The Perception of Fragrance Mixtures: A Comparison of Odor Intensity Models

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A comparison of two psychophysical odor intensity models and their effect on the prediction of the odor character for perfume mixtures is presented. The odor value (OV) and Power-Law models were applied together with previously developed perfumery ternary diagram (PTD®) and perfumery quaternary diagram (PQD) methodologies to map the perceived smell of quaternary and quinary fragrance mixtures. A diffusion model was used to simulate the evolution of liquid and headspace concentrations. The evaporation of perfumes starts with a fast ethanol release, then the diffusion of the fragrant components. The composition paths were predicted through the evaporation lines plotted in the PQD. The two odor intensity models present differences in the initial perfume impact, but after some time tend to similar profiles. The Power-Law predicted higher ethanol intensities than the OV model, due to its exponent. Introducing water in perfume formulation fixes ethanol in the solution, thus reducing alcohol perception.
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Introduction

The development of new, high added-value products and the processes to produce them demands both process and product engineering knowledge. First and foremost, such products have to go through several stages till reaching the market: design, development, optimization, production, and testing.[1–5] This is the reason why product engineers need to have knowledge and expertise in multiple scientific areas inside chemical engineering. Extending the current limits of product's performance has now become a key factor for Product Engineers who must hand out innovative and valued products, technologies and services to the market. The development of perfume engineering itself represents a particular case in the field of Product Engineering, inside the Flavor & Fragrance multi-billion dollar market. For its part, Flavor & Fragrances represents a commercially relevant and profitable area where scientific knowledge must be combined with creativity.[6,7]

The formulation of perfumes involves the combination of a wide variety of fragrances (from natural, natural-identical, and synthetic origin) in the order of thousands. This is the role of the perfumer, combining different fragrant notes in a trial and error procedure, until the desired scent or odor character is found. The perfumer has to smooth the odor profile of a formulation so that there will be no discontinuities in the perceived odor as the different fragrant components evaporate. The amount of concentrated fragrance (or essential oils) in a perfume formulation can vary widely, from 10–20% for some compounds to trace levels (ppm) for others. In the formulation process, perfume concentrate is usually incorporated in ethanol. Additional water is used for the more dilute forms.[8] The classification of perfumes can be done with respect to the concentration of the perfume concentrate[9] or to its olfactory family. In what concerns our

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Table 1. Perfume Classification in Terms of the Composition of Perfume Concentrate and Water (in volume)

Type	Perfume Concentrate (%)	Water (%)
Extrait or Parfum	15–30	1–3
Eau de parfum	8–15	9–13
Eau de toilette	4–15	10–18
Eau de cologne	3–5	20–40
After shave	2–8	30–50
Splash cologne	2–3	30–50

work, the first is highlighted for the purpose of the study of the odor intensity and is described in Table 1.

According to its composition a perfume may be classified into different types, as defined by the ratio of concentrate and solvent (ethanol/water). The amount of water that is introduced into the perfume mixture depends on the nature of the perfume composition and the percentage of oil. Water is desirable because it reduces the sharp odor of alcohol and the price of the finished product.[10] The selection of the fragrances and their exact combination to design a perfumed product relies on a variety of parameters like the odor contribution to the overall scent, its stability, the performance in the products to be perfumed (impact, tenacity, diffusion, and volume[11–13]), its safety in use and cost. During the development of a fragrance, perfumers experimentally evaluate the odor character as it evaporates off a paper blotter and diffuses in the air above it. While both processes occur the character or tonality of the perceived odor (the dominant smell) necessarily changes, once fragrant species do not evaporate at the same rate.[14,15] The study of the evaporation processes from fragrant mixtures has largely been studied since the performance of such products is often defined by the fragrance perception. In the literature there are several studies in this area namely: its application to the release of fragrant molecules from microcapsules for textile applications,[16] the evaporation of fragrances from the skin,[17,18] the release of bioactive volatiles encapsulated in copolymers,[15] and also of remark the research in the evaporation from emulsions with algebraic approaches which can have applications on pharmaceutics and cosmetics.[19–21] However, the high complexity of perfume mixtures, due to the multiplicity of interactions and the number of components present in solution renders it difficult to predict a priori headspace compositions.[22] Additionally, fragrant molecules have to be captioned by the human olfactory receptor cells and its interpretation in the brain has to be considered. Here, two aspects are relevant: on the one hand, the quantification of the odor intensity of a fragrance; and on the other hand, the discrimination and identification of the overall odor character and the fragrances present in a multicomponent mixture. For its part, the odor intensity will be discussed in this work along with the prediction of the odor character in the air and some insight in that area will be provided ahead.

