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Study of the Thermodynamic Equilibrium of Fragrance Mixtures, Limonene, Linalool and Geraniol, using the Unifac and Cosmo-Sac Models and the Estimation of their Combined Properties in Binary, Ternary and Quaternary Mixtures

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Abstract: Perfume is a non-ideal complex mixture of chemicals originating from the extraction of essential oils and these oils are volatile components extracted from plants, some animals, or even synthesized. For this reason, to compose a fragrance, there are countless possibilities to combine one element and another, which makes the process slow and expensive. Therefore, in this study, we will combine three components of the most known and accepted in the cosmetic industry that make up most essential oils, they are Limonene, linalool, and geraniol. The effect of these combinations generates an influence on the diffusive behavior, on the volatility of the mixture and on the odor intensity of its constituents, due to molecular interactions, its physicochemical properties and the presence of liquid and vapor phases. Therefore, some thermodynamic models and calculations involving vapor-liquid balance, EVL, are the most used tools to predict perfume performance and quality. In general, these models start from the activity coefficient, which measures the non-ideality of the mixture, by the modified Raoult's law, which associates this coefficient to the vapor pressure and to the compositions in each phase. However, being of industrial interest, the use of modeling and process simulations capable of optimizing the time and cost of a product, the research seeks to investigate the application of thermodynamic models of the COSMO and UNIFAC type to estimate the VLE of real mixtures of fragrances, through literature review and computational analysis. The use of the COSMO-SAC thermodynamic model will help to obtain the activity coefficient and the sigma profiles of a combination among the components studied, through the JCOSMO computational package. The UNIFAC model and Raoult's Law for ideal gas/solution will contribute to the estimation of the VLE curves of binary mixtures, the diffusive behavior of fragrances and the fugacity and activity coefficients of binary, ternary and quaternary mixtures, through the process simulator DWSIM. The results obtained showed agreement with the expected behavior, according to the literature. Regarding the efficiency in the use of thermodynamic models, which facilitate the VLE studies of different fragrances and the interactive behavior of these components when mixed, in order to reduce the number of experiments and optimize the process. The biggest challenge of the research was to find programs that could facilitate the analysis of VLE curves, such as the complete JCOSMO, which is not available for free access.

Keywords: Fragrances, Volatility, Thermodynamic Models, Liquid-Vapor Equilibrium, COSMO-SAC, UNIFAC, JCOSMO, DWSIM

Introduction

Perfume is a non-ideal complex mixture of chemical products originating from the extraction of essential oils, whose physicochemical properties vary according to the polarity, solubility, volatility, and odor intensity of its constituents (Mata and Rodrigues, 2006; Xavier *et al.*, 2020). The essential components are components extracted from plants and some animals, with wide applicability in the animal market, being their use in pharmaceutical, cosmetic, and cleaning products, whose classification follows an olfactory pyramid, according to the volatility time of each one of them (Almeida, 2016).

Fragrance volatility studies comprise the application of the activity coefficient, γ_i , which estimates the non-ideality of these mixtures in the vapor-liquid equilibrium, VLE. This equilibrium is reached when the rates of evaporated liquid and condensed vapor are equal¹. This application can be facilitated through the use of some thermodynamic models, among which are the UNIFAC² and COSMO-SAC³ (Lin and Sandler, 2002) models described in this study.

In addition, its use is of fundamental importance for the analysis and design of processing units in the chemical industry. These models were created to reduce or replace the experimental tests used in the combination of the most diverse types of fragrances and their behavior in the mixture (Valente, 2016; Van Ness, 2007).

The activity coefficient of a substance in a mixture corresponds to a number that represents the intensity of the interactions between the components and the effect of the molecular structure⁴, is a measure of the non-ideality of substances in the liquid phase⁵. When γ_i tends to 1,0, it is said that the component hardly notices the presence of the other substances⁶, while, if $\gamma_i \neq 1,0$ the component identifies the presence of the other substances, behavior characteristic of real mixtures (Xavier *et al.*, 2020).

The fragrance branch has expanded over time and new scented molecules were created from pre-existing ones, allowing perfumers to have infinite combinations. However, when creating or discovering a molecule, specialists verify its potential for use in aromatic products, through a systemic analysis⁷ of its behavior in different solutions, so that the combination between them is pleasant and accepted in the market (Mata and Rodrigues, 2006; Xavier *et al.*, 2020).

Therefore, the study is not simple. Because it contains a variety of aromatic molecules and, consequently, an

infinity of combinations, the process becomes complex, time-consuming and expensive. Therefore, several thermodynamic models have been proposed that predict the behavior of volatile molecules and the effect of real mixtures, through the activity coefficient and the vapor-liquid balance, VLE, of these mixtures. The advantage of the models lies in the reduction of costs and analysis, through experimental data and variables already defined in each one of them (Mata and Rodrigues, 2006; Xavier *et al.*, 2020).

However, being of industrial interest, the use of modeling and process simulations capable of optimizing the time and cost of a product, the research seeks to investigate the application of thermodynamic models of the COSMO and UNIFAC type to estimate the ELV of real mixtures of fragrances, containing limonene, linalool and geraniol. The choice of these components is due to their presence in numerous essential oils and the knowledge of formulations in cosmetics.

Materials and Methods

As perfume is a complex mixture of volatile components, the characterization of fragrances is important to detect in which note of the olfactory pyramid that component is structured, or even to study the behavior of these components present in the mixture. In this case, limonene, linalool, geraniol, and ethanol were combined as a base solution for this characterization, composing binary, ternary and quaternary mixtures, to predict the characteristics of the mixture, estimate the volatilization time and the vapor composition.

Several odor intensity models were created to facilitate calculations involving the physical magnitude perceived by the stimuli. The dominant odor in a mixture can be found in the vapor composition and, to predict this composition above the diluent, in general, alcohol, it is necessary to know some physicochemical properties of the mixture and the phase equilibrium.

The thermodynamic model used is the COSMO-SAC which, through quantum mechanics, can estimate the solvating power of a solute in a solvent, submerged in a perfect conductor. The vapor-liquid equilibrium was predicted using the modified Raoult's Law, in which the vapor pressure was determined by the Antoine equation and the activity coefficient was estimated by the COSMO-SAC and UNIFAC models.

The work presented is theoretical and experimental, based on research and literature review. Among the main references, the authors Rafael de Pelegrini Soares stand out, in mathematical modeling and simulations and Hendrick C. Van Ness, in the field of thermodynamics. Added to the

¹Vaporization is directly dependent on temperature, while condensation is directly dependent on pressure.

²UNIFAC-Universal Quase-chemical Functional-group Activity Coefficients.

³OSMO-COnductor-like Screening MOdel Segment Activity Coefficient

⁴A spatial arrangement or more stable conformations of the molecule.

⁵In the gas phase, this interaction is more difficult to happen under low or moderate pressures, because the molecules are more spaced from each other.

⁶The substance interacts in the mixture as if it were pure, so they are assigned the condition of an ideal gas.

⁷Quality index, formulation, combined raw material, packaging, and the final evaluation of the product.

research of scientific articles, studies in the literature on perfumes, the liquid-vapor balance, models based on the activity coefficient, such as UNIFAC and COSMO-SAC, physicochemical properties of the components and their influence on the chemical industry. In addition to the use of computer programs such as (JCOSMO, 2022) to obtain the activity coefficient and (DWSIM, 2022) for the analysis of the ELV curves of the binary mixtures. Both programs, DWSIM and JCOSMO, were chosen because they have a simple methodology and are available on the internet.

This text has been divided into sections, each covering an essential topic for estimating and predicting ELV calculations and applying the COSMO-SAC and UNIFAC models. Starting with the concepts of perfume, fragrances, and aromas, their physical-chemical properties, and thermodynamic models. Next, we have the results of the effect of the properties of the components limonene, linalool, and geraniol, when combined in the presence and absence of the diluent (ethanol), through the sigma profile and the VLE curves of the binary mixtures. Finally, it concludes with the validation of these models through comparison with experimental data from the literature and observations of the results collected by the DWSIM simulator and the JCOSMO computer program.

Perfumes, Aromas and Fragrances

One of the most sublime perceptions of human beings is their olfactory capacity, which allows them to recall memories of the smells that marked their childhood, such as the smell of their mother, breast milk, the environment, food, and their own body. Even the appropriation for the personal use of perfumes, combined with their body odor. Studies show that each human being has a characteristic odor and the choice of perfume, as well as the combination of fragrances, is related to this odor (Lenochová *et al.*, 2012). This explains the lower and higher attraction to different types of fragrances or blends.

Its origin is associated with the burning of wood and dry leaves, whose smoke produced was given as an offering to the gods of the time. Later, other materials were incorporated for the production of incense and hence the name per FUM which means "to smoke". Perfumes for personal use emerged in Egypt with the purpose of social hierarchy. Initially, its production was based on the extraction of animal and vegetable raw materials, and today, seeking to combine new fragrances and reduce costs, in addition to environmental impacts, many mixtures are synthesized in laboratories, through ecologically sustainable processes (Dias and da Silva, 1996).

By definition, perfume is a complex mixture of organic compounds called fragrances. And the fragrance is a volatile chemical compound with a molecular mass of less than 300 Da (Daltons), perceptible through the human

olfactory system. Originated from the Latin fragrant which means "aroma, smell, odor, color, perfume" (Mata and Rodrigues, 2006).

