2) *Rub-out*: the application of the product on the skin;
3) *After-feel*: the evaluation of the effect of the product on the skin after application.

2.1.4 Emulsion stability

Emulsion stability is a major concern for the formulator. As emulsions are thermodynamically unstable, they tend to separate over time and under the effect of external forces and/or perturbations. Physical destabilization of emulsions mainly proceeds through four distinct phenomena, namely coalescence, Ostwald ripening, flocculation, and creaming or sedimentation (**Fig. 2** from [47]). A detailed description of these phenomena can be found elsewhere [48].

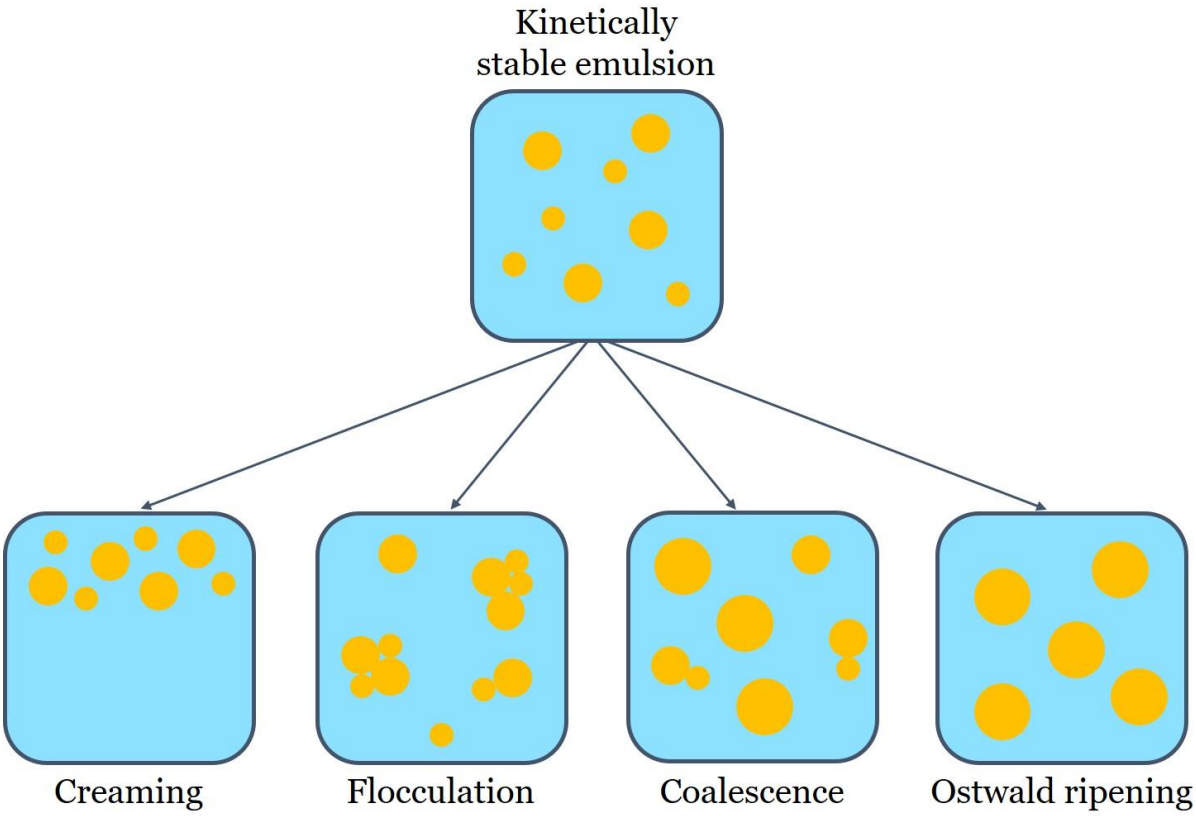


Figure 2. Mechanisms involved in O/W emulsion destabilization

The occurrence and the rate of emulsion destabilization depend on several physicochemical parameters [42]:

- the particle size distribution and the density difference between the droplets and the continuous phase;
- the magnitude of the attractive versus repulsive forces;
- the solubility of the dispersed droplets in the continuous phase;
- the stability of the liquid film between the droplets.

Interaction forces between droplets govern emulsion stability. Van der Waals forces are distant–dependent attractive interactions between atoms or molecules. In order to counteract the van der Waals attraction, it is necessary to create a repulsive force. Two main types of repulsion can be distinguished depending on the nature of the surfactant used [42]: (i) electrostatic repulsion and (ii) steric repulsion (**Fig. 3** from [49]).

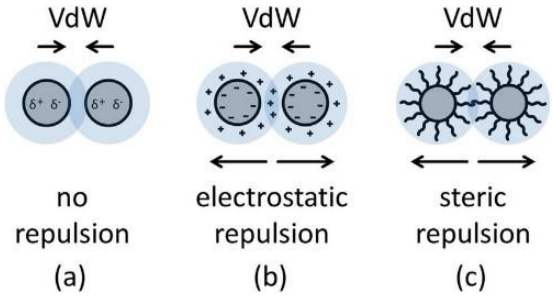


Figure 3. Force balancing of attractive van der Waals (VdW) interactions (a) with repulsive electrostatic (b) and repulsive steric interactions (c) to achieve colloidal stability ; from Matter [49]

Ionic surfactants stabilize emulsions by the formation of an electrical double layer on the surface of the droplet, creating a repulsive electrostatic barrier keeping the droplets apart. Non-ionic and polymeric surfactants stabilize emulsions by providing steric repulsion, which occurs due to the presence of adsorbed surfactant or polymer layers at the surface of the dispersed phase droplet. The portion of the molecule in the continuous phase provides steric hindrance and impedes droplets from coalescing together [1].

2.2 Fragrance

2.2.1 Fragrance composition

Fragrance is a complex blend of isolated odorant molecules. Approximately 3000 ingredients are currently available for the creation of fragrance compositions, and there is a wide diversity of chemical functions represented. The most represented chemical families are esters, alcohols, ketones, aldehydes, hydrocarbons, and musks. Molecules can be of synthetic or natural origin. Essential oils and absolutes are examples of natural extracts often used in perfumery [1]. They are obtained from botanical raw materials such as plants or parts of plants (flowers, seeds, leaves and fruits). Essential oils are obtained by steam distillation, dry distillation or by a suitable mechanical process without heating, whereas absolutes are produced through organic solvent extraction and solubilization in ethanol. The obtained extracts are complex mixtures, containing between 10 and 100 components. An example of a feminine fragrance composition from 2016 can be found in **Table 2** (from [4]). It is composed

of isolated fragrance molecules such as benzyl acetate and coumarine, registered molecules like Florol® and Lilial® and natural extracts such as *Galbanum* essential oil and jasmine absolute. IFRA (International Fragrance Association) standards allow for evaluation and regulated use to ensure that fragrance products are used safely.

Table 2. Composition of a feminine fragrance with a floral scent, from Fernandez [4]

Compound	Weight (g)
Florol®	200
Benzyl acetate	40
Styrallyl acetate	120
Vetyveryl acetate	560
10-undecenal (10%)	80
Hexyl cinnamaldehyde	80
Ambrettolide (10%)	100
Allyl ionone (1%)	80
γ-undecalactone (1%)	160
Frambinone (1%)	80
Blackcurrant bud absolute	100
Coumarine (10%)	140
Cyclosia® base	500
Galbanum essential oil	60
Cloves essential oil	20
Isobutlquinoleine (10%)	40
Phenoxyethyl isobutyrate	20
Jasmin absolute	240
Levocitrol	440
Lilial®	40
Ethyl linalool	140
Lyral®	260
Iralia®	460
Oakmoss absolute (50%)	320
Hédione®	1140
Neroli essential oil	120
Patchouli essential oil	40
Phenylethyl alcohol	760
Sweet orange essential oil	80
Polywood®	160
Rosa Centifolia absolute	120
Benzyl salicylate	440
Santal essential oil	260
Stemone®	60
Tonalid® (10%)	130
Vanilline (1%)	50
Acetyl cedrane	1640
Ylang extra essential oil	140
Jacinth absolute	160
Rose absolute	160

Other than its olfactive profile, the most important property of any molecule used in a fragrance composition is its volatility. Odorous molecules are volatile molecules, which are diffused in the air and can be detected by humans through their olfactory system. Very volatile materials comprise the "top note" of a finished perfume, those of intermediate volatility and tenacity are called the "middle notes," and the low volatility, tenacious products constitute the "base notes". Compositions evolve over time as fragrance molecules evaporate in order of volatility. When sprayed on the skin, the top note might last for five to ten minutes, the middle notes for a few hours and the base notes for several hours or even days, but the exact rate depends on the individual fragrance, the delivery system, and the substrate [1].