The scientific study of the phenomena of perception has inspired perfumers and psychophysicists for long time. Several issues put the mind of these specialists to the test. How do we perceive and interpret a stimulus coming from the outside world? What stimuli are we capable of process? Which is the relationship between a stimulus magnitude and the sensation perceived?

The quest for the answer of some of these questions started to be sketched out only by the end of the 19th century. Since then and until our days, the search for a primary question is still going on: How precisely does a sensation (output) vary with a stimulus (input)?

Perception can be defined as the means by which we receive, collect, and interpret information from the outside world. It is the sensory experience by which we gain information about the properties of the environment around us, allowing us to act within it. In what concerns to odor perception, the olfactory system is remarkably capable of detecting and identifying thousands of odorants through the olfactory receptor cells.[23] It is even able to collect scents at lower concentrations than analytical instruments such as gas chromatographs. The odor sensations can be perceived from single aromas or fragrances, but also from mixtures, which may have hundreds of compounds. In the latter case a complex summation of odors occurs, turning difficult to characterize it in a physical way and often resulting in a unitary perception of a smell (e.g., coffee).[24]

Odor Intensity Models

Psychophysics is a scientific field of Psychology that deals with the integration between physical stimuli and its psychological interpretation, giving some mathematical relationships for that. There are some models in this area based on experimental studies to establish this relationship. A brief description of the most significant models is given below, starting from the first experimental models till our days. The Power Law and the odor value (OV) model will be compared throughout this work using the PTD® and PQD methodologies to predict the odor intensity of perfume mixtures. The effect of water on perfume formulation will also be addressed, once it is a component widely used in perfumery, and playing an important role in the release of the fragrances and the odor character.

The Weber-Fechner law

The first relationship between a stimulus and its perceived sensation to be postulated was based on Weber's theories, first published in 1851.[25] However, only a few decades later, in the 1870s Weber's empirical theories were mathematically expressed by Fechner.[26,27] The Weber-Fechner law stated that as stimulus strength grew geometrically (by constant ratios) the sensation magnitude increased arithmetically, or in other words, the magnitude of the psychological sense would be proportional to the logarithm of the ratio of physical stimulus:

$$\psi = k \cdot \log\left(\frac{S}{S_0}\right) \tag{1}$$

where ψ is the sensation magnitude, k is a positive constant factor, S is the stimulus magnitude, and S_0 is the threshold of the magnitude of the physical stimulus.

However, physicists and psychologists contended that this logarithmic law could not be applicable to all perceptual continua. Nonetheless, this law persisted for more than a century mainly due to the fact that the critics had never come up with a scientific alternative but only contrary arguments. One of the major questions that psychophysicists put to this law concerns the fact that it was based on indirect experiments and indirect measurements of magnitude sensation.[27] Modern psychophysicists support their ideas on direct measurements, thus diminishing errors that are difficult to eliminate in such a sensorial science.

At the beginning of the 20th century, many psychophysicists criticized the theories proposed by Weber-Fechner but they still failed to submit an alternative. It was not until the 30s that the first direct methods were applied in the area of Psychophysics.

The power law

These direct methods shown that, to a first-order approximation, the ratio scale of magnitude perception was a power function. But would some power law distribution be capable of describing different perceptual continua?