These terms are often used in different areas and are related to the dilution of the formula in alcohol. For example, perfume is the term used for personal use, whose dilution in alcohol is much less, therefore, stronger than an ambient scent. The fragrance is a term used for the environment, whose dilution in alcohol is greater and therefore weaker and aroma is a term used in olfactory and cosmetic marketing (Xavier *et al.*, 2020).

In general, perfumes are composed of two basic components, a diluent, and a fragrance. The diluent, mostly alcohol, serves to dilute all oils and essences, to obtain an expected concentration for the product and is present in greater quantities. And the fragrance is a combination of aromatic substances of animal, vegetable, or artificial origin, attributed by notes by the cosmetics industry. This combination can contain from 20 to 40% of aromatic compounds dissolved in alcohol, being directly linked to the concentration of the essence. The higher the concentration of the essence, the longer the fixation time on the skin and the lower its volatility (Xavier *et al.*, 2020; Gomes, 2019).

As for the time of volatilization and the intensity of the molecules, the cosmetic industry usually classifies fragrances in notes, through an olfactory pyramid. Figure 1 shows a scale of notes of a perfume and the participation of different fragrances in those notes.

The base or base notes comprise the least volatile part and, therefore, are heavier and longer to be perceived. This makes the perfume last and is where the woody, sweet, balsamic, and spicy notes are found, among others. Can be felt from 8 h to 1 day (Dias and da Silva, 1996; Xavier *et al.*, 2020).

The middle or middle notes are more volatile than the base notes and correspond to the "heart" of the perfume, as soon as the top note begins to disappear. Among them are floral, green, and fruity and can be felt for periods of 15 min to 8 h. Finally, at the top of the pyramid are the top notes or top notes, which are the most volatile and therefore lighter and more easily felt than the others and can last from a few minutes to 2 h. The most common are citrus and menthol (orange, lemon, bergamot, mandarin, and lavender, for example) (Dias and da Silva, 1996; Capuani, 2015; Xavier *et al.*, 2020).

The natural fragrances characteristic of perfumes was obtained from essential oils⁸, extracted from plants, flowers, and roots and within this group, whose molecular mass varies from 200 to 300 Da (Daltons), there is a wide variety of scented components. Figure 2 shows some of these main components, among them geraniol and linalool, which are the most abundant monoterpenes and, consequently, more important, used in the production of perfumes.

⁸The main fragrance agent is formed by 20 to 60 different components in various concentrations, the main ones being present in relatively high levels, 20 to 70%.

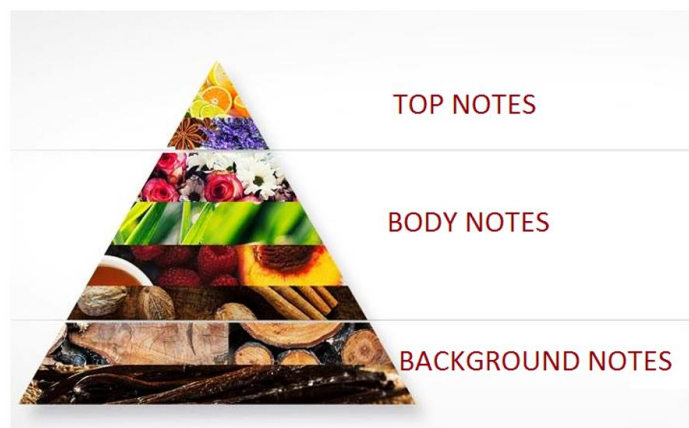


Fig. 1: A perfume's note scale, including different fragrances attributed to the time of volatilization (Havrê, 2020)

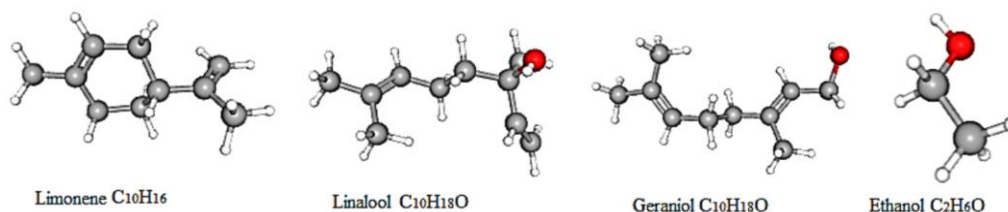


Fig. 2: Some of the main components of natural essential oils (Adapted from PubChem, 2021a, b, c)

Both geraniol and linalool are major components found in jasmine, lavender, and palmarosa. Geraniol can also be found in roses and linalool in bergamot. Limonene can be found in caraway, bergamot, eucalyptus, orange, lemon, and juniper (Xavier *et al.*, 2020). Attributing to the notes of the olfactory pyramid, limonene belongs to the top notes, and geraniol and linalool to the middle notes. Ethanol serves as a baseline study for solvation (Teixeira *et al.*, 2011).

The fragrance market is broad, covering the food, pharmaceutical, personal care products, cosmetics and perfumery (HPPC) sectors, and cleaning products, among others. Concerning HPPC, according to the Brazilian Association of Personal Hygiene, Perfumery and Cosmetics Industry (Abihpec), the sector grew 4.2%, reaching a factory billing of R\$55.7 billion in the production of these items. And in 2019, Brazil remained in the fourth position in the world ranking of fragrance consumption, earning US\$6.676 billion (EUROMONITOR, 2020). Concerning essential oils, the main raw material for the production of fragrances, Brazil has a considerable prominence, mainly in the export of oranges, responsible for 50% of the world's production (Gomes, 2019; Speziali, 2012).

Therefore, the study of fragrances has aroused great interest, especially regarding the synthesis of the

molecules that make up essential oils, and the variability of mixtures and their combinations. In addition, the olfactory capacity of the human being, resulting from the chemical stimulus⁹ and the olfactory apparatus, allows them to detect numerous substances present in the air in concentrations lower¹⁰ than a gas chromatography equipment, despite not being able to distinguish several aromatic components present in the same mixture. (Xavier *et al.*, 2020).

Physicochemical Properties of Fragrances Volatility

The human olfactory system is only able to perceive the smell of a substance because of its volatility. More volatile substances tend to be perceived more easily, but for a short time, while less volatile substances are more difficult to perceive, but can be felt for a longer time. In mixtures with two or more volatile components, as is the case with perfumes, fewer volatile substances are felt after the volatilization of substances above it and belong to the group of base notes or base notes (Pavani, 2014; Xavier *et al.*, 2020).

By definition, the volatility of a substance is the ability to change from a liquid state to a vapor state over time and is positively associated with vapor pressure, as it measures the tendency of a liquid to evaporate. The higher

⁹These properties are directly involved in the effect of mixtures.

¹⁰With an accuracy of 10⁻¹⁸ g.

the vapor pressure of a fragrance component, the lower its evaporation rate and, consequently, the greater its ability to remain in the mixture (Pavani, 2014).

As mentioned, fragrances are felt over time after they start to volatilize. But, in addition, the application distance is a fundamental factor that measures the intensity of the components, the long-term effectiveness, and the diffusion of these compounds in the environment.

In perfumes, aromas and fragrances, the choice of volatile organic components takes into account not only the fragrances that are most attractive to the human sense of smell, but those whose molecules are light enough to spread through the air. A curious fact is that the perception of smell changes from one person to another, that is, the same fragrance can be felt differently between people. This is because each human being has different genetics and, depending on the changes in the genome, the smell receptors can undergo changes, making the odor not the same between one person and another (Ciencia, 2022).

Steam Pressure

Being one of the most essential physicochemical properties in the design of chemical engineering processes, the vapor or saturation pressure comprises the external pressure necessary for the isolated system, under a given temperature, to remain in thermodynamic equilibrium. It is the pressure exerted by the vapor of a given constituent, when in thermodynamic equilibrium. It can be expressed as a measure of the vaporization tendency of a pure substance or as a measure of volatility, in the case of liquid-vapor mixtures, so that the vaporization and condensation rates are equal (Pavani, 2014; Carneiro, 2012).

One of the laws that helps in the process of identifying real mixtures is the modified Raoult's Law, since it starts from the ideal conditions for gas and solution and, from that point, compares the behavior of the mixture attributing to the activity coefficient (Carneiro, 2012; Xavier *et al.*, 2020).

When studying the components separately, as being a pure substance, which transits discontinuously between the phases, liquid, and vapor under constant pressure and temperature conditions, it is usual to use the Clausius Clapeyron¹¹ relation. It says that: "When an infinitesimal amount of pure liquid is evaporated at constant temperature and pressure, the Gibbs free energy remains constant for the two phases coexisting in equilibrium" (Almeida, 2016).

In this study, an integrated form of the Clausius equation, which depends on the enthalpy of vaporization and the temperature, diffused by the Antoine equation, was used to calculate the vapor or saturation pressure of each component of the mixture. However, the parameters of this equation are estimated by correlations of

experimental data using the CSGC-PRV model proposed by, which is based on the principle of Riedel's (1954) theory of corresponding states. Equation 1 expresses this theory following the Antoine equation:

$$\ln P^{sat} (kPa) = A - \frac{B}{T(K) + C} \quad (1)$$

Diffusivity

Diffusivity is understood as the ability of a substance to mix with another substance and can be divided into molecular and convective diffusivity. The first refers to the absence of mechanical action that promotes diffusion and the transport of matter takes place through molecular interactions. The second is the action of forces that promote the diffusion and transport of matter as a result of the movement of the medium, such as thermal diffusivity and mass diffusivity (Cremasco, 2002, p. 26).