2.2.2 Fragrance properties

The evaporation properties of a fragrance can be understood by applying the laws of the physical chemistry of mixtures [3]. Many characteristics of fragrances are based on their cohesive properties. Polarity, solubility and volatility are important examples and are described by different parameters presented below.

2.2.2.1 Hydrophobicity

The partition coefficient (P) is the ratio of the concentrations of a compound in a mixture of water and octanol. Therefore, the partition coefficient measures the balance between the hydrophilic and hydrophobic characters. Partition coefficients often expressed in logarithmic form log P (**equation 2**), are useful in estimating the affinity and distribution of fragrance molecules in the O and W phases of an emulsion.

$$\log P = \frac{\log C_{oct}}{\log C_{water}} \qquad \textbf{equation 2}$$

where C_{oct} and C_{water} are the concentration of the compound in octanol and in water respectively. A low value of log P (log P < 1) means that the compound is more soluble in

water than in octanol, which reveals some hydrophilic character. Conversely, a high log P value (log P > 3) means that the compound is more soluble in octanol than in water, which reveals some lipophilic character. **Table 3** gathers the log P values of some fragrance molecules. As an example, acetate esters are commonly used in the fragrance industry. One can see that log P increases with the alkyl chain length, due to increased hydrophobicity.

2.2.2.2 Solubility parameter

The solubility parameter, denoted δ, is a measure of the cohesive forces existing in a molecule and constitutes a way of predicting if one material will bond with and dissolve in another. There are four types of cohesive forces within molecules: the van der Waals forces (London, Keesom and Debye interactions) and the hydrogen bonding force. Hansen solubility parameter can be calculated (**equation 3**) considering the London dispersion forces δ_D, the Keesom polarity forces δ_P and the hydrogen bonding forces δ_H:

$$\delta = \sqrt{\delta_D^2 + \delta_P^2 + \delta_H^2}$$ **equation 3**

The Debye forces, which are always small in absolute values, are neglected as a first approximation. Vaughan [50], [51] was interested in the possible applications of the solubility parameter for the formulation of cosmetic products and determined the δ of nearly 150 cosmetic raw materials. By studying the behavior of ingredients incorporated into ternary water/oil/surfactant systems, he established that compounds with a solubility parameter δ < 9 tended to solubilize in the oil phase (as β-pinene in **Table 3**), whereas compounds with a solubility parameter δ > 12 tended to solubilize in the aqueous phase (as vanillin in **Table 3**).

2.2.2.3 Volatility

From a chemical point of view, the volatility of a compound describes its tendency to vaporize, that is to say, to pass from a condensed state (liquid or solid) to a gaseous state. The

more volatile the compound, the faster it evaporates. The measurement of the vapor pressure of a compound makes it possible to account for its volatility. Raoult's law (**equation 4**) states that for a single component in an ideal solution,

$p_i = p_i^* x_i$ **equation 4**

where p_i is the partial vapor pressure of the component, p_i^* is the equilibrium vapor pressure of the pure component and x_i is the mole fraction of the component in the solution.

In practice, when an odorant compound is introduced into a sample, its distribution coefficient K (**equation 5**) between the vapor and liquid phases is measured to evaluate the volatility [28]. The latter is expressed as the ratio of the molar or mass concentrations of an odorant in the two phases:

$K = \frac{C_a}{C_S}$ **equation 5**

where C_a and C_S are the concentrations of the odorant in the air and in the sample, respectively. One can determine K_{water}, the partition coefficient of odorants between air/water. In the case of lipophilic compounds, the concentration in water should be inferior to the solubility limit. It is also possible to determine $K_{product}$, the partition coefficients of odorants between air and product for the dispersed systems or emulsions, and to calculate the retention R (equation 6) to predict potential interactions between the fragrance and the emulsion ingredients:

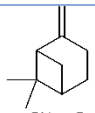
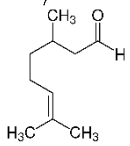
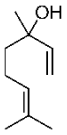
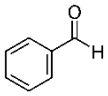
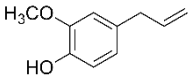
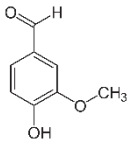
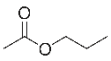
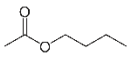
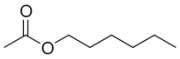
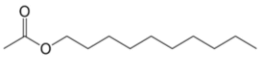
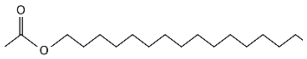
$R = \frac{K_{water} - K_{product}}{K_{water}} \times 100$ equation 6

K_{water} (also noted K_{aw}) is used as a reference for all types of volatile compounds to determine R (Table 3); theoretically, one could also use another reference, K_{oil} for instance. If R=0, no

interaction is expected. A negative value of R indicates a salting-out effect, increasing the release rate of fragrance compounds. Conversely, a positive value of R translates the occurrence of interactions between fragrance and emulsion ingredients, limiting fragrance release [52].

To summarize, several parameters can be considered to give an estimation of fragrance release from emulsions. Log P takes into account the hydrophilic and hydrophobic characteristics of a fragrance molecule and gives an indication on its partition in emulsion phases. The solubility parameter is a complementary way of predicting in which emulsion phase a fragrance molecule will be dissolved. Knowledge of fragrance molecule location in the emulsion can be used to apprehend its release. In an O/W emulsion, fragrance molecules dissolved in the aqueous phase are expected to be released faster than those dissolved in the oil phase. Finally, retention can be used to predict fragrance-emulsion interactions, that would affect fragrance release. In practice, solubility parameters are not always known (**Table 3**, adapted from [5]) and may differ from one source to another as they are hard to measure. Furthermore, they are based on an approximation and depend on the temperature. However, it is to note that solubility parameters are anticorrelated to Log K_{aw}. This latter coefficient can be measured for all volatile compounds. Conversely, log P values of most fragrance molecules are known and can be found in common databases. Thus, log P appears to be a useful and complementary parameter to estimate fragrance release from emulsions. Additionally, interfacial tension of volatile amphiphiles such as fragrance molecules can be measured. This parameter is not often discussed in the literature, but could be used to predict fragrance affinity with the emulsion phases. However, this technique is very sensitive to experimental conditions. To obtain reliable measurements, an important amount of raw materials of high purity is required.

Table 3. Chemical structures, solubility parameters, octanol-water and air-water partition coefficients (Log P and Log Kaw respectively) of some fragrance molecules, from Herman [5]

	Chemical structure	Solubility parameter (δ)	Log P[1] (25°C)	Log K_{aw}[1] (25°C)
β-pinene		8,03	4,16	0.82
Citronellal		8,83	3,30	- 1,56
Linalool		9,62	2,97	- 3,06
Benzaldehyde		11,0	1,48	- 2,96
Eugenol		11,12	2,27	- 5,71
Vanillin		12,34	1,21	- 7,06
Propyl acetate		9,02	1,24	- 2,05
Butyl acetate		8,93	1,78	- 1,94
Hexyl acetate		-	2,83	- 1,66
Decyl acetate		-	4,79	- 1,04
Hexadecyl acetate		8,06	7,74	- 0,30

[1] Calculated using the *EPI* suite

To conclude, dermocosmetic emulsions are complex mixtures of various types of ingredients having different physicochemical properties. They are not thermodynamically stable and thus require some energy and a certain concentration of surfactants to be formed. Their complex structure is responsible for their physical properties (including texture), and their ability to entrap and release cosmetic actives and fragrance. Fragrance is a blend of natural extracts and individual odorant components (between 10 and 100), diluted in a solvent. When added to a dermocosmetic emulsion, individual fragrance molecules partition between the emulsion

phases depending on their physicochemical properties. This is likely to affect emulsion properties such as their structure, stability and texture. Furthermore, one could expect emulsion structure to impact fragrance release. The rest of this review aims to highlight the effect of fragrance on dermocosmetic emulsions structure, stability and texture on the one hand, and the effect of emulsion structure on fragrance release on the other hand.