This first mathematical equation relating sensation magnitude with physical stimulus for perceptual continua was proposed by Stanley Smith Stevens (1906–1973), an American psychologist. The Stevens Psychological Law or the Power Law set forth that sensation (ψ) was proportional to stimulus (S) raised to an exponent (n), so that

$$\psi = k \cdot S^{\mathrm{n}} \tag{2}$$

The power law has been observed for perceptual judgments of physical stimuli like brightness, loudness, taste, smell or size, and of nonphysical stimuli like utility of money, products, and services. Adapting Eq. 2 for the measurement of odor intensity, it is possible to express that

$$\psi = \left(\frac{C^{\mathrm{g}}}{\mathrm{Thr}}\right)^{n} \tag{3}$$

where C^{g} is the concentration of an odorant in the gas phase (g/m^3) and Thr is its concentration threshold on air (g/m^3). This equation can be plotted in a log–log scale to obtain a linear relationship between a stimulus and the perceived sensation where the slope equals the exponent n. The concentration threshold and the exponents for the power law can be obtained in the literature from compilations of data for several odorant species.[11,28–30]

The principle of the power law lays on the assumption that equal stimulus ratios tend to produce equal sensation ratios.[27] In fact, Stevens' experiments consisted in asking observers that were presented with different intensity stimuli to make a numerical or category judgment of their subjective experience. The use of direct methods in opposition to the indirect methods revealed that a power law was behind the explanation of different perceptual continua. Equally interesting was also the discovery by Stevens that the value of the exponent n was different for each perceptual continuum. He found that in the case of brightness it was $n = 0.5$ (point source); loudness, $n = 0.6$ (sound pressure); smell, $n = 0.6$ (for heptane); taste, $n = 1.3$ (sucrose) or $n = 1.4$ (salt); or electric shock, $n = 3.5$ (current through the fingers). It is worth to mention that although the power law has had a great impact and applicability since then till our days, it is not universally valid once it does not hold from zero to infinity.[27]

However, this law has still some drawbacks that are first perceptible from Stevens' experiments. In fact, it was not performed a direct test of the power law but a fitting to experimental data that showed to be correlated by a power function.[31] Stevens' tests also missed out any personal differences between the subjects. Additionally, the power function did not always hold when data were considered separately from individual respondents.[32] Equally moot is when backgrounds are introduced in continua measurements (e.g., background noise in loudness or background scent in olfaction) where it is seen that the shape of the magnitude estimation functions sharply deviate from the power function.[33] There are some other variables that affect perception magnitude like adaptation or human sensory modification, among others.[34] Finally, it is important to highlight that it was shown that the loudness function, for example, is less steep at moderate levels than at low and high levels, and that near threshold the average slope is about unity or slightly higher.[35]

It is a straightforward reasoning that the psychophysical power law is a nonlinear relationship between the strength of some stimulus and its sensory magnitude. It is feasible to admit that odor perception follows such a law, where at some point the increase in the odorant concentration will not produce an increase in the odor perception due to the saturation of the odor receptor cells. This way if the exponent is lower than unity ($n < 1$), it is called compressive and the odor intensity increases slowly with the concentration; for exponents equal to unity ($n = 1$) there is a linear relationship between concentration and perceived sensation which are linearly proportional; and finally, if the exponent is higher than unity ($n > 1$), it is said to be expansive and odor intensity increases more rapidly than the concentration. Whereas sugars tend to produce power function exponents for sweetness slightly greater than 1 with a mean of 1.33, acids tend to produce exponents smaller than 1 for sourness.[36] In olfaction, the majority of the odorants seem to generate power functions with exponents smaller than unity, and for the compilation of data used the median was 0.35.[30] In what concerns to the exponents used in this work they were obtained from a data compilation.[30] This compiled data has a weighting coefficient attributed to each author based on statistics (index of profile similarity), followed by averaging and standardization of the exponent values.