Thermal diffusivity refers to the heat transfer expressed by the temperature variation of the material when subjected to a cooling or heating process and mass diffusivity comprises mass transfer, whose driving force is the concentration difference and the transport resistance associated with the interaction between the solute and the solvent, with the external action (Carneiro, 2012).

The diffusivity of fragrances makes it possible to analyze the behavior of each component and influence the olfactory perception of the human being, located at a distance from the source of the application, as well as the intermolecular interactions that will influence the liquid-vapor balance, in the phase evaporation process. liquid and air diffusion. All this is of fundamental importance in the quality of the perfume, as it determines its intensity and its duration in the vapor phase (Carneiro, 2012).

In this way, the diffusivity is directly related to the efficiency of the fragrance that reaches your skin, since some of them, such as perfumes and deodorants, is applied at a certain distance from the skin. Is this distance enough to make the perfume interact with the environment before reaching our skin? and if it interacts with the environment, will the fragrance that reaches our skin have the same interaction, or will it provide the same intensity of the expected odor?

Hydrogen Bonding

Atoms and molecules interact with each other through interactions known as Van der Waals forces. Intermolecular interactions reflect on the geometry of the molecule and intramolecular interactions reflect on the phase change of a substance, influenced by the distance between molecules.

¹¹By keeping the temperature and pressure in the system, the phase changes constant increases the maintenance of energy, which favors the phase change as the volume and potential of the system increase.

They can occur through the sharing or donation of electrons, according to the distribution of their charges and the tendency to repel or attract them. It is directly linked to the electronegativity of the atom, if it is electronegative, it means that it will have a greater tendency to attract electrons to its valence orbital, otherwise, it indicates that it will tend to repel these electrons (Van Ness, 2007). In addition, the distance between them can influence this interaction.

In quantum mechanics, the electronic distribution is given by the number of electrons in the atom, however, the interaction occurs in the last orbital, in which there are empty spaces capable of accommodating a pair of electrons. The more orbital the atom is, the greater the distance between its nucleus and the electrons in the last shell and, consequently, the smaller this interaction. However, it becomes easier for another atom to bond by Van der Waals¹² forces, which are hydrogen bonds, dipole-dipole, or dipole-induced (Melo and Guedes, 2020).

The dipole-dipole interaction occurs in polar molecules of opposite charge in which electrons are donated from one atom to the other. The induced dipole type interaction occurs between nonpolar molecules through the sharing of electrons. By definition, hydrogen bonding is the interaction by the attraction of a hydrogen atom belonging to one molecule, with an electronegative atom, for example, fluorine, oxygen, or nitrogen, belonging to another molecule and concerning the three bonds, the hydrogen bond is the strongest because it occurs in more electronegative atoms (Melo and Guedes, 2020).

Since solvation is a molecular interaction between different species, acting as a solute or solvent, by hydrogen bonding, there is the species that donates and the one that receives the hydrogen. In the “pure” solvation, there is no association between these species (Van Ness, 2007). Further on, the COSMO-SAC model will be studied with the contribution of the activity coefficient equation, which relates the energetic effects of the molecular interactions of the solution, tracing a sigma profile.

Vapor-Liquid Equilibrium (VLE) and Fugacity and Activity Coefficients

Being a static condition, where no change is observed in the macroscopic properties of the system concerning time, equilibrium implies the balancing of all variables that can change this condition, so that two or more phases are in equilibrium. For example, the absence of temperature gradients (thermal equilibrium) and the absence of pressure difference (mechanical equilibrium) (Xavier *et al.*, 2020; Almeida, 2016).

Both conditions are achieved if the chemical equilibrium is achieved, that is, the chemical potential of

an x component (μ_x) in a phase must be the same as the chemical potential of this component at all other phases of the system. As shown in Eq. 2, by definition, the chemical potential corresponds to the partial molar Gibbs energy and can be written according to the measured variables such as temperature, pressure, and the number of mols of each component (Xavier *et al.*, 2020):

$$\mu_x = \left(\frac{\partial G}{\partial n_x} \right)_{T, p, n_{j \neq x}} \bar{G}_x \quad (2)$$

However, because it presents mathematical inconveniences, this potential is not usually used directly in phase equilibrium analyses. In a phase with multiple components, when a substance is very diluted or when the system pressure tends to zero, the energy tends to less infinity. With this, a change of variable, called fugacity, is used to describe the criterion of chemical equilibrium. Fugacity indicates the tendency of a substance to escape the phase by itself and is expressed by Lewis. Eq. 3 shows this expression:

$$\mu_i - \mu_i^0 = RT \ln \left(\frac{f_i}{f_i^0} \right) \quad (3)$$

When associated with the excess Gibbs free energy, there is a relationship between the partial molar Gibbs energy above component *i*, as the difference in the Gibbs energy of a substance in the mixture in its ideal gas state (G_i) and an ideal solution (G_{iD}) and the relationship between the fugacity of component *i* in a mixture and the fugacity of this same component in an ideal solution are given as the activity coefficient. This coefficient, Eq. 4, indicates the tendency of the species to be expelled from the phase and is related to the intensity of the interactions between the components and the effect of the structure:

$$\gamma_i = \frac{f_i}{f_i^{id}} \quad (4)$$

$$\text{So, } \mu_i - \mu_i^0 = RT \ln(\gamma_i)$$

When γ approaches 1.0, it says that the component feels little of the presence of the others, that is, it interacts as if it were alone. Thus, in an ideal solution, the fugacity is the fugacity when pure weighted by its composition in the mixture. Equation 5 rewrites the activity coefficient as:

$$\gamma_i = \frac{f_i}{x_i f_i} \quad (5)$$

¹²These forces vary in intensity due to the distance R (atomic radius) between the atoms.

In both cases, the escape or expulsion of the substance depends on the conditions of the environment and the effects of the presence of other components, involving liquid phases.

In phase equilibrium in which there is direct contact between the phases, liquid, and vapor in an isolated system, after a certain time, it reaches a final state in which there is no tendency for changes to occur in its interior, macroscopically. The pressure, temperature, and composition of both phases reach an equilibrium. Furthermore, the fugacity of each of the components of the mixture is the same for both phases. This behavior is called Vapor-Liquid Equilibrium (VLE) (Van Ness, 2007; Foust, 1982).

In it, some models are used to find the pressures and compositions of each phase, such as Raoult's law, which is only exact for VLE whose hypotheses comprise the vapor phase as being an ideal gas and therefore can be used only under low or moderate conditions of temperature and pressure. And the liquid phase corresponds to an ideal solution, which can be validated in the presence of chemically similar components (Van Ness, 2007; FOST, 1982). Equation 6 is the mathematical expression that reflects these hypotheses:

$$y_i P = x_i P_i^{sat} \quad (6)$$

where, x_i = mole fraction in the liquid phase, y_i = mole fraction in the vapor phase, P_i^{sat} is the vapor pressure of pure species i at system temperature, and P is the partial pressure of species i . However, this model only serves to study simple cases of VLE or as a standard method of comparison concerning a more complex system. This, in turn, takes into account a realistic VLE system, employing deviations from the ideality of solutions in the liquid phase, activity coefficient. With this, Eq. 7 writes Raoult's modified law as:

$$y_i P = x_i \gamma_i P_i^{sat} \quad (7)$$

In the VLE, if the liquid phase and temperature are already known and, in addition, since the sum of all the molar fractions of this phase is 1.0, the pressure can be calculated by the sum of all species at the bubble point given by Eq. 8 and the vapor composition by Eq. 9:

$$P = \sum_i x_i \gamma_i P_i^{sat} \quad (8)$$

$$y_i = \frac{x_i \gamma_i P_i^{sat}}{P} \quad (9)$$

In addition, we can use Antoine's Eq. 2 to express the vapor pressure of the fragrance components proposed in the work, as shown in Table 1, estimated by Almeida (2016, p. 77) through the contribution of the CSGC-PRV method.

For the calculation of the activity coefficient to predict the VLE, some thermodynamic models are used, such as the UNIFAC model and the COSMO-SAC model, which are based on Eq. 10, associated with the Gibbs free energy:

$$RT \ln \gamma_i = \left(\frac{\partial G^{exc}}{\partial n_i} \right)_{T,P,n_{j \neq i}} \quad (10)$$

Statistical Thermodynamics is an area of physics that correlates to the macro and microscopic properties of matter, such as Gibbs free energy, entropy, heat, and work. On a larger scale, intended for Process Engineering, it is possible to calculate the activity coefficients of species i as a function of the temperature and composition of an arbitrary mixture. As a function of pressure, the activity coefficient is written as a state function.