3 Effect of fragrance on emulsion structure, stability and texture

When fragrance is added to an emulsion, the odorant molecules are distributed in the system between the various phases of the emulsion (oil and aqueous phases, interface and headspace). Fragrance molecules may then have an impact on the emulsion structure, stability and texture. This will also change the balance of fragrance components in the air above the emulsion, consequently changing the fragrance perception [1]. Understanding the effect of fragrance on the emulsion matrix is critical to predict the kinetics of fragrance release and the stability of the finished product.

3.1 Effect of fragrance on emulsion structure

Fragrance molecules can impact the structure and organization of the emulsion. Fragrance is composed of molecules typically spanning the entire range from nonpolar to moderately polar, causing the fragrance mix to separate and partition into the different phases of the emulsion, based on their physicochemical properties (polarity, hydrophobicity, solubility parameter, molecular structure, size and shape) [1]. A classic O/W emulsion is composed of a continuous phase, mainly water, a dispersed phase, usually oil-based, and the interface between these two phases. The continuous phase can also contain micelles or areas of liquid crystal structures. Thus, one can distinguish highly nonpolar areas in the core of micelles and liquid crystal structures and a highly polar area as the external phase. Most cosmetic

emulsions are stabilized by lamellar liquid crystal phases, thus studies found in the literature mostly deal with this type of system. For instance, Zhang *et al* [17], [23] studied the location of three fragrance molecules of various hydrophobicity (limonene, phenylethyl alcohol and benzaldehyde) in a cosmetic emulsion containing lamellar liquid crystals. The authors showed that limonene, which is the most hydrophobic compound and the only aliphatic one, tended to enter the space between the terminal methyl groups of the non-polar chains, between two layers of surfactants (zone C, **Fig. 4** from [17]).

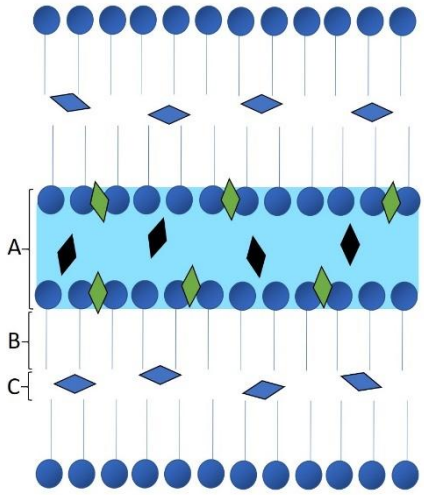


Figure 4. Schematic drawing of hydrophobic (blue diamonds), hydrophilic (black diamonds) and amphiphilic (green diamonds) fragrance molecules in a lamellar liquid crystal, adapted from [17]. Zone A : aqueous layer and hydrophilic headgroups ; Zone B : hydrocarbon chains ; Zone C : space between end methyl groups where oil can be solubilized

The variation in the length of the non-polar chains of the surfactant creates empty spaces within the lamellar bilayer, resulting in some disorder. Limonene, which is composed of a short hydrocarbon chain, can then fit into these spaces and fill the void, increasing the order of the system. Phenylethyl alcohol, which is the most hydrophilic compound, is able to bind with the polar heads of the surfactants (zone A). Benzaldehyde, which is more hydrophobic, can penetrate along the hydrophobic chains of surfactants (zone B). Herman [5] came to similar conclusions when investigating the influence of polarity and solubility parameters on

the location of five fragrance compounds (phenylethyl alcohol, amyl alcohol, hydroxycitronellal, β-pinene and vanillin) in a typical cosmetic emulsion containing liquid crystals. He reported that β-pinene, like many other non-polar compounds with a solubility parameter $\delta < 9$ and a negligible number of oxygen-containing groups, was found in the dispersed phase at the core of micelles. Hydroxycitronellal was located on the surface of the micelles, while phenylethyl alcohol, vanillin and most compounds with a solubility parameter $\delta > 11$ and thus more polar, were located in the continuous phase. Amyl alcohol, which is moderately polar, can fit into the lamellar phases. Other factors such as size, molecular structure, and surface properties of the fragrance molecules influence their location in the emulsion structure [53]. Likewise, Moucharafieh *et al* [54] showed that aliphatic hydrocarbons, such as limonene, had a significant solubility in lamellar liquid crystals, whereas the solubility of aromatic molecules such as phenylethyl alcohol and benzaldehyde in these structures is limited. Moreover, the presence of unsaturation increases the polarizability and rigidity of the fragrance molecules, which then tend to position themselves along the surfactant molecules. The steric hindrance of cyclic alcohols plays a key role in their ability to form hydrogen bonds, which affects their solubilization and thus their location [55].

As a consequence, the partitioning of fragrance molecules within the different phases can modify the emulsion organization. Tokuoka et al [15] established the ternary phase diagrams of surfactant/water/perfume systems containing a non-ionic ($C_{16}POE_{10}$) or an anionic (SDS) surfactant and six fragrances, namely d-limonene, α-hexyl-cinnamaldehyde, α-ionone, benzyl acetate, linalool, and eugenol. For the non-ionic surfactant, the results showed that an increase in hydrophilicity of the perfume resulted in an increase in the domains of the normal and inverse micellar solution phases respectively (L_1 and L_2), and a decrease in the domains of the hexagonal and the lamellar liquid crystal phases, respectively (LC_l and LC_h). Fragrance-surfactant interactions also impact emulsion structural organization. The use of an anionic

surfactant resulted in a decrease in the domains of the liquid crystalline and lamellar phases, for all fragrance molecules. This shows that the non-ionic surfactant has more affinity with the fragrances than the anionic surfactant, making it more difficult to form crystalline phases. The comparison of the phase diagrams of limonene (the most hydrophobic fragrance) and eugenol (the most hydrophilic fragrance), in the presence of both surfactants, allows visualizing these results (Fig. 5 and 6 from [15]).

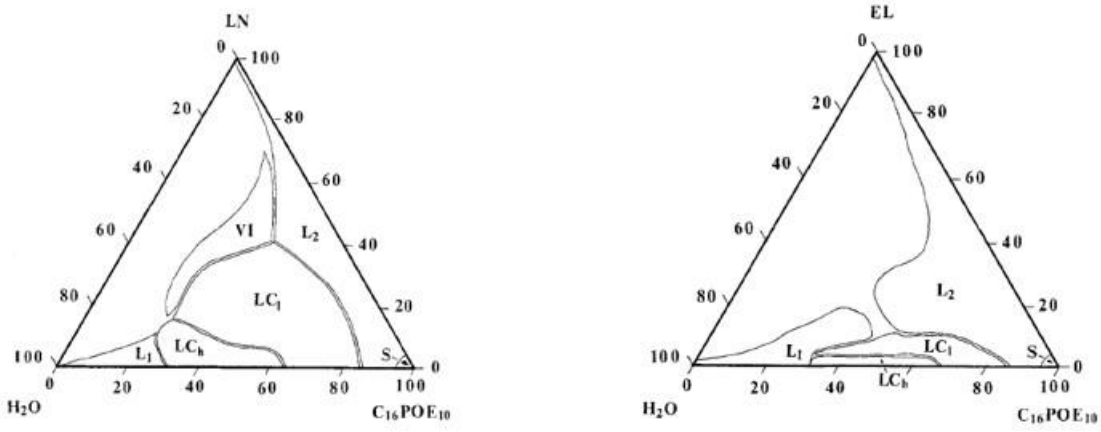


Figure 5. Phase diagrams of C16POE10/water/limonene and C16POE10/water/eugenol systems, from Tokuoka [15]; L1 and L2: micellar direct and inverted isotropic phases; LCh and LCI: hexagonal and lamellar liquid crystalline phases; VI: viscous isotropic solution phase; S: phase including a crystalline surfactant in equilibrium with other kinds of phases.