The odor value

The odor value concept expresses the relationship between stimuli and perception by a linear function. This linear law is shown by Eq. 4, being applied to the measurement of the odor intensity.[11,12,29,37–40]

$$\mathrm{OV} = \frac{C^{\mathrm{g}}}{\mathrm{Thr}} \tag{4}$$

This linear law is a special case of the Power Law for $n = 1$. Then, there will be a linear relationship between odor concentration and its perceived intensity. Some authors,[11,41] have referred the OV model because of its simplicity and data availability. Values for concentration threshold can be obtained from the literature in data series for numerous fragrant species.[11,28,29]

We have used the OV model in previous studies with application in olfactory sensation showing fair agreement between simulated and experimental results.[42] Nonetheless, some authors point out that this linear law does not hold for all the range of stimuli magnitude, and particularly at high values of the stimulus where it deviates from the experimental data.[43]

So far, experimental studies performed on sensory perception have shown that at sufficiently high concentrations, the experimental data based on human sensory panels followed approximately power functions with exponents smaller than unity. However, at lower concentrations, and especially near-threshold concentrations, the slope of the curves was close to unity. Very recently, a new scientific approach of a similar linear law, called the law of asymptotic linearity, was presented.[43] This law states that all subjective magnitudes grow linearly with the intensities of the stimuli that evoke them near their thresholds.

In brief, multisensory experiments found in the literature together with its biophysical and biological fundamentals have shown good agreement with both the Power Law and the Linear Law (OV model) for sensory perception in different perceptual continua. In this work, a comparison between these two laws will be done with application on the olfaction of perfume mixtures. The prediction of the odor perception will be modeled with both laws using some chemical engineering methodologies, like the PTD® and the PQD for the representation of the odor character.

The PTD® and PQD Methodologies

The starting point behind the PTD® methodology[12,44] was the combination of two concepts from perfumery and chemical engineering: the perfume pyramid structure proposed by the perfumer J. Carles[45] and the triangular diagrams used for ternary systems in chemical engineering. The classic pyramid changed the view of perfume formulation, by considering that the basis of the perfumes was a tripartite structure with three types of fragrant notes: top, middle and base notes. Following this line of thought, top notes would be the most volatile species in a perfume mixture, evaporating faster and contributing for the initial perceived impact. Middle notes would act as bridge notes between the top and base notes. As the scent of the top notes starts to fade out, these middle notes would become more strongly perceived. Finally, the base notes, constituting the core of the perfume, would last longer in the liquid phase and so being smelled only some hours after application, and persisting for days or even months. These ideas are combined with the engineering ternary diagrams in the previously developed PTD® methodology.[12,46]

This way, at each perfume composition it is possible to predict the odor intensity of single fragrant components by using one of the aforementioned odor intensity models (Power Law or OV) and represent the odor character in the PTD®. Both models consider the ratio between the actual concentration in the headspace and the odorant concentration threshold value. The latter can be found published in compilation of data sets, while the first can be predicted using some concepts of chemical engineering, and more specifically of Thermodynamics. The gas phase above the liquid (headspace) can be considered as an ideal phase since the gas molecules are highly diluted, while in the liquid phase nonidealities should be considered due to the presence of molecular interactions. Taking into account these assumptions the relationship between both phases can be expressed to the light of the modified Raoult's Law, and the concentration of the odorant species in the headspace (C_i) can be traduced as:

$$C_i^{\mathrm{g}} = \frac{y_i M_i P}{RT} = x_i \gamma_i \frac{M_i P_i^{\mathrm{sat}}}{RT} \tag{5}$$

where x_i represents the liquid mole fraction of component i, M_i is its molecular mass, γ_i is the liquid activity coefficient, P_i^{sat} is the saturation pressure of pure component i, R is the universal gas constant, and T is the absolute temperature.