Thermodynamic Models

Model UNIFAC

The UNIFAC model (UNIQUAC Functional-group Activity Coefficients) was proposed by Fredenslund, based on the UNIQUAC methodology. In this model, both the combinatorial term and the residual term shown in Eq. 11, are based on the method of the contribution of groups, that is, the local environment of a molecule in a solution can be modeled as the probability of molecular configurations of the solution as a whole. This is a predictive model, since all molecular interactions are replaced by interactions between functional groups and, thus, the model depends indirectly on experimental data (Ferrarini, 2017; Xavier *et al.*, 2020):

$$\ln \gamma_i = \ln \gamma_i^{res} + \ln \gamma_i^{comb} \quad (11)$$

This model presents wide applicability in the calculation of interactions in mixtures, exhibiting positive or negative deviations from Raoult's law and it serves as the basis for other models that allow the change of residual and combinatorial terms and can add new functional groups to obtain better results following the solution studied. The combinatorial contribution refers to the study of the entropic effects according to the difference in the shape and size of the molecules, being calculated from the pure properties of the substances, while, the residual contribution, refers to the study of the interactions of the groups in the mixture, resulting from the intermolecular forces.

As this model is adjusted for each pair of functional groups, there are numerous parameters and consequently, many experimental data of properties involving mixtures, such as steam pressure and activity coefficient are required. In addition, the model is limited to isomers and cannot identify the polarization of one functional group by the presence of another in the same molecule (Valente, 2016).

Model COSMO-SAC

COSMO models were developed by, based on the classic models of the coefficient of activity. It is a mathematical approach based on Gibbs excess free energy,

whose calculations start from the molecule inserted into a cavity formed within a perfect conductive medium, which induces a distribution of loads on a surface (Maciel and Da, 2012; Schneider *et al.*, 2018).

The COSMO-SAC (Segment Activity Coefficient) type, created by Lin and Sandler in 2002, is an adaptation of the COSMO-RS (Realistic Solvation) model that unites COSMO calculations with the Staverman-Guggenheim equation to determine the activity coefficient. This coefficient, γ_i , is based on the energy required for the removal of the loads distributed on the surface and around the molecule, in a real state. The interaction with the solvent (continuous medium) produces a distribution of loads in the perfect conductor, generating a probability density known as profile-sigma, estimating the actual effects of solvation of a solute in a solvent and then predicting its behavior in a mixture¹³ (Maciel and Da, 2012; Soares and Staudt, 2020).

Figure 3 shows the quantum model of energy, distribution of apparent surface loads of benzene and acetone molecules, submerged in a perfect conductor (a), in which there is no interaction, and submerged in a partially excluded conductor (b), where there is an interaction between the molecules due to the inductive effect (Soares and Staudt, 2020).

When a molecule is placed inside a cavity in a perfect conductor, the electric field must be zero, thus, an induced charge appears on the surface of this cavity to cancel the charge induced by the molecule in that region. (Xavier *et al.*, 2020).

The red color denotes regions of higher electron density with which it will induce positive charges, while the blue color denotes regions of lower electron density and will induce negative charges. In green, the electron density is neutral. In all cases, it measures the molecules' ability to interact or their deviation from ideality (Gerber, 2010; Soares, 2011).

The COSMO-SAC method, proposed by Lin and Sander, predicts the behavior of mixtures by the activity coefficient based on the distribution of induced charges of the isolated molecules, in a liquid phase (Gerber, 2010; Soares, 2011).

In this study, we will study the use of the COSMO-SAC methodology to estimate the behavior of a fragrance mixture through the excess Gibbs free energy as a function of the activity coefficient.

Mixtures involving polar substances show a much greater deviation from ideality than mixtures involving non-polar substances, as these polar molecules can have a high electron density capable of binding to other molecules and breaking this perfect conductor.

COSMO-SAC Method used to Estimate the Gibbs Free Energy as a Function of the Activity Coefficient

Among the most diverse models proposed to describe the relationship of the activity coefficient with temperature and mixture composition, there is the model based on excess Gibbs free energy. As it is a state function, it is independent of the path taken from the start point to the endpoint, in addition to being an easily measurable property, dependent on T, P, and the chemical composition of the mixture. Equation 12 was obtained by adjusting Eq. 11:

$$G_i^{exc} = RT \ln \gamma_i \quad (12)$$

Obtained starting from the fundamental relations of the properties, in the generalized form, Eq. 13, in which:

$$d\left(\frac{nG^{exc}}{RT}\right) = \frac{nV^{exc}}{RT} dP - \frac{nH^{exc}}{RT^2} dT + \sum_i \frac{\bar{G}_i^{exc}}{RT} dni \quad (13)$$

When the $\ln \gamma_i = 0$, $\gamma_i = 1$, that is, the activity coefficient is equal to 1, it corresponds to the ideal behavior of the gases. In cases where the pressure is low or moderate, the vapor phase of the mixture can be considered an ideal gas. Lin and Sandler's COSMO-SAC model defines Eq. 11 as the expression for obtaining the activity coefficient, in which the residual term is expressed by Eq. 14 and the combinatorial term by Eq. 15:

$$\ln \gamma_i^{res} = \frac{\Delta G^{res} / s}{RT} - \frac{\Delta G^{res} / i}{RT} \quad (14)$$

$$\ln \gamma_i^{comb} = \ln \left(\frac{\phi_i}{xi} \right) + \frac{z}{2} q_i \ln \left(\frac{\phi_i}{\phi_i} \right) + li - \frac{\phi_i}{xi} \sum_j^{xij} \quad (15)$$

The term $\ln \gamma_i^{res}$ corresponds to the residual contribution and is related to the energetic effects of molecular interactions in the solution such as hydrogen bonds, electrostatic differences, and dispersion. It is calculated as the difference between the free energy to restore charge around the solute molecule in solution, s and to restore charge to a pure liquid, i. The $\ln \gamma_i^{comb} = \ln \gamma_{i/s}^{SG}$ corresponds to the combinatorial contribution of Staverman-Guggenheim (SG). This combinatorial term refers to the purely entropic, non-energetic part, which considers the mixture of substances of different sizes. Then Eq. 16 is obtained by substituting Eq. 14 and 15 into Eq. 11:

¹³ The polar portion of the solute or the region of higher electron density, due to inter and intramolecular interactions, connects to the solvent molecules.

$$\ln \gamma_i = \frac{\Delta G_i^{res} / s}{RT} - \frac{\Delta G_i^{res} / i}{RT} + \ln \left(\frac{\phi_i}{x_i} \right) + \frac{z}{2} q_i \ln \left(\frac{\theta_i}{\phi_i} \right) + li - \frac{\phi_i}{x_i} \sum_j x_i l_j \quad (16)$$

where, $\Delta G_{i/s}^{res}$ corresponds to the difference between the free energy of charge restoration of solute i in solution s expressed by Eq. 17, defined as the sum of the product between the sigma profile of the mixture and the logarithm of the activity coefficient of the segment of area for all surface charges:

$$\frac{\Delta G_i^{res} / s}{RT} = n_i \sum_{\sigma_m} p_i(\sigma_m) \ln \Gamma_s(\sigma_m) \quad (17)$$

where, n_i is the total number of segments in a solvent molecule, $\Gamma_s(\sigma_m)$ is the activity coefficient for the area segment with charge density σ_m , calculated by Lin and Sandles using statistical mechanics, whose formulas are defined by Eq. 18 and 19:

$$\ln \Gamma_s(\sigma_m) - \ln \left\{ \sum_{\sigma_n} p_s(\sigma_n) \Gamma_s(\sigma_n) \exp \left[-\frac{\Delta W(\sigma_m, \sigma_n)}{RT} \right] \right\} \quad (18)$$

$$\ln \Gamma_s(\sigma_m) - \ln \left\{ \sum_{\sigma_n} p_i(\sigma_n) \Gamma_i(\sigma_n) \exp \left[-\frac{\Delta W(\sigma_m, \sigma_n)}{RT} \right] \right\} \quad (19)$$

For molecules to interact, there must be an exchange of energy necessary to obtain a pair of segments m, n , whose contributions come from electrostatic interactions or the maladjustment of charge of hydrogen bonds, in addition to non-electrostatic interactions and dispersion. Equation 20 defines this exchange:

$$\Delta W(\sigma_m, \sigma_n) = \left(\frac{\alpha'}{2} \right) (\sigma_m, \sigma_n)^2 + c_{hb} \max[0, \sigma_{acc} - \sigma_{hb}] \min[0, \sigma_{don} - \sigma_{hb}] \quad (20)$$

α' is the load misfit constant expressed by Eq. 21:

$$\alpha' = f_{pol} \left(\frac{0,3(a_{eff})^{3/2}}{\epsilon_0} \right) \quad (21)$$

In which ϵ_0 = vacuum permittiveness constant = $2,395 \times 10^{-4}$ (e² mol/kcal Å) and f_{pol} is the polarization factor. Equation second term. 21 quantifies the contribution of interactions related to hydrogen bond formation, where c_{hb} is the hydrogen bond constant, σ_{hb} is the cutting sigma for hydrogen bond and σ_{acc} and σ_{don} are the highest and lowest values of σ_m and σ_n . Table 2 shows

all the global parameters of the COSMO-SAC mathematical model.