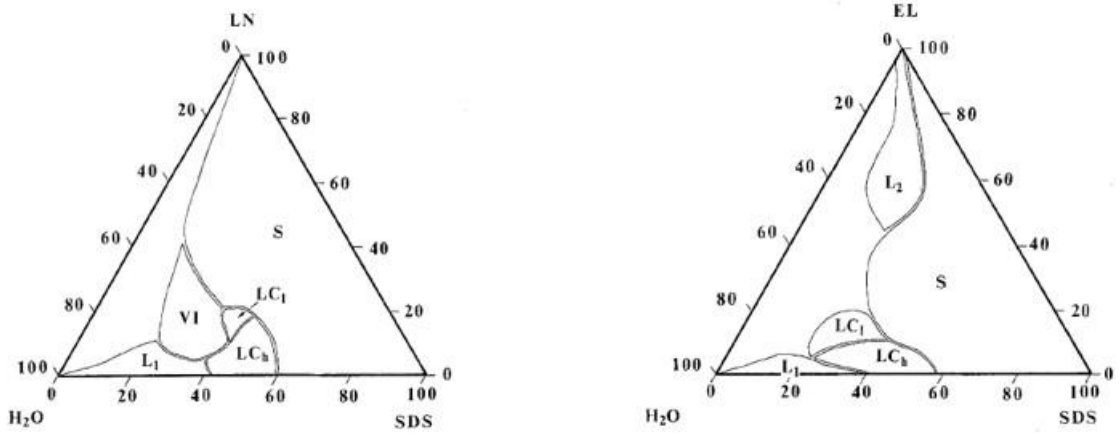


Figure 6. Phase diagrams of SDS/water/limonene and SDS/water/eugenol systems, from Tokuoka [15]; L1 and L2: micellar direct and inverted isotropic phases; LCh and LCI: hexagonal and lamellar liquid crystalline phases; VI: viscous isotropic solution phase; S: phase including a crystalline surfactant in equilibrium with other kinds of phases.

Kayali *et al* [56] showed that the location of a fragrance molecule between two surfactant layers (zone C, **Fig. 4**) results in an increase of the inter-lamellar distance d_0. This distance is not modified if the fragrance molecule is located along the hydrophobic chains of the surfactants (zone B), whereas it decreases if the fragrance molecule is inserted between the polar heads of the surfactants (zone A). Tokuoka *et al* [13] obtained different results when studying the solubilization of fragrance compounds in SDS micelles. They reported that the solubilization of non-polar compounds in the core of the micelles (zone C) had no significant effect on their size, whereas the solubilization of polar compounds between the surfactant molecules (zone B) led to an increase in the diameter of the micelles. Additionally, the location of odorant molecules in lamellar structures greatly affects the curvature of the surfactant layer [57]. When fragrance molecules penetrate the surfactant layer, the volume of the hydrophobic chain and the cross-sectional area of the polar head of the surfactant increase. To minimize this effect, the film curvature becomes negative (or less positive). A phase transition to a more lipophilic system then takes place.

These studies suggest that fragrance-surfactant intermolecular interactions affect the structural organization of the emulsions. However, these results were obtained by studying model ternary systems containing only one fragrance molecule at a relatively high concentration. In practice, dermocosmetic emulsions are more complex systems, fragrance contains many odorant molecules and is present at a much lower concentration in a final product. The effect on microstructure should be less important.

These previous studies did not draw a relationship between partition of molecules in emulsified systems and the final odor. However, Van Ruth *et al* [31] demonstrated a correlation between headspace concentration of hydrophobic compounds such as α-pinene and the odor intensity of the final product. This study reveals the importance of understanding the partitioning of odorants molecules.

3.2 Effect of fragrance on emulsion stability

The effect of fragrance on emulsion stability can be considered from a physical or chemical point of view. Although it is often assumed that fragrance can destabilize emulsions, there are very few studies in the literature about this topic.

3.2.1 Physical stability

As discussed in the previous section, the fragrance-surfactant interactions can affect the stability of lyotropic and liquid crystal phases present in water/surfactant/fragrance systems [15], [23]. The fragrance/surfactant ratio governs the different amphiphilic association structures present and the phase changes occurring in the system, which is responsible for variations in emulsion stability. The presence of lamellar liquid crystals stabilizes emulsions, whereas the presence of hexagonal liquid crystals does not improve the stability. When inverse micelles are formed, they are adsorbed into the macroscopic oil droplets, destabilizing the emulsion. When no liquid crystal phases are present, optimum stability is due to the match of the oil phase density to that of the continuous phase. In some cases, fragrance molecules can act as amphiphiles and be located at the oil-water interface. For example, polar fragrance molecules located on the surface of the micelles can compete with the hydrophilic heads of the surfactants. Consequently, surfactant molecules can be displaced and leave the interface [5], destabilizing the emulsion. The size, shape and number of micelles in a solution greatly influence its viscosity. The incorporation of fragrances can alter these three parameters by changing the surface properties of the micelles, and lead to an increase or alternatively a decrease in the viscosity of the system [3]. This can result in the breaking of the emulsion.

3.2.2 Chemical stability

Cosmetic emulsions are complex matrices composed of many ingredients with different structures. Several papers have reported the existence of interactions between fragrance and other ingredients of the formulation [3], [5], [6]. The reaction of an aldehyde or ketone with a

primary amine leads to the formation of Schiff bases, which can cause an undesirable bright yellow coloration. The best-known Schiff base example is probably aurantiol, which results from the reaction of hydroxycitronellal and methyl anthranilate. These interactions can also lead to changes in odor, with the development of acidic or rancid notes, or a decrease in the intensity of the perceived odor [5]. Matrix composition, including pH or the presence of salt or metals, can lead to the destabilization of fragrances [6]. Exposure of systems to heat or UV light can accelerate these deteriorations. Indeed, many cosmetic products are colored, creating light-stability problems when fragrances are present. Some fragrance chemicals, such as benzaldehyde, create free radicals when exposed to UV. In the free radical state, they can react with the color-generating structures and cause pronounced discoloration [3].

3.3 Effect of fragrance on emulsion texture

3.3.1 Interactions between texture and fragrance

The literature about the influence of fragrance on the textural properties of cosmetic emulsions is very scarce. Texture is a complex and multidimensional parameter that mainly refers to the touch sense. Texture properties of cosmetic emulsions are evaluated during the application to the skin. Different attributes are used to properly evaluate the skin feel of topical creams according to the first phase, named appearance, the pick-up or the rub-out phases as well as in the last phase, after absorption, named residual appearance [58]. Better understanding the effect of fragrance on the textural attributes remains an unexplored field, in particular during application to the skin. Conversely, several studies have investigated the impact of aroma on the textural properties of food emulsions. As fragrance and aroma compounds have very similar physicochemical properties, the behavior of such volatile compounds in emulsions can be comparable. The use of knowledge on the effect of aroma on the texture of food products may be extended to the cosmetic field, especially when studying the consistency, firmness or thickness.

Some papers reported evidence of the impact of aroma compounds nature on the textural properties of food products. Pangborn and Szczesniak [59] studied various aroma compounds and observed an impact of butanoic acid on the perceived viscosity of thickened solutions, but no effect of acetaldehyde, acetophenone and dimethyl sulfide. In a real food product such as low-fat stirred yogurts, Saint- Eve *et al* [60] reported that the perception of texture was dependent on the flavor. Indeed, yoghurts with butter and coconut notes were perceived thicker than yoghurts with green notes (green apple, almond), which were perceived smoother and more fluid. Conversely, other studies found that aroma did not modify the perception of food products texture. Tournier [61] studied the interactions between aroma and texture of six dessert creams with 3 levels of structure and 2 different aromas. The results showed no significant effect of aroma on the perception of consistency, granularity or smoothness of dessert creams. Such results highlight that interactions between texture and aroma depend on the products and the aroma compounds used and that no general rules can be driven from those examples.

Depending on the mechanisms involved, one can generally distinguish two possible origins: either the fragrance/aroma modifies the texture of emulsions from a physicochemical point of view, or the fragrance/aroma influences the perception of the texture from a sensory or cognitive point of view.

3.3.2 Effect of fragrance on rheological properties

The effect of fragrance on emulsion texture can be explained by a modification of the rheological properties of the systems. Rheological measurements are very useful to characterize the flow properties of emulsions and to predict their behavior during manufacturing, in packaging or in final use when applied to the skin. Some of the differences in perceived viscosity previously cited have been attributed to the alteration in the Newtonian behavior (rheological properties) of the thickened solutions produced by the addition of aroma

substances. As an example, Pangborn and Szczesniak measured the intrinsic viscosity of the solutions of hydrocolloids and attributed the changes in perceived viscosity induced by butanoic acid to changes in rheological behavior. Likewise, Paçi Kora *et al* [62] studied yogurts presenting different amounts of fruity flavoring agents. The differences in perceived thickness between yogurts were also perceived without aroma stimulus (panelists wore nose clips), but with a smaller amplitude. This study suggests that aroma has an impact on the texture of emulsion perceived by panelists due to changes in rheological properties. Moreover, not only physicochemical mechanisms made it possible to explain texture-aroma interactions but also cognitive phenomena since the effect is more pronounced when panelists did not wear nose clips. This cognitive effect is discussed in section 3.3.3.