The activity coefficient γ_i, is a parameter that measures the deviations of the liquid phase from ideal behavior. For an ideal solution the activity coefficient equals unity ($\gamma_i = 1$), while for a nonideal solution $\gamma_i \neq 1$, evidencing deviations from Raoult's Law. For perfume mixtures, the activity coefficient can be understood as a measure of the tendency of a molecule to stay in the liquid solution or to be "pushed out" into the headspace (and thus being more strongly perceived). Activity coefficients can be obtained from experimental vapor–liquid equilibrium (VLE) data or calculated with predictive methods. In our work, the UNIFAC method[47,48] was used for calculation of activity coefficients of the fragrance species.

Therefore, for a multicomponent perfume mixture having N fragrant components, it is possible to predict the N different odor intensities (ψ, OV) in the headspace, each one corresponding to a single fragrant species, considering Eqs. 4 and 5:

$$\psi_i = \left[\gamma_i x_i \left(\frac{P_i^{\mathrm{sat}} M_i}{\mathrm{Thr}_i} \right) \left(\frac{1}{RT} \right) \right]^n \tag{6}$$

where the exponent n can be equal to unity when considering the OV model or different when the Power Law model is applied.

The odor perception of a multicomponent mixture, that is the odor character resulting from the combination of different scents, can be expressed by the Strongest Component model. This odor perception model states that in the multiplicity of odorant components present in the gas phase, that having the highest odor intensity will be more strongly perceived and thus better recognized by the human nose, although there is a mixture of perceived scents in the air[49,50]:

$$\psi_{\max} = \max\{\psi_i\}, i = 1, \ldots, N \tag{7}$$

Accordingly, the PTD® methodology presents itself as a tool for mapping the character of fragranced products by showing in a ternary diagram the compositions where each component is most strongly perceived. However, when applied to quaternary mixtures this methodology is conditioned by the fact that it cannot show the whole behavior of the odor distribution, and is not applicable to higher multicomponent mixtures.

Table 2. Properties of the Odorant Components

	Name	Molecular Formula	M_i (g/mol)	P_i^{sat} (Pa)	Thr_i (g/m^3)	$\frac{P_i^{\text{sat}} \cdot M_{wi}}{\text{Thr}_i \, R \cdot T}$	$D_{i,\text{air}}$ (m^2/h)	n[*]
A	Limonene[†]	$C_{10}H_{16}$	136.2	20.5×10^{1}	2.45×10^{-3}	4.60×10^{3}	2.214×10^{-2}	0.37
B	Geraniol[†]	$C_{10}H_{18}O$	154.3	26.7×10^{-1}	2.48×10^{-5}	6.70×10^{3}	2.138×10^{-2}	0.36
C	Vanillin[†]	$C_8H_8O_3$	152.2	16.0×10^{-3}	1.87×10^{-7}	5.25×10^{3}	4.111×10^{-2}	0.31
	Galaxolide	$C_{18}H_{26}O$	258.4	72.7×10^{-3}[‡]	6.30×10^{-7}[§]	1.20×10^{4}	1.924×10^{-2}	0.36
S	Ethanol[†]	C_2H_6O	46.07	72.7×10^{2}	5.53×10^{-2}	2.44×10^{3}	4.469×10^{-2}	0.58
	Water	H_2O	18.01	3.17×10^{3}	–	–	9.132×10^{-2}	–

[*] Ref. 30.
[†] Ref. 11.
[‡] Ref. 51.
[§] Ref. 52.

To overcome such difficulties, the PQD methodology[12,46] was recently developed, being able to represent in tetrahedric diagrams the whole behavior of quaternary mixtures. It can also be applied to quinary systems by representing the compositions in a solvent free-basis. These two methodologies can be used together as will be seen throughout this work. In a PQD, it is possible to map the quaternary or pseudo-quinary compositions where one odorant species has the maximum odor intensity, called the perfumery odor volumes. Each odor volume is limited by surfaces where two fragrant components share the maximum odor intensity. These surfaces intersect at lines which are the compositions where three components have the same maximum odor intensity. The studied odorant components and their physical and sensorial properties are presented in Table 2.