According to studies by Maciel and Da (2012), “obtaining the activity coefficient is based on the energy required to remove the charges distributed on the surface and return the molecules to the real state”. The calculation of this energy difference is performed based on the profile of charge density probabilities called the sigma profile. Returning to the general activity coefficient equation, (Eq. 16) the term $\Delta G_{i/i}^{res}$ corresponds to the free energy of charge restoration of pure solute i , and the third term:

$$\ln \gamma_i^{comb} = \ln \left(\frac{\phi_i}{x_i} \right) + \frac{z}{2} q_i \ln \left(\frac{\theta_i}{\phi_i} \right) + li - \frac{\phi_i}{x_i} + li - \frac{\phi_i}{x_i} \sum_j x_i l_j$$

where:

$$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j}$$

which corresponds to the normalized volume fraction:

$$\theta_i = \frac{r_i^p x_i}{\sum_j r_j^p x_j}$$

Is the normalized fraction of surface area:

$$li = \left(\frac{z}{2} \right) * (r_i - q_i) - (r_i - 1)$$

where, z is the coordination number, x_i is the molar fraction of the liquid phase, r_i and q_i are normalized areas and volume parameters expressed by:

$$r_i = \frac{V_i}{r}$$

$$q_i = \frac{A_i}{q}$$

V_i is the volume and A_i is the surface area of the cavity formed in the conductor by component i , obtained through quantum methods. Thus, substituting Eq. 18 and 19 in Eq. 12 and simplifying these expressions, we obtain Eq. 22 which relates the coefficient of component i in the solution:

$$\ln \gamma_i / s = n_i \sum_{\sigma_m} p_i(\sigma_m) [\ln \Gamma_s(\sigma_m) - \ln \Gamma_i(\sigma_m)] + \ln \gamma_i / s \quad SG \quad (22)$$

This new equation relates the sigma profile to the probability distribution of finding a surface segment of the molecule that has a charge density, sigma:

$$A_i = \sum_a A_i(\sigma)$$

$$p_i(\sigma) = \frac{n_i(\sigma)}{n_i} = \frac{A_i(\sigma)}{A_i}$$

$$n_i = \sum_m n_i(\sigma) = \frac{A_i}{a_{eff}}$$

where, A_i corresponds to the total area of the cavity occupied by the molecule, $A_i(\sigma)$ is the total area of all surface segments that contain a charge density, a_{eff} is the effective surface area of a surface segment that corresponds to the area of charge contact between different molecules. For solvents formed from different molecules, the sigma profile of the mixture becomes the weighted average of the sigma profiles of all components involved.

The experimental COSMO-SAC model can be summarized in Fig. 4, which begins with the quantum study of molecules, starting from the ideal condition of solvation, a perfect conductor. A graph is drawn for the profile of the pure substance and the mixture, then these profiles are related to the activity coefficient of

the charge segments, thus obtaining the activity coefficient of the molecule.

In the first step, the apparent charge distribution induced on the surface of the molecule is determined in the hypothetical condition in which the solute is submerged in a perfect conductor, an ideal solvent so that the activity coefficient can be calculated through the data provided by quantum analyzes (molecule characteristics, charge distribution), as exemplified in Fig. 2 for benzene and acetone (Maciel and Da, 2012).

In the second step, with the three-dimensional shape of the molecule, a graph is made in two dimensions, known as a sigma profile, for each of the substances contained in the mixture. This profile is traced through the equations mentioned above, therefore, a computational method is used to simplify the calculations called JCOSMO.

In the third and last step, there is the diagram profile with which the activity coefficient for each load segment of this profile is evaluated. Both segments, sigma profile and activity coefficient, are combined to obtain the activity coefficient of each component of the mixture (Maciel and Da, 2012).

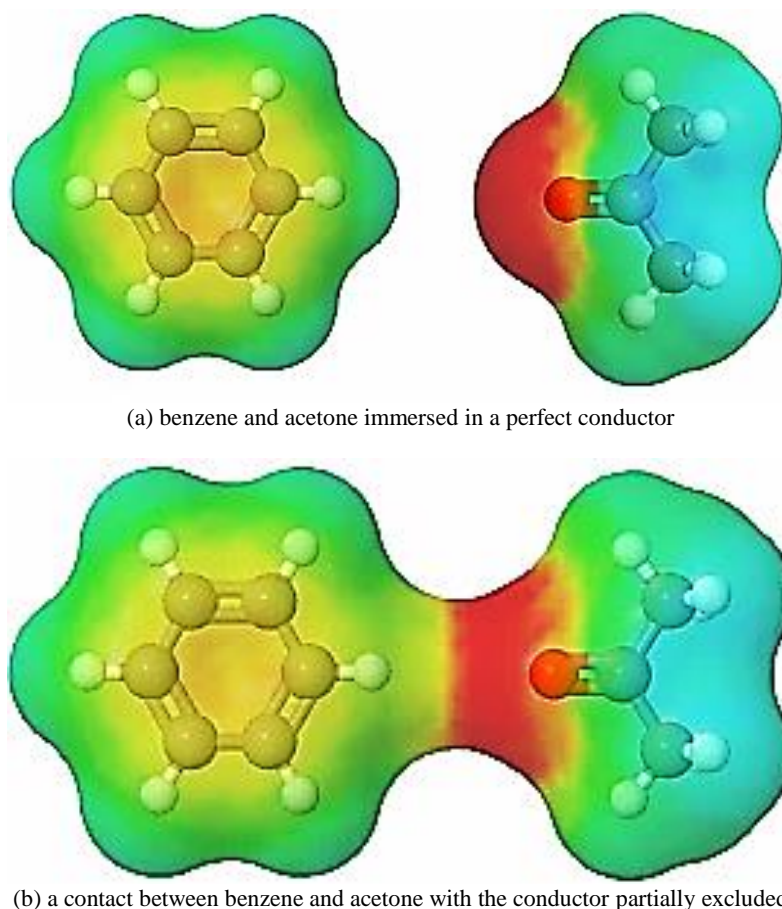


Fig. 3: Behavior of benzene and acetone molecules concerning the solvation effect (Gerber, 2010; Soares, 2011)

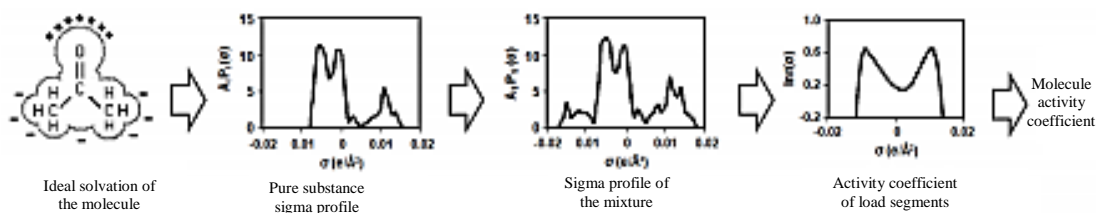


Fig. 4: Schematic diagram of the COSMO-SAC model (Gerber, 2010)

Table 1: Antoine type coefficients (Adapted from Lima, 2016)

Compound	A	B	C	T _b (K)	P _i ^{sat} (kPa)
Ethanol	18,9119	3803,098	-41,068	351,52	761,02
Geraniol	18,0921	7187,399	0,995	503,02	106,25
Limonene	16,0002	5143,156	0,490	4,51	100,53
Linalool	15,0854	5216,496	0,998	468,15	113,85

Table 2: Global parameters of the COSMO-SAC model (Adapted from Gerber, 2010)

Parameter	Description	Value	Unit
a _{eff}	Effective area of a standard surface segment	7,0025	Å ²
z	Coordination number	10,0000	-
r	Normalized volume parameter	66,0069	-
q	Normalized surface area parameter	79,0053	-
Chb	Hydrogen bond constant	85580,0000	Å ⁴ /molL e ²
σ _{hb}	Cutting sigma	0,0084	e/Å ²
f _{pol}	Polarization factor	0,6917	-

This model has wide applicability, both in qualitative and quantitative analysis. In the case of quantitative analysis, the COSMO-SAC model predicts the behavior of deviation from ideality through the difference in size and shape of molecules, charge misfit, and hydrogen bonding.

The actual calculation of the activity coefficients starts from the resolution of Eq. 19 and 20, once for the pure compound and once for the mixture. The probability $p_i(\sigma)$ is represented through the graph seen in the diagram in Fig. 4. This profile for a molecule corresponds to a two-dimensional representation of the distribution of induced charges on its surface. On the abscissa axis, charge densities σ are shown, which normally vary between -0.02 and $+0.02$ e/Å², and on the ordinate axis, the area of the molecule that has that charge density is shown. The integral under this curve gives the total charge of the molecule and this sigma profile is unique for each molecule (Xavier *et al.*, 2020).

Results and Discussion

Analysis of Sigma Profiles of Fragrances using the COSMO-SAC Model

As seen earlier, the sigma profile of a substance or a mixture determines the apparent charge distribution that is induced on the surface of the molecule, due to the presence of free electrons.

Figures 5 and 6 show the sigma profile of ethanol as a function of its charge distribution, correlating with the equations involving hydrogen bonds, to calculate the activity coefficient applied to ethanol mixtures. This model was generated with the aid of the computer program JCOSMO, the first thermodynamic model based on Quantum Mechanics in Brazil (Gerber, 2010). The colors, blue and red in the pie chart in Fig. 5 show the regions where hydrogen bonds can occur, remembering that the blue regions induce negative charges, the red region induces positive charges and the green regions are neutral regions.