Concerning cosmetic emulsions, fragrance may also have an impact on the rheological properties of systems and consequently affect texture perception. Terescenco *et al* [63] studied the rheological properties and the texture of cosmetic emulsions varying from their oil phase. A cetearyl alcohol/cetearyl glucoside emulsifier was used for its ability to form lamellar phases. Using wide-angle X-ray diffraction, the authors demonstrated that the composition of the dispersed oil phase influenced the lamellar organization, which was dominated by α-gel structuration for oils without heteroatom and by lamellar liquid crystals combined to α-gel for oils with heteroatom. These differences in the lamellar organization can be explained by the differences in emollients structure and hydrophobicity, as evidenced by interfacial tension measurements against water. Rheological measurements highlighted different elastic and flow behaviors between the emulsions. Moreover, the influence on texture was evidenced. This study suggests that fragrance molecules of different structures and polarity may similarly modify the rheology and texture of systems by impacting the organization of emulsions and thus be at the origin of physicochemical interactions.

3.3.3 Cognitive effects

Some authors hypothesized that the impact of fragrance on texture perception may be of cognitive origin. Several papers reported evidence that a change in the stimulation of one sense may influence perception in another [64]. There is vast literature on the influence of color on odor perception from a cognitive point of view. However, there is less information about the cross-modal effects of the sense of smell on the perception of texture. A study from Demattè *et al* [65] demonstrated that the presence of an odor could modify the tactile perception of fabric softness. The authors supposed that the cross-modal interactions could rely on an associative mechanism learned through repeated exposure to particular odor tactile combinations, or that a bias could have been introduced by the presence of a pleasant odor making the perception of the fabric texture more pleasant (in this case softer), or finally that the presence of a pleasant odor could have induced a general change in participants mood that would have been reflected in their response (i.e. softness ratings).

Very few studies have been conducted on the influence of fragrances on the tactile properties of cosmetic emulsions. Gonçalves *et al* [66] studied the influence of the presence and type of fragrance on the sensory perception of cosmetic creams, with two types of fragrance, sweet flowers and fennel, and without fragrance. The formulations containing fennel fragrance were preferred by the testers, whereas the fragrance-free formulations were the least appreciated. Fennel fragrance is widely used in cosmetic products in Brazil (where the study was conducted), thus olfactory memory can explain testers' preference for this fragrance. The floral fragrance is less known, which could explain its lower acceptability (**Fig. 7** from [66]).

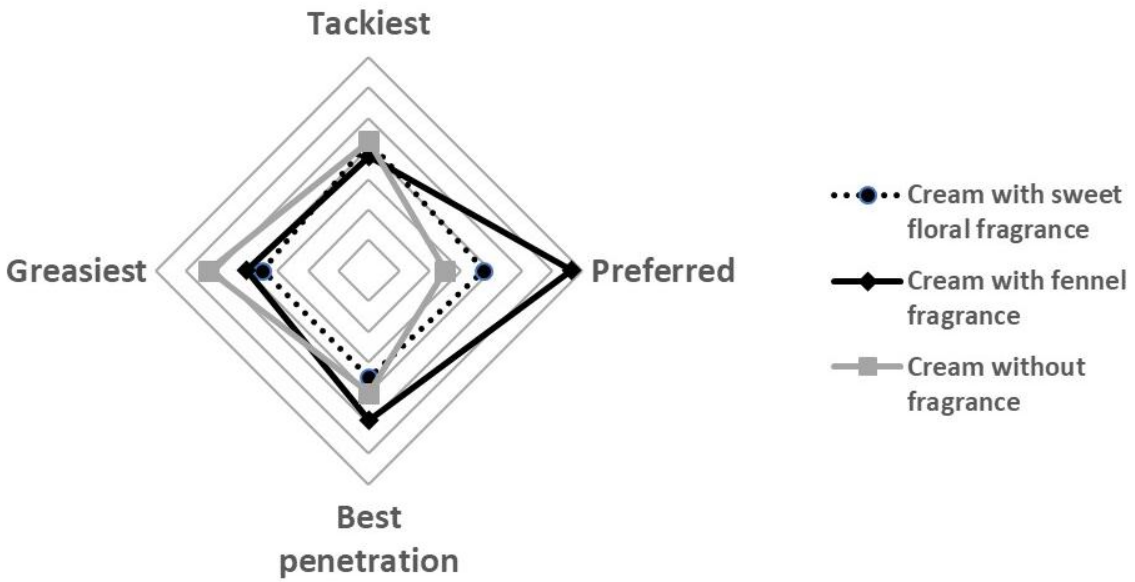


Figure 7. Preferred formulations and formulations that presented the best-perceived penetration, greasiness and tackiness. (CR) Cream formulations; (G) Gel formulations; (A) sweet flowers fragrance, (B) fennel fragrance; from Gonçalves [66]

Furthermore, differences were observed in the perceived efficacy, greasiness, spreadability, stickiness and absorption kinetics of the formulations. The authors explained that the personal preferences of the panelists, associated with their olfactory memory could be at the origin of the perceived differences. Indeed, it is possible that the fennel fragrance is considered lighter and more refreshing by the panelists than the floral fragrance, which is stronger and sweeter. Likewise, Churchill *et al* [64] investigated the cross-modal interactions of odor and touch, to establish whether fragrance modified the textural characteristics of a shampoo. Sixteen fragrances were added to the same shampoo base, and the perceived textural characteristics of shampoo usage on hair during and after washing were assessed by a panel. The authors found that differential effects on the perceived texture and feel of the hair could be observed from shampoos. Viscosity measurements were conducted and apparently shampoos differed solely in odor characteristics. The fragrances *Citrus* and *Rose Jasmine* increased the perception of positive consumer attributes like creamy, silky, smooth, conditioned, and manageable. On the other hand, the fragrances *Leafy* and *Camphor* increased the perception of sticky and tacky attributes. Furthermore, the liking attributes of some of the fragrances were found to correlate

positively with positive texture attributes and to correlate negatively with rather unpleasant texture attributes. However, the most preferred products, namely those fragranced with *Citrus* and *Rose Jasmine*, received the highest scores on positive attributes and the lowest on negative ones, which might indicate a halo effect, that is a general impression of a stimulus that biases the evaluation of the stimulus on a seemingly unrelated characteristic. Other artefacts such as dumping and context effects can influence the panel responses. Dumping occurs if the considered list of attributes does not sufficiently cover all observed perceptions, opinions or judgements. Panelists will then ‘‘dump” their assessment onto another available attribute, resulting in an artificial enhancement of scores on other scales. Context effect is the tendency to contrast sensory attributes with their surrounding context. It is also possible that previous experience and cognitive association could have influenced the perceived odor of the products, changing the perception of the touch and feel characteristics. Based on this study, bias linked to the study of cross-modal interactions were evidenced.

To summarize, fragrance can either modify the rheological properties of emulsions, impacting their viscosity and texture, or be at the origin of cognitive interactions that could influence the perception of texture and product performance. Fragrance also plays a great role in the purchase decision and overall liking of cosmetic products. It is thus essential to be able to control its release from the final product. The next section of this review aims to describe the effect of the emulsion composition and structure on fragrance release. In the case of cosmetic emulsions, the release of fragrance before, during and after application on the skin must be considered.

4 Effect of emulsion matrix on fragrance properties

The creation of a fragranced cosmetic product is a complex task. In addition to fragrance, cosmetic formulations contain various ingredients such as water, organic solvents, surfactants, polymers, pigments, proteins, chelating agents, preservatives, and others [67]. Fragrance

release is not only driven by the physicochemical parameters of volatile molecules, but also by their interactions with the constituents of the product (e.g. skin lotion, detergent) and/or the substrate (e.g. skin).

4.1 Chemical stability of fragrance in cosmetic formulations

Herman studied the stability of fragrance compounds in cosmetic emulsions and the undesired consequences of their destabilization [1]. He reported that many odorant chemicals were not stable in extreme environments such as high and low pH formulations. This can lead to undesired reactions as it is the case for esters, which readily hydrolyze at high and low pH, resulting in the formation of carboxylic acids with a distinctly rancid odor. Phenols can also be very unstable as they are very sensitive to oxidation and can undergo autoxidation, leading to severe color changes. Aldehydes are easy to oxidize or reduce, even under the mildest conditions. Aldehydes can also condense with primary amines to form Schiff bases, contributing to the ageing of the fragrance and leading to color changes of the formulation. Ketones are much less reactive than aldehydes but are easily reduced to secondary alcohols. An important property of fragrance blends is the great diversity of chemical functions of the individual molecules. The presence of different chemistries elevates the odds for the fragrance molecules to react with each other and with specific formulation ingredients to impart instability issues such as color and viscosity shifts, changes in odors, and reactions with the packaging material.