Diffusion Model

The diffusion of fragrant components and the effect on perception of perfumes was also studied in this work to the light of the two odor intensity models. A perfume diffusion model based on Fick's 2nd Law was developed to simulate the evaporation and diffusion rates of fragrant molecules from liquid solutions. The unsteady-state mass balance described by the partial differential equation (PDE) for the gas phase and the mass balance between the liquid and gas phases (ODE) are presented in Eqs. 8 and 9, with the corresponding initial and boundary conditions to solve the system of equations:

Gas Phase:

$$\frac{\partial y_i}{\partial t} = D_{i,\text{air}} \frac{\partial^2 y_i}{\partial z^2}$$

$$\textbf{\textit{Initial Condition}}\text{:}\quad t = 0 \qquad y_i = y_{i_0} = 0$$

$$\textbf{\textit{Boundary Conditions}}\text{:}\; t > 0 \quad z = 0 \quad y_i = \frac{\gamma_i P_i^{\text{sat}}}{P}$$

$$x_i = \frac{\gamma_i P_i^{\text{sat}}}{P} \frac{n_i}{\sum\limits_i n_i} \qquad z = z_{\max}\; y_i = 0 \qquad (8)$$

Liquid Phase:

$$\frac{dn_i}{dt} = D_{i,\text{air}} A_{lg} c_{\text{T}} \left. \frac{\partial y_i}{\partial z} \right|_{z=0}$$

$$\textbf{\textit{Initial Condition}}\text{:}\quad t = 0 \qquad n_i = n_{i_0} \; or \; x_i - x_{i_0} \qquad (9)$$

where $D_{i,\text{air}}$ is the diffusivity of component i in the air, $c_{\text{T}} = P/RT$ is a positive constant once the gas is considered ideal, y_{i_0} and x_{i_0} are the initial mole fraction of component i in the gas phase and in the perfume liquid mixture, respectively. Finally, n_i and n_{i_0} are the number of moles and the initial number of moles of component i in the liquid phase, respectively. These equations were integrated for the time span, $[t, t_{\max}]$ and distance, $[z, z_{\max}]$ where $z_{\max} = 2m$. The total number of moles present in the liquid solution was set to $n_{\text{T}} = 1$ mmol and the area of liquid–gas interface, $A_{\text{lg}} = 0.071$ m^2.

The simulations for the perfumery ternary diagram (PTD®) and the perfumery quaternary diagram (PQD) methodologies were run using the MATLAB software. Routines and functions were developed in MATLAB as well as the prediction of the activity coefficients (γ_i) using the UNIFAC method. The calculations over the space variable were set to second-order approximations to the solution on the specified mesh values. The computation of the nonlinear systems of equations were solved numerically using the optimization toolbox from MATLAB, adapted to the nature of the problem studied.[53–55] Further details and conditions used for this perfume diffusion model were previously reported in the literature.[12,13]

Results

The two odor intensity models considered in this work (Power Law and OV) were applied for the simulation of different quaternary and quinary perfume systems. The top note (A—limonene) and the middle note (B—geraniol) were the same for all systems, while the selected base notes (C) were vanillin and galaxolide for system 1 and 2, respectively. Moreover, the selected solvent (S) was ethanol for quaternary systems, and a mixture of ethanol/water for quinary systems.

The effect of the selected odor perception model is first analyzed using the PTD® methodology (Figure 1), instead of the PQD, since it is easier to get a better perception of the variations in the odor zones by plotting the ternary subsystems that constitute the quaternary system. These ternary subsystems represent the faces of the PQD tetrahedric diagram, where there are $n - 1$ components present in the mixture. Figure 2 shows the corresponding four ternary subsystems (A+B+C), (A+B+S), (A+C+S), and (B+C+S) for the quaternary perfume systems studied in this work, considering both the OV (top) and the Power Law (bottom) models.