All these profiles were taken from the master's research, written by Vanessa Barbieri Xavier (2020), under the guidance of professors Paula Bettio Staudt and Rafael de Pelegrini Soares and available in the open LVPP database (<https://github.com/lvpp/sigma>). However, the research was limited to understanding the programs that govern the database and, consequently, the codes written to obtain these profiles, since the objective of showing it was to analyze and validate the load induction regions. And from that, explain the interactions between them.

Figures 7, 8, and 9 show, respectively, the sigma profiles of the components linalool, geraniol, and limonene.

In both figures, the region with the highest peak is part of the region where there is no charge density. In non-polar molecules such as limonene, the sigma profile is zero, as it is non-polar, the charges are evenly

distributed throughout the region. Negative sigma indicates the region where there is interaction with positive charges of the molecule, while positive sigma indicates the molecule's tendency to interact with the negative part of another molecule. The presence of hydroxyl groups in the molecules of geraniol, linalool, and ethanol, according to quantum mechanics, causes a region of higher electron density (>0) due to the electronegativity of oxygen, enabling interaction by hydrogen bonding (Gerber, 2010; Xavier *et al.*, 2020).

The COSMO-SAC model resembles the UNIFAC due to the discretization of the molecule before the activity coefficient is calculated. COSMO-SAC divides the molecule into charge segments and calculates the interaction between these segments, with statistical thermodynamic theories, which correlate with the macro and microscopic properties of matter and it is quantum mechanics that gives the model a strong predictive character. The UNIFAC model divides the molecule into functional groups and calculates the interaction between these groups through experimental data.

Using the same computer program, the profile of the binary mixture of ethanol and limonene was traced (Fig. 10) and it was observed that the region of an absence of charge density of limonene is much larger than that of ethanol, due to its polarity. In addition, the ethanol molecule has regions of greater induction of negative and positive charges than limonene. This implies little interaction between the two components.

Analysis of the Fragrance Activity Coefficient using the COSMO-SAC Model

The activity coefficient of a substance in a mixture corresponds to a number that represents the intensity of interactions between the components and the effect of the molecular structure, being a measure of the non-ideality of substances in the liquid phase. When γ_i approaches 1.0, the component is said to hardly feel the presence of other substances, while if $\gamma_i \neq 1.0$ the component feels the presence of other substances, a characteristic behavior of real mixtures. Eq. 23 demonstrates this logarithm of the activity coefficient and Eq. 24 the expression associated with a binary mixture (Xavier *et al.*, 2020).

$$\ln \gamma_i = \frac{G^{exc}}{RT} \quad (23)$$

$$\frac{G^{exc}}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \quad (24)$$

The activity coefficient of a species in solution tends to a unit value when the species tends to become pure. In the case of binary mixtures, $\ln \gamma_1$ and $\ln \gamma_2$ tend to zero when the molar fraction of the liquid phase tends to 1. When this fraction tends to 0, species 1 and 2 become

infinitely diluted, consequently, the coefficient becomes finite. So, when x_2 tends to 0 and x_1 tends to 1, G^{exc}/RT , tends to zero. The opposite is also true (Van Ness, 2007). That way, Eq. 24 can be rewritten by getting to Eq. 25:

$$\frac{G^{exc}}{RT} = \ln \frac{\gamma_1}{\gamma_2} \quad (25)$$

The curves of the coefficient of activity of the mixture between ethanol and limonene at 300 K were obtained using the JCOSMO program, as shown in Fig. 11, based on Gibbs excess free energy curve, in green in the diagram, given by Eq. 24. According to the diagram, the net phase presents a positive deviation for both constituents. In addition, it is observed that the logarithm of the ethanol activity coefficient reaches the finite unit value ($\ln \gamma_1^\infty$) of 2.97 when its molar fraction, x_1 , approaches 0.0 (see the curve in red). The logarithm of the D-limonene activity coefficient reaches its finite unit value ($\ln \gamma_2^\infty$), of 1.48 when its molar fraction tends to 0.0 ($x_1 = 1.0$) (see blue curve).

It is worth mentioning that, as the computational program JCOSMO is as recent as the thermodynamic model COSMO-SAC, the availability and access to the free tool is simple, and therefore, it does not recognize all the components studied. Thus, the research was limited to showing the behavior by the program only of the binary mixture between limonene and ethanol.

Analysis of VLE Curves of Binary Mixtures using the UNIFAC model and Raoult's Law

Using the DWSIM chemical process simulator, it was possible to trace the VLE curves of the binary mixtures: Limonene-linalool, limonene-geraniol, and geraniol-linalool, in a constant pressure heating process of 1 atm (101325 Pa), as shown by Figs. 12, 13, 14, 15, 16 and 17, using Raoult's law-Gas/ideal solution and the UNIFAC model.

In all of them, the region of the subcooled liquid corresponds to the area below the bubble point line and the overheated steam region corresponds to the area higher than the dew point line. The space between the two surfaces (lines) comprises the region where the two phases, liquid, and steam, coexist in the equilibrium (Van Ness, 2007 p. 265).

The bubble point represents the first vapor bubble that appears when the temperature of a liquid is increased to constant pressure and composition. The dew point is the point at which the last drops of liquid disappear, that is, the extent to which the temperature increases, the number of steam increases, and, consequently, the number of liquid decreases, under pressure and constant composition (Van Ness, 2007 p. 266).

Table 3: Properties of the combined components in binary, ternary and quaternary mixtures

Properties		Limonene	Linalool	Geraniol	Ethanol	Air
1-Liquid-phase	Activity coefficient	1,0	1,0	1,0		
	Fugacity coefficient	0,0	0,0	0,0		
	Diffusion constant	$2,805 \times 10^{-9}$	$2,796 \times 10^{-9}$	$2,775 \times 10^{-9}$		
2- Liquid-phase	Activity coefficient	1,0	1,0	1,0	1,0	
	Fugacity coefficient	$2,551 \times 10^{-3}$	$8,192 \times 10^{-6}$	$2,803 \times 10^{-6}$	$7,779 \times 10^{-2}$	
	Diffusion constant	$2,918 \times 10^{-9}$	$2,908 \times 10^{-9}$	$2,887 \times 10^{-9}$	$3,037 \times 10^{-9}$	
3- Liquid-phase	Activity coefficient	1,0	1,0	1,0		84,0
	Fugacity coefficient	$2,551 \times 10^{-3}$	$8,192 \times 10^{-6}$	$2,803 \times 10^{-6}$		85327,7
	Diffusion constant	$3,435 \times 10^{-9}$	$3,424 \times 10^{-9}$	$3,398 \times 10^{-9}$		–
3-Vapor-phase	Activity coefficient	392,06	122068,00	356801,00		$9,846 \times 10^{-4}$
	Fugacity coefficient	1,00	1,00	1,00		1,00
	Diffusion constant	∞	∞	∞		$1,053 \times 10^{-10}$
4- Liquid-phase	Activity coefficient	1,00	1,00	1,00	1,00	84,0
	Fugacity coefficient	$2,551 \times 10^{-3}$	$8,192 \times 10^{-6}$	$2,803 \times 10^{-6}$	$7,779 \times 10^{-2}$	85327,7
	Diffusion constant	$3,377 \times 10^{-9}$	$3,366 \times 10^{-9}$	$3,341 \times 10^{-9}$	$3,515 \times 10^{-9}$	–
4- Vapor-phase	Activity coefficient	392,06	122068,00	356801,00	12,85	$9,846 \times 10^{-4}$
	Fugacity coefficient	1,00	1,00	1,00	1,00	1,00
	Diffusion constant	∞	∞	∞	$3,782 \times 10^{-11}$	$9,083 \times 10^{-11}$

Source: Author, 2021

Table 4: Molar fraction of the components in the vapor phase, for the different models and experiments at 296 k

Experiment	COSMO-SAC				UNIFAC				Y _{Lim}	Y _{LOH}	Y _{Ger}	Y _{EtOH}
	Y _{Lim}	Y _{LOH}	Y _{Ger}	Y _{EtOH}	Y _{Lim}	Y _{LOH}	Y _{Ger}	Y _{EtOH}				
0,9430	0,0567	–	–	0,9558	0,0442	–	–	0,9537	0,0463	–	–	–
–	0,9400	0,0599	–	–	0,9500	0,0500	–	–	0,9512	0,0488	–	–
0,9720	–	0,0279	–	0,9905	–	0,0095	–	0,9914	–	0,0086	–	–
0,8960	0,0578	0,0461	–	0,9167	0,0446	0,0386	–	0,9088	0,0490	0,0422	–	–
0,0477	0,0045	0,0011	0,947	0,0255	0,0017	0,0004	0,9725	0,0211	0,0014	0,0003	0,9771	–

Source: Xavier *et al.* (2020)

Table 5: Activity coefficient predicted by the COSMO-SAC model for fragrance mixtures at 296 k

System	COSMO-SAC			
	Y _{Lim}	Y _{LOH}	Y _{Ger}	Y _{EtOH}
Binary	1,08	1,80		
		1,00	1,03	
Ternary	1,12		2,28	
	2,07	1,01	1,02	
Quaternary	2,72	1,00	0,95	1,14

Source: Xavier *et al.* (2020)