4.2 Effect of matrix composition on fragrance properties

When added to a finished product, it is not uncommon for the odorant character of fragrance to be altered, even in the absence of a chemical reaction. Indeed, differences in perception have been reported when the same fragrance was introduced at the same concentration into different products [9]. This suggests that perfumes interact with the ingredients of

formulations, which influences their release. Understanding fragrance-matrix interactions is therefore essential to achieve optimal formulations considering retention and/or salting-out effects of ingredients. But despite the importance of these phenomena for the industry, literature on the behavior of perfumes incorporated in different cosmetic matrices is still insufficient. However, there have been numerous studies on the influence of the food matrix on the release of aroma compounds. They have shown that aroma release is mainly influenced by the composition of the water and oil phases of the emulsion, which determine the possible interactions between ingredients. We will use these works to extend the conclusions to cosmetic emulsions that have close compositions.

Table 4. Physicochemical parameters of studied fragrance molecules

	Molecular weight (g/mol)	Solubility parameter	Vapor pressure at 25°C (mmHg)	Log P
α-pinene	136,2	8,0	4,75	4,83
Limonene	136,2	8,0	0,20	4,57
Linalool	154,3	9,6	0,016	2,97
Geraniol	154,3	10,2	0,021	3,56
Vanillin	152,1	12,3	0,002	1,21

Sources : The Good Scents Company and Herman [5]

4.2.1 Composition of the water phase

4.2.1.1 Impact of the solvent

The affinity of fragrance compounds with the solvent has an impact on their release. Most of the time, water is used as the solvent constituting the continuous phase of O/W emulsions. Often, ethanol can also be found as solvent in fragrance composition. Indeed, it was found that the solvent could profoundly influence the headspace composition of the volatile components, and the fragrance substantivity [68]. Fragrance molecules behave differently as their affinity with the solvent differs. Hydrophilic compounds can interact with water molecules through H-bonding or van der Waals interactions [69], which affects their air/water partition and may induce retention phenomena for the most polar ones. Additionally, Almeida

et al [37] developed a model to describe the evaporation and permeation profiles of fragrance systems (α-pinene, limonene, and linalool diluted in ethanol) from porcine skin using a Franz diffusion cell. They found considerable differences between the experimental and predicted values for the permeation coefficients, proving that the permeation coefficient parameter is dependent on different factors, including interactions between fragrances and matrices (e.g., ethanol and lotion). Indeed, the polarity of the diluent affects the solubility properties of the fragrance [3]. Limonene and α-pinene (nonpolar molecules) have less affinity with water and ethanol (polar molecules), they were found to be pushed out of the solution explaining the faster release and low permeation of these odorants as compared to linalool (see Log P, solubility parameters and vapor pressures in **Table 4**). In turn, linalool (amphiphilic molecule) was released more slowly as a result of its affinity with ethanol together with its low vapor pressure. These interactions affect the headspace concentration of odorants. Teixeira *et al* [70] established a model to predict and analyze the behavior (evaporation, performance, evolution) of fragrance mixtures in ethanol as a function of time. They showed that an increase in the ethanol mole fraction resulted in faster evaporation of limonene. Indeed, the addition of ethanol increases the average polarity of the liquid phase, which causes accelerated evaporation of non-polar top notes such as limonene. Conversely, the authors found that the mole fractions of geraniol and vanillin increased in the liquid phase with increasing ethanol mole fraction since these compounds are less volatile and more polar.

4.2.1.2 Impact of salt

Salts are used in cosmetic emulsions as viscosity control, preservative, buffer, chelating, or exfoliating agents, and have the property to enhance fragrance release due to the well-known salting-out effect. An increase in the salt concentration induces an increase in the air/water partition coefficients, and thus an increase in the release of most volatile compounds. This is due to the salt dissociation in water into ions, characterized by a decrease in the available

solvent in the liquid phase, thus a decrease in solubilization of volatile compounds [71, 72]. This effect is more pronounced for hydrophobic compounds, which are less soluble in water and will therefore be more released [73].

4.2.1.3 Impact of the texturing agents

In cosmetic emulsions, texturing agents are added to adjust the sensory perception of the final product. These texturing agents are mainly polysaccharides such as starch and gums (guar, xanthan, carrageenan) or synthetic polymers. Among many examples, they can be used as thickeners, emulsifiers, stabilizers and gelling agents. Some authors have modified the nature and/or the concentration of texturizing agents in food emulsions, which led to various textures (more viscous, firmer) that had different effects on the perception of the flavor. Indeed, the addition of thickening agents induces a modification of the structural properties of the solutions which can have an effect on the mobility and the release of the flavor compounds. Polysaccharides, when used as a thickening and stabilizing agents in formulations, are commonly known to reduce flavor release [74]. Two phenomena may be involved in the decrease in volatile compounds release from solution as compared with water. The first one corresponds to an increase in the solution viscosity, more specifically when macromolecular chains overlap inducing a steric hindrance to diffusion. The second phenomenon is related to specific interactions that may retain small molecular species and reduce their mobility in the media [75].

Secouard *et al* [76] studied the release of limonene from aqueous solutions containing xanthan at different concentrations. They reported that the release rate of limonene was markedly slowed down when xanthan gum was present at a concentration above its critical concentration C*, which evidences the occurrence of interactions. Indeed, at C > C*, the polysaccharide chains overlap, allowing the occurrence of intra- and intermolecular interactions between the chains that strongly favor the formation of non-polar regions, able to

trap low-polar compounds such as limonene. In gelled systems, the addition of gelling agents creates a structured network that can also affect the release of flavor compounds. The presence of a dense network leads to the reduction of the diffusivity of volatile compounds, slowing down their migration to the matrix–air interface. Many studies have been carried out using different gelling agents as carrageenan, pectin or gellan gums [77]. Finally, Savary *et al* [75] studied the release of two different hydrophobic fragrance compounds (α-terpineol and ethyl decanoate) from aqueous solutions containing acacia gums with different emulsifying properties. They found a strong correlation between the retention of the compounds and the emulsifying properties of the gum. Indeed, they established that good emulsifying properties were linked to gums able to induce hydrophobic interactions, thus sharply reducing the release and mobility of fragrance compounds in solution.

4.2.2 Composition of the oil phase

Interactions between fragrance compounds and the oil phase depend on the physicochemical properties of the volatile compounds, but also the nature and composition of the oil phase. Hydrophobic compounds are generally more retained in the oil phase than hydrophilic compounds. This can be explained by the fact that hydrophobic compounds are able to form hydrophobic interactions with the oil phase. Besides, hydrophobic compounds being mainly dissolved in the inner oil phase of the O/W emulsions, they first have to diffuse from the oil droplets to the aqueous phase to be released in the headspace, which generally inhibits this process [69]. Several publications [28], [31] report that the volume fraction of the oil phase influences the release of the aromatic compounds. Chung *et al* [34] showed that cherry flavors present in the ice cream were released faster and perceived with greater intensity as the fat content in the ice cream decreased. Similarly, Dadali *et al* [32] reported that the release of vanillin decreased with increasing fat content in margarine. This can be explained by the fact that hydrophobic interactions increase with fat content, therefore hydrophobic compounds are

more retained and less released. Moreover, oil/water partition coefficients of odorant compounds depend on the nature of the oil phase as mentioned in [25] with the comparison of sunflower and olive oils. The chain length and degree of unsaturation as well as the physical state (solid or liquid) of the fat can impact the volatility of flavor compounds. Relkin *et al* [27] studied emulsions containing either hydrogenated palm kernel oil or anhydrous milk fat presenting various percentage of solid-to-liquid fat. Thus Roudnitzky *et al* [33] showed that the volatility of some flavors varied significantly with the percentage of the oil phase in the solid-state in a food matrix, while no dependence was found when the oil phase was in the liquid state. A possible explanation is that most aroma compounds are only soluble in liquid fat, thus a high amount of solid fat reduces their solubility and increases their release in the vapor phase [25].