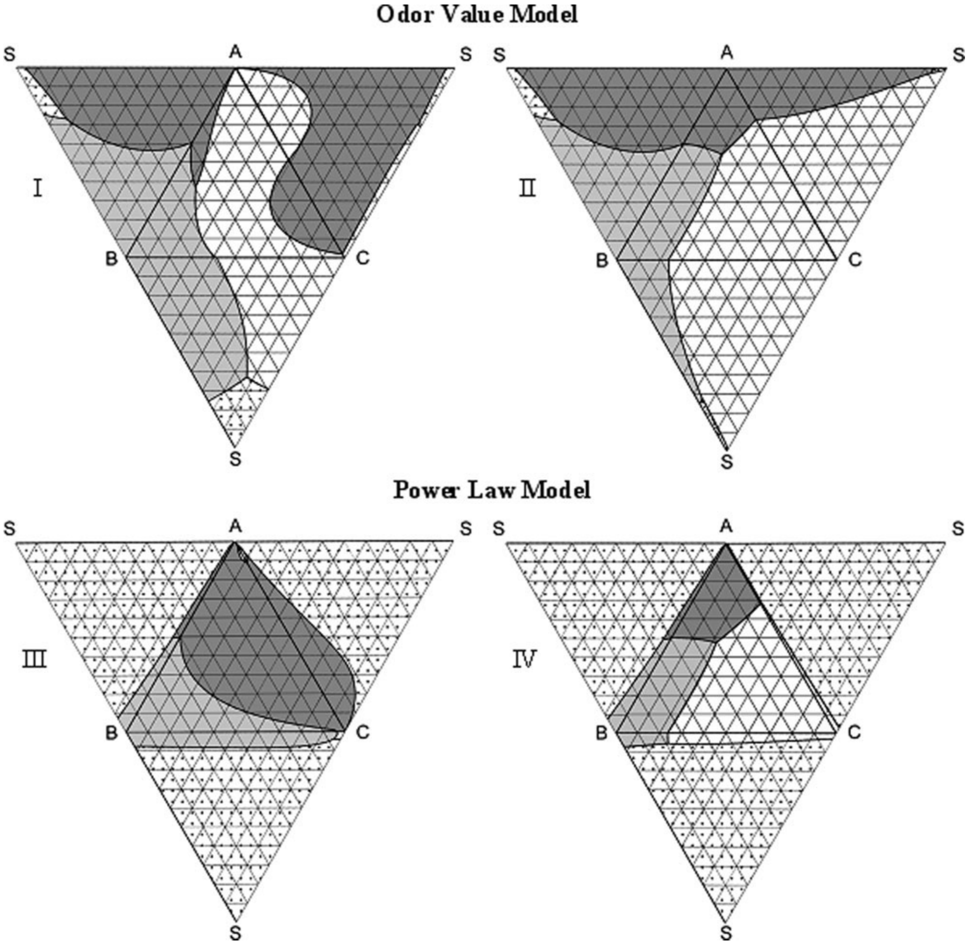

Figure 1. PTD® of the different ternary subsystems of the two quaternary mixtures.

A: Top note (dark gray, limonene), B: middle note (light gray, geraniol), C: base note (white, I–III: vanillin, II–IV: galaxolide), S: solvent (dotted, ethanol). Top diagrams simulated using the OV model (I–II), bottom diagrams with Power Law model (III–IV).

Through Figure 1 it can be easily seen that there are significant differences in the shapes of the odor zones and in the distribution of the odor character when the two odor intensity models are applied. Comparing the top (OV model) with the bottom diagrams (Power Law model) the predominance of the odor of the solvent increases significantly. This is due to the fact that ethanol has a much higher exponent, resulting in higher initial odor intensities. It is seen that for the ternary mixture (ABC) of the perfume system 1, the application of the Power Law changes significantly the odor character, since vanillin is only perceived near the corner C. On the other hand, for perfume system 2, the simulation with the Power Law does not change much the inner PTD.

However, viewing these ternary subsystems does not give us any specific insight into the quaternary perfume mixture, that is, the composition points located inside the tetrahedron. To see the whole behavior of the quaternary perfume system, it is presented in Figures 2–5 the PQD, for the two perfume systems using both odor intensity models, with the different fragrance volumes highlighted for each odorant component.