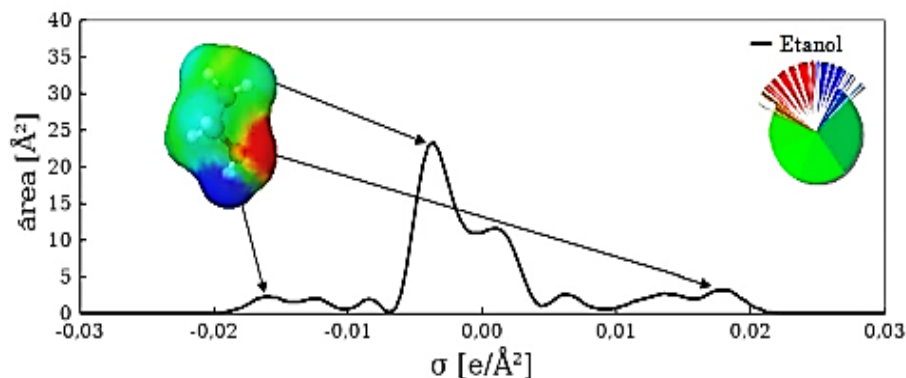


Fig. 5: Sigma profile for the ethanol molecule (Xavier *et al.*, 2020)

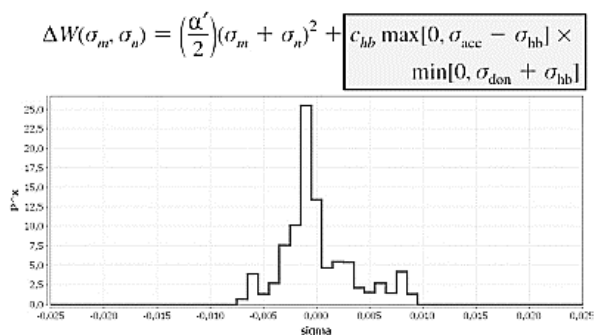


Fig. 6: Sigma profile of ethanol, described by the second term of the energy exchange equation (GERBER, 20120)

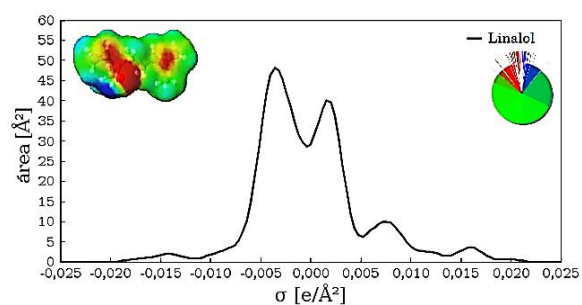


Fig. 7: Sigma profile for the linalool molecule (Xavier *et al.*, 2020)

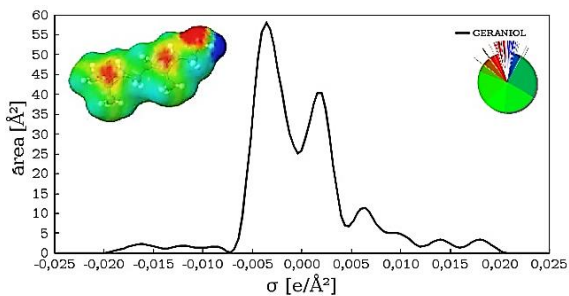


Fig. 8: Sigma profile for the geraniol molecule (Xavier *et al.*, 2020)

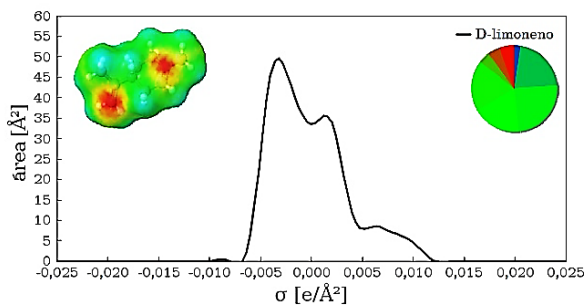


Fig. 9: Sigma profile for the limonene molecule (XAVIER *et al.*, 2020)

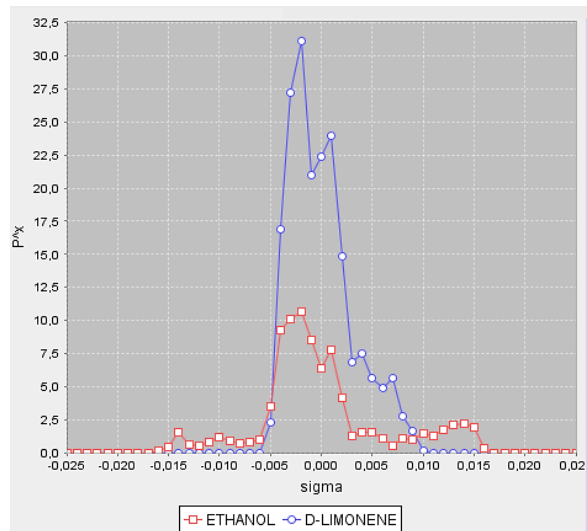


Fig. 10: Sigma profile of the binary mixture of ethanol and limonene

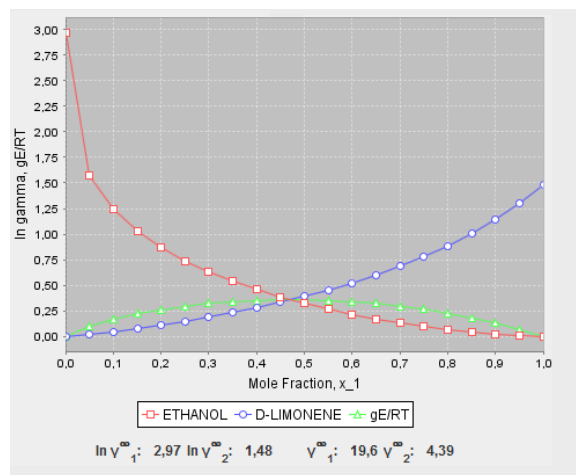


Fig. 11: Activity coefficient of the binary mixture of ethanol and limonene

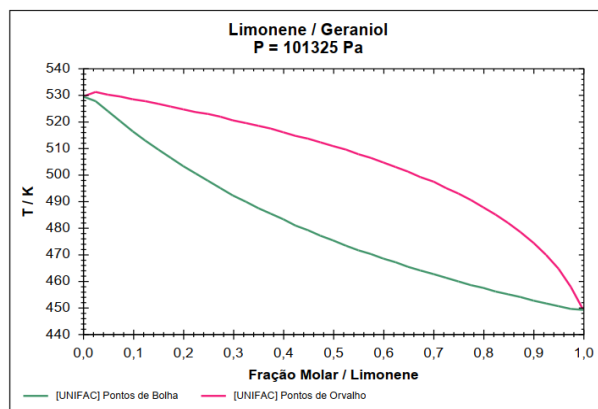


Fig. 12: VLE curve of the binary mixture Limonene and Geraniol by the UNIFAC model

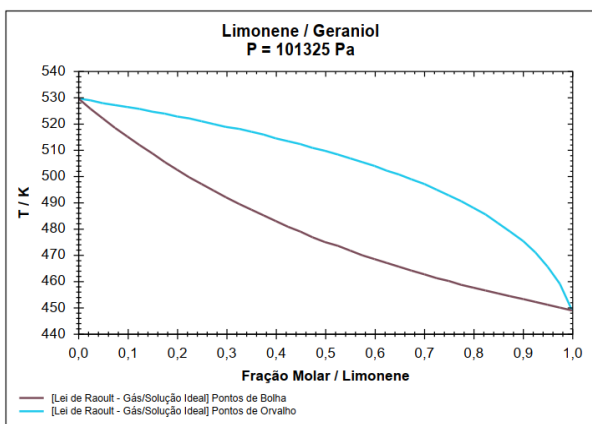


Fig. 13: VLE curve of the binary mixture Limonene and Geraniol by Raoult's law

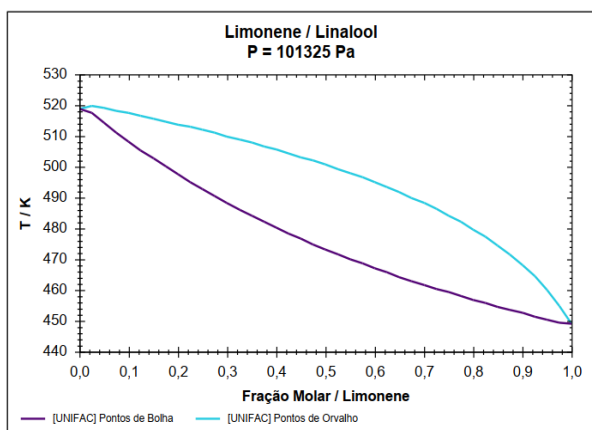


Fig. 14: VLE curve of the binary mixture Limonene and Linalool by the UNIFAC model