4.2.3 Surfactants

The kinetic and thermodynamic stability of O/W emulsions greatly depends on the adsorbed layer of surfactants at the oil-water interface [69]. The concentration of surfactant has an influence on the nature of the interface, on its interfacial area and on the quantity of surfactant adsorbed at this interface, which may influence fragrance release. Bortnowska [69] showed that the relative retention of aroma compounds was higher in emulsions formulated with 2wt% emulsifier than in the respective emulsions prepared with 1wt% emulsifier, whatever the aroma compound hydrophobicity. This result suggests that poor coverage of the surfaces of the oil droplets probably decreased the resistance to mass transfer of aroma compounds from oil droplets to the water phase. Similarly, Dadali *et al* [32] showed a decrease in the release of aromatic compounds with increasing surfactant concentration in a model margarine matrix. The authors suggested that the surfactants adsorbed at the interface strengthened its mechanical properties, making the release of aromatic compounds more difficult. It is interesting to note that superficial and interfacial tension measurements could help

corroborate these hypotheses, but they were not taken into consideration in these studies. Landy *et al* [28] studied the influence of the surfactant nature on the release of two aromatic compounds (ethyl butanoate Log P = 1,80 and ethyl hexanoate Log P = 2,82) from aqueous solutions of sodium casein or sucrose stearate. They found that the nature of the surfactant had no significant effect on the volatility of ethyl butanoate, whereas a significant effect was observed on the volatility of ethyl hexanoate revealing differential hydrophobic interactions with the surfactant. On the other hand, when these compounds were introduced into emulsified systems with a triolein oil phase, no significant impact of the nature of the surfactant was observed on the volatility of ethyl hexanoate. Authors supposed that ethyl hexanoate was mainly retained in the oil phase. Conversely, the volatility of ethyl butanoate was lower in the presence of sodium casein than in the presence of sucrose stearate. Ethyl butanoate is more polar and is influenced by the nature of surfactants at the O/W interface. Bortnowska [69] conclude that aroma compounds interacted to a greater extent with natural emulsifiers such as proteins. A significant correlation between flavor retention and surfactant HLB was also reported by Bortnowska [69]. Addition of surfactants with HLB value lowering from 40 to 11, to the emulsions containing 1wt% emulsifier generally increased relative retention of hydrophobic compounds.

To conclude, interactions between fragrance molecules and matrix ingredients can modify fragrance release (**Table 5**). These interactions can be predicted by considering the physicochemical properties of the ingredients (e.g polarity and hydrophobicity), using log P and retention index for example.

Table 5. Summary of the effects of emulsion matrix ingredients on fragrance release

	Effect on fragrance release/retention	References

WATER PHASE		
Solvent	Polar solvents (water, ethanol) have affinity with polar fragrance molecules → retention of polar molecules; release of non-polar molecules	[37], [70]
Thickeners	Increase in viscosity → retention of fragrance molecules	[74]–[77]
Salt	Salting-out effect → release of fragrance molecules	[71]–[73]
OIL PHASE		
Emollients	Hydrophobic interactions → retention of hydrophobic fragrance molecules; increase of retention with increasing oil phase percentage	[69] [28], [31-32], [34]
Waxes	Fragrance molecules are less soluble in solid oils → release of fragrance molecules	[33]
Surfactants	High concentration → retention of fragrance molecules Low HLB → retention of hydrophobic fragrance molecules	[32], [69]

4.3 Effect of matrix structure on fragrance properties

Fragrance release from emulsions can be affected by the emulsion structure, characterized by the nature and viscosity of the dispersed phase, the amphiphilic association structures present and the size of the oil droplets.

4.3.1 Impact of microstructure

Fragrance molecules are distributed in emulsion between the oil and the water phases or at the interface according to their chemical affinity. In O/W emulsions, a lipophilic molecule will be found mainly in the inner oil phase and its release requires the diffusion of the molecule in oil, the transfer through the O/W interface, the diffusion in the water before the release in the headspace. For polar molecules, the path is more direct since only diffusion in water is required to be released in the headspace. Additionally, the nature of the dispersed phase (water or oil) influences the release rate of fragrance compounds. Salvador *et al* [30] reported a higher release rate of diacetyl (polar compound mainly located in the water phase) from an O/W emulsion than from a W/O emulsion with the same composition.

The diffusion of spherical particles in a liquid follows the Stokes-Einstein equation (**equation 7**), which states that the diffusion coefficient is inversely proportional to the viscosity of the medium:

$$D = \frac{k_B T}{6 \pi \eta r}$$ **equation 7**

where D is the diffusion coefficient ($m^2.s^{-1}$), k_B is Boltzmann's constant, T is the temperature (K), η is the dynamic viscosity of the solution (Pa.s) and r is the radius of the spherical particle (m).

Viscosity is one of the most important parameters that influence the value of the diffusion coefficient of fragrance compounds in liquid systems. Several authors observed a decrease in the release of aromatic compounds and their perceived intensity with increasing viscosity of the medium [78]. The nature and amount of amphiphilic association structures present in a system can also affect fragrance release. Van Ruth *et al* [31] reported that hydrophobic odorants incorporated in emulsions were more retained due to their affinity with hydrophobic cavities formed by surfactants. They also showed an increase in the retention of hydrophilic compounds caused by higher micelle concentrations, which suggests interactions between these compounds and micelles. Seuvre *et al* [24] showed that the release of ethyl hexanoate and ethyl butanoate was different in a biphasic or emulsified system, highlighting the effect of microstructure. The size of the droplets of the emulsion was also found to have a strong effect on both the release and perception of volatile compounds. Charles *et al* [78] showed that the effect on flavor release from O/W emulsion depends on the hydrophobicity of the volatile compounds. The release of the most hydrophilic compounds (log P < 1,3) is higher in the emulsion with the larger droplet size (> 85 µm), as compared to the emulsion with the smaller droplet size (20 µm). The increase in droplet size is associated with a decrease in viscosity, facilitating flavor release from the water phase. Conversely, the release of hydrophobic

compounds (log P > 1,5) is higher when the oil droplet size is smaller. A decrease in droplet size results in a decrease in the quantity of surfactants adsorbed at the interface and in an increase in the interfacial surface area, thus increasing the rate of transfer of the hydrophobic compounds from oil to water. Droplet size also had an influence on the sensory profile and intensity of the smell of the flavor compounds. Conversely, Landy *et al* [28] found that the size of the dispersed phase droplets had a limited or no effect on the release of aromatic compounds present in the matrix. The parameter that should be rather considered is the interfacial area.

4.3.2 Impact of texture

Many authors have also hypothesized the occurrence of cognitive interactions between texture and fragrance. Tournier [61] studied the impact of the texture of dessert creams on the perception of flavor. She found out that liquid dessert creams were perceived more intense in flavor than more consistent dessert creams. This trend is in agreement with the results of Saint-Eve *et al* [79] who showed that for the same composition, less viscous yoghurts were perceived more intense in strawberry flavor than more viscous yoghurts. In such studies, authors hypothesized cognitive interactions since no difference in flavor release was observed using in vivo measurements [80].

Moreover, other sensory properties can affect our perception of flavor, such as color and sound. One could imagine that such cognitive interactions also occur in fragranced cosmetics. For example, it is possible that the appearance (color) and texture of cosmetic products influence the perceived smell of the product. However, to our knowledge, there is no data in the literature on that topic.

4.4 Application on skin

The final step of dermocosmetic emulsion usage is the application on the skin. *Stratum corneum* (SC) is the outermost layer of skin, and is thus the first line of defense for the body,

serving an essential role as a protective skin barrier against infections, mechanical stress and chemicals [81]. Thus, it is critical concerning the skin's interaction with cosmetics. The overall chemical and physical characteristics of the skin surface will be partly determined by those of the SC itself, partly by those of structures which feature on the SC such as hair follicles and sweat glands, and partly also by the hydrolipidic film at the surface of the SC [82]. Despite their great importance, the interactions between fragrance and skin surface are poorly documented in the literature. Understanding the release process of fragrance from skin is necessary to avoid skin irritation that can be caused by fragrance penetration into the SC, and can aid in the design and performance evaluation of fine fragrances and fragranced products.

When a fragranced emulsion is spread on the skin, it breaks due to the manual shear applied. As the skin surface is hydrophobic, the oil droplets spread on the surface, while the water and other volatiles are evaporated in a short time. As the water evaporates, the surfactant concentration increases and the fragrance can then be re-emulsified [35], retarding its evaporation and thus muting its character and impact [1]. The residual film left on the skin after complete evaporation of water is composed of the oil phase, most of the fragrance and the surfactants. After application, fragrance dissipates from the skin over time through a combination of evaporation and absorption into the SC by passive diffusion [83] (**Fig. 8**).