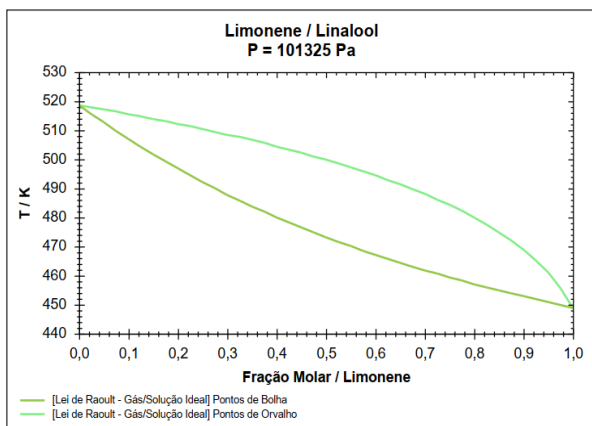


Fig. 15: VLE curve of the binary mixture Limonene and linalool by Raoult's law

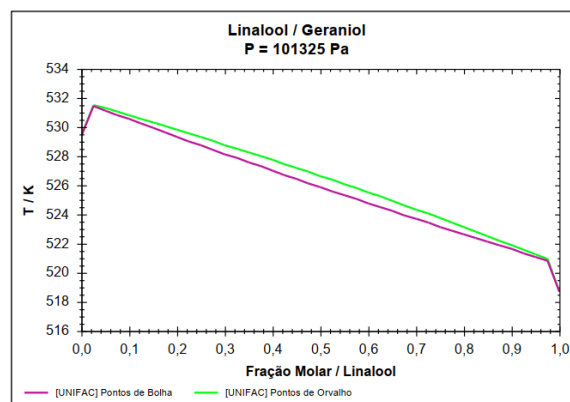


Fig. 16: VLE curve of the binary mixture Linalool and Geraniol by the UNIFAC model

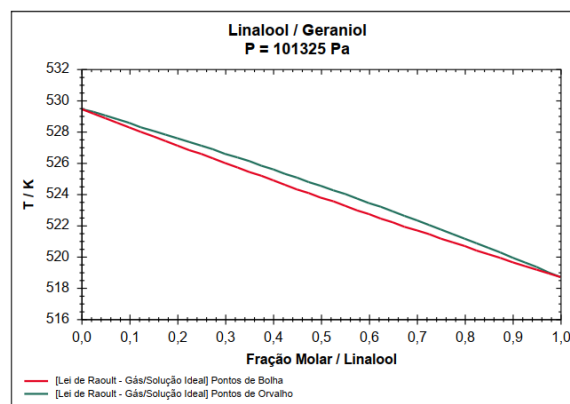


Fig. 17: VLE curve of the binary mixture Linalool and Geraniol by Raoult's Law

According to the figures, both models show similarities regarding the behavior of the VLE curves of the binary mixtures. However, if we compare the behavior of the limonene/linalool (Fig. 14 and 15) and limonene/geraniol (Fig. 12 and 13) graphs with the linalool/geraniol graph (Fig. 16 and 17), we observe a reduction in the phase where these components coexist at equilibrium in the bubble point and dew point temperature range (532-518 K). This can be explained by the isomerism of these components, that is, they have the same molecular formula ($C_{10}H_{18}O$), but the bonds between atoms are constituted differently, which makes their behavior similar.

In addition to the ELV curves of the binary mixtures, with the DWSIM simulator it was possible to estimate the properties of the components in the liquid phase and in the vapor phase, in 4 different combinations, binary, ternary and quaternary in the presence or absence of air, at a temperature of 298, 15 K and pressure of 101.325 kPa (1 atm.). The results are shown in Table 3, by Raoult's Law-Ideal Gas/Ideal Solution.

It is important to note that the VLE curves obtained by the DWSIM simulator provide a behavior close to the ideal of binary mixtures, for both models, UNIFAC and Raoult's Law. And to validate these behaviors, it would be interesting to carry out experiments in the laboratory. However, for the purpose of obtaining the physicochemical properties of these combined components and estimating the ELV curves, the use of the simulator was efficient.

From the table, it can be seen that, both in the liquid phase and in the vapor phase, the components limonene, linalool, and geraniol, when combined in the presence of ethanol and/or air, kept their activity and fugacity coefficients constant. It is interesting to note that, according to Raoult's law for ideal gas/ideal solution, in the liquid phase the components hardly feel each other's presence, which is demonstrated by the activity coefficient equal to 1.0. In the vapor phase, this representation is given by the fugacity coefficient equal to 1.0. On the other hand, the diffusion constants of each component were changed due to the composition of the mixture.

Since the diffusion coefficient indicates the tendency of a substance to diffuse in a medium, the higher this coefficient, the easier diffusion becomes. Thus, we can observe that the diffusive behavior of limonene, linalool, and geraniol, although very small, were approximate¹⁴ in all combinations.

However, in the presence of ethanol and ethanol and air, the diffusion capacity was even lower concerning the first mixture of fragrances in the liquid phase. In the vapor phase, what is observed is the minimum diffusivity of ethanol and air and the maximum diffusivity of these fragrances. When switching from the liquid phase to the vapor phase, the components easily mix with the medium, due to the low molecular interaction between them and the disordered movement of the molecules, characteristic of gases.

So if we could see the interaction of these fragrances with our skin and the environment, we would realize that, depending on the distance from the source of the application, these molecules would spread through the air, and part of them, reaches our skin, providing a pleasant sensation. The intensity with which we feel the perfume is linked not only to diffusion but also to the intensity of odor and concentration in the vapor phase, which causes a sensation that reminds us of childhood, places, or people.

Validation of COSMO SAC and UNIFAC Thermodynamic Models

Through the experiments carried out by Vanessa Barbieri Xavier *et al.* (2020, p. 41-46) to estimate the liquid-vapor balance of binary, ternary and quaternary mixtures between the Limonene (Lim), Linalool (LOH), Geraniol (Ger), and Ethanol (EtOH) mixtures, from the COSMO-SAC model and, by the experimental data and

the calculation of molar composition in the vapor phase, of these mixtures performed by Teixeira *et al.* (2011, p. 9390-9400), from the UNIFAC model, it was possible to validate the efficiency of these models, concerning the behavior of molecules, their properties, and their interaction capacity. The results are shown in Table 4 and 5.

The results show that the molar fractions of the vapor phase predicted by the UNIFAC and COSMO-SAC models are close to the real values found experimentally. In mixtures containing ethanol, greater deviations are observed for limonene, concerning linalool and geraniol, due to the weak interaction with ethanol due to the formation of hydrogen bonds, even with the approach for multiple hydrogen bond energies used, according to explains Xavier *et al.* (2020, p. 48).

In addition, the activity coefficients predicted by the COSMO-SAC model do not show a significant deviation from ideality, that is, due to the components having similarities in their structure, taking the activity coefficient close to unity, such as the binary mixture linalool and geraniol. However, it was expected that there would be strong positive shifts for mixtures containing less polar compounds such as limonene and more polar compounds such as geraniol and ethanol. In fact, what is observed are much higher values of the activity coefficient for limonene and much lower values for geraniol (in ternary and quaternary mixtures).

Conclusion

Therefore, we can conclude the efficiency of the models in representing the behavior of different fragrance mixtures, based on the modified Raoult's law and the physicochemical properties of each component studied.

The sigma profiles represented by the COSMO-SAC model clearly showed the possible regions of the interaction of the molecule, either by hydrogen bonding or by charge induction. The VLE curves obtained by the process simulator allowed the evaluation of the region in which the components coexist in equilibrium when combined two by two.

The experimental and theoretical activity coefficient of the UNIFAC and COSMO-SAC models validated the behavior concerning deviations from ideality, that is, they resulted in the real behavior of these mixtures of binary, ternary and quaternary fragrances. The diffusivity constants of these combinations also allowed us to assess how much these components diffuse in the medium, both in the liquid and vapor phases.

In practice, the intensity with which we feel the perfume is linked not only to the diffusion but also to the odor intensity and the concentration in the vapor phase, which causes a sensation that brings us back to childhood, places, or people.

¹⁴This fact is evidenced by the values of the diffusion constants.

As for the limitations of the research, the availability and access to the free tool of the computer program JCOSMO being simple, it does not recognize all the components studied. Therefore, only the sigma profile and the activity coefficient of the binary mixture limonene and ethanol were demonstrated. In addition, the VLE curves obtained by the DWSIM simulator provide a behavior close to the ideal of binary mixtures, for both models, UNIFAC and Raoult's Law. And to validate these behaviors, it would be interesting to carry out experiments in the laboratory. However, for the purpose of obtaining the physicochemical properties of these combined components and estimating the ELV curves, the use of the simulator was efficient.

As a proposal for future work, it is possible to study the interactive behavior of other fragrance components and carry out experiments in the laboratory in order to compare the results obtained with the theoretical estimated by the thermodynamic models. The models studied in this study, UNIFAC and COSMO-SAC, despite being based on different analyses, showed an efficiency in the results of the activity coefficients and in the molar fractions of the mixtures formed through the combinations of the components limonene, linalool and geraniol. The UNIFAC model starts from the group contributions method and the COSMO-SAC model starts from the molecule inserted in a cavity formed inside a perfect conducting medium, which induces a distribution of charges on a surface.

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Author's Contributions

Lavínia Mota Cristianismo Silva: Participation as a student, developing research, analysis, and writing of the work.

José Izaquiel Santos da Silva: Participation as an advisor, helping in the development and correction of the work.

Rogério Alexandre Alves de Melo: Participation as a collaborator in the correction of the work.

Edilaisa Januário de Melo: Participation as a collaborator in the correction of the work.

Ethic

This study and the ethical aspect were approved by the authors and collaborators of the Universities, UFVJM and UNICAMP.

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