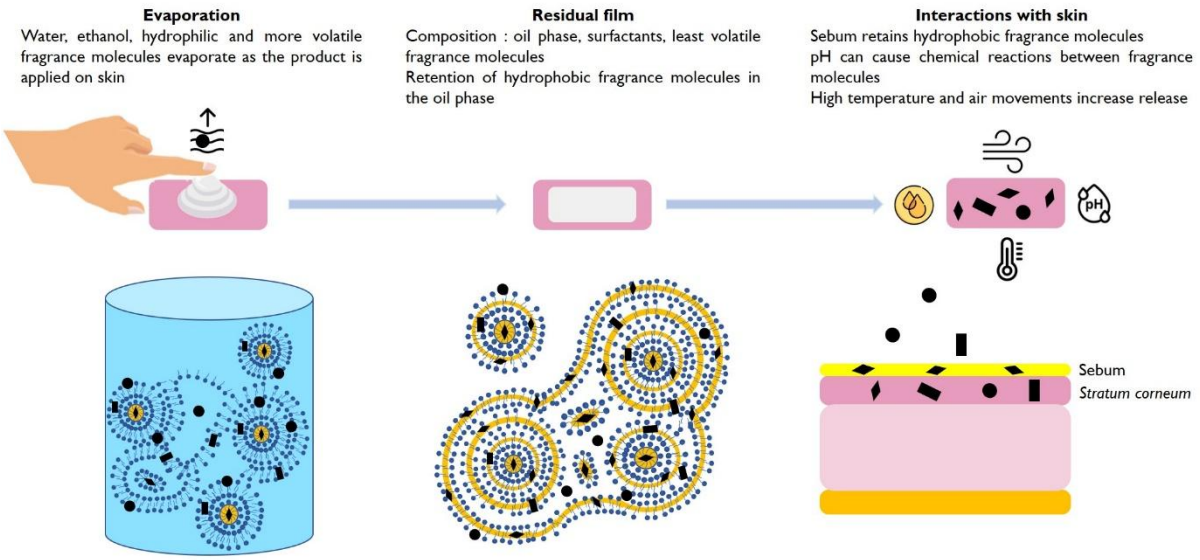


Figure 8. Timeline of fragranced emulsion application on skin, and parameters influencing fragrance release

The evaporation rate of a fragrance from the skin depends on the physicochemical properties of each fragrance molecule (volatility, molecular weight, vapor pressure, and log P) and the interactions occurring among the formulation ingredients and with the skin. Highly volatile and skin-permeable components such as ethanol and top notes dissipate rapidly, whereas less volatile, higher molecular weight compounds may reside on the skin surface for a substantial period of time. The evaporation of the more volatile compounds may lead to significant surface cooling, delaying the evaporation of other components by depressing their vapor pressure. Hence, a complete description of the evaporation process involves the solution of combined heat and mass-transport problem involving concentrated solutions with multiple ingredient interactions. Skin absorption makes the problem even more complex because the skin is a heterogeneous membrane composed of multiple layers of substantial complexity [84]. The individual interactions of skin with the many different components of perfume are complex in themselves, but no doubt other factors also contribute. It is known that perfume behavior on the skin can vary from individual to individual. However, it is unknown which parameters from the skin are responsible for this variation. Perfume diffusion from the skin

could be influenced by several biological parameters, namely skin surface (surface properties, pH, temperature), skin hydration, trans epidermal water loss (TEWL), sebum and air movements above the skin surface [85]. Several studies attempted to understand and predict fragrance evaporation from the skin [37], [38], [82]–[88]. Behan *et al* [82] were among the firsts to explore physical and chemical interactions between skin and fragrance. They quantified the differences in fragrance behavior when on the skin and when on a relatively inert surface (ceramic tile), using headspace analysis and solvent swabbing techniques to monitor fragrance concentrations on and above the surface in use. The results demonstrated that fragrance components, especially the more volatile ones, were slower leaving the skin than ceramic tile. The authors concluded that the interaction responsible was mainly with the SC lipidic material. Depending on their nature, polarity and size, fragrance compounds are more or less able to interact with the skin. Hydrophobic compounds have a certain affinity with the skin lipids and were, therefore, more retained on the skin's greasiest areas, and conversely, the presence of perspiration drove off very hydrophobic materials such as terpene hydrocarbons. Moreover, the presence of bacteria on the skin may give rise to chemical changes due to oxidation and/or hydrolysis. The authors compared odorant molecules of different natures and showed that chemical reactions could take place in contact with the skin. For example, they observed the oxidation of aldehydes, the acetalization of acetals at acidic pH (skin pH around 5) or the hydrolysis of esters when they are applied to areas rich in microbes such as the armpits.

Fragrance diffusion from the skin is also influenced by chemical interactions between fragrance molecules. Vuilleumier *et al* [38] measured the diffusion rate of two very close fragrance compositions applied on the forearm of a human volunteer, using dynamic headspace technology. The first fragrance composition, Vector A, comprised 11 ingredients. Vector B containing the same 11 ingredients, and a musk acting as a fixative agent was also

included. The addition of the musk resulted in a reduction of the initial evaporation rates of the other components present in Vector B. These findings suggest that the fixative agent lowers the thermodynamic activity of the other fragrance ingredients, thereby retarding their absorption and evaporation. This effect appears to be greatest for the most volatile components, providing strong evidence for interactions between these components and the musk. Recently, researchers discovered that olfactory receptors (OR) present at the surface of the skin could be activated by specific fragrance molecules, and play a beneficial role for the skin. Busse *et al* [89] and Tsai *et al* [90] found that the activation of different OR transcripts by Sandalore® (a synthetic sandalwood odorant), isononyl alcohol and cyclohexyl salicylate were found to promote keratinocyte migration and proliferation, inflammatory process and secretion of cytokines, positively impacting wound healing. Duroux *et al* [91] evaluated the effect of Rose extract on skin stress. They found that phenylethyl alcohol (the major constituent of the extract) activated some ORs, inducing an anti-stress response in skin which reduced the appearance of under-eye dark circles.

To conclude, fragrance diffusion from the skin depends on many parameters, including fragrance–skin interactions which are governed by fragrance physicochemical properties but also by skin biological parameters, fragrance–fragrance interactions and fragrance–solvent interactions. However, the whole picture is not well understood, and the literature about this topic is still scarce.

5 Conclusion

Fragrance is widely used in personal care products, and its role is crucial for consumer acceptance and performance assessment of products. Fragrance is a complex mixture of odorant chemicals, but its exact composition is kept secret by manufacturers. The volatility, polarity, and stability of the individual fragrance chemicals mainly determine the performance of the fragrance in diverse media. When incorporated in dermocosmetic emulsions, fragrance

chemicals partition between the different phases according to their physicochemical properties, which has an important effect on odor intensity. Furthermore, fragrance can alter the emulsion microstructure, and interact with specific ingredients of the formulation impacting product odor, color, viscosity, texture and stability. Fragrance was also found to influence the perceived texture and performances of cosmetic products, due to cognitive interactions.

On the other hand, the composition and structure of dermocosmetic emulsions are thought to affect fragrance release, although literature about this topic is very rare. However, many studies highlighted the impact of physicochemical properties of aroma molecules, nature and concentration of surfactant, water:oil ratio and interactions with matrix ingredients on the release and perception of aroma chemicals in food emulsions. Regarding the great chemical similarities between fragrance and aroma compounds and of both matrices, one could reasonably think that these results can be transposed from food to cosmetic emulsions. When applied to the skin, emulsion structure changes due to water evaporation. The residual film left on skin contains most of the fragrance, which can then react with skin lipids and be re-emulsified, influencing its character and evaporation rate.

Fragrance is often the last ingredient added to the base formulation and can affect stability and viscosity of the formulation. To avoid unpleasant interactions between fragrance and cosmetic matrices, it is important to consider the foresee the addition of fragrance to the formulation as early as possible. Knowledge of the structure, polarity and volatility of fragrance molecules is necessary to predict possible interactions with the cosmetic formulation. Compatibility with the other ingredients of the formulation such as salt, viscosity adjusters and pigments should also be taken into consideration. Finally, very little information is available in the literature about the superficial and interfacial properties of fragrances, although it could help in understanding and predicting their behavior in emulsions. Furthermore, such knowledge could

be useful to apprehend fragrance interaction with the skin and to avoid skin irritation which is a major concern for the cosmetic and pharmaceutical industries.

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