The PQDs for both perfume systems studied here show that when the Power Law model is applied to account for the odor intensity, the fragrance volumes of the odorant compounds are significantly reduced while the fragrance volume of ethanol increases. It is observed when comparing Figures 2 and 3 that the odor volume for vanillin is significantly smaller when the Power Law model is considered, being reduced to two small volumes near the corners of limonene and vanillin. This means that when considering a nonlinear odor intensity model, the Stevens' Law as opposed to the linear OV model, the result is that the range of simulated compositions where ethanol has higher intensity is greater. It is important to highlight that the PQD methodology maps the odor character near the source of the perfume mixture that is at the gas–liquid interface. This effect in the prediction of the odor intensity near the source of the perfume is mainly dependent on the exponent (n) for the single fragrances. A comparison between the two different odor intensity models can be seen in Figure 6, where the Power Law model is plotted against the linear OV concept, considering the exponents (*n*) in Table 2 for each fragrance.

The use of a power law to relate odor stimuli and the perceived olfactive sensation, results in a significant difference in odor intensity relatively to the linear law. It is seen also from Figure 6, that the predicted odor intensity of ethanol reaches values much higher than for other fragrant components, due to the fact that its exponent is significantly higher than all others. Additionally, the slope of the ethanol curve

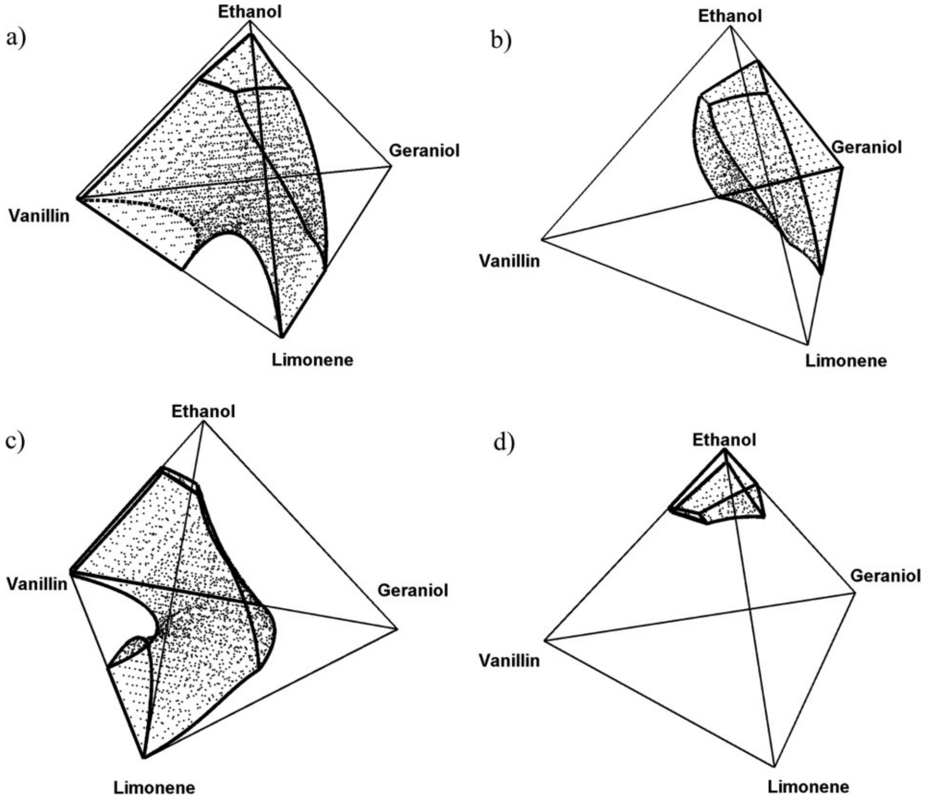

Figure 2. Perfumery fragrance volumes considering the OV model for the odor perception in system 1: (a) limonene, (b) geraniol, (c) vanillin, (d) ethanol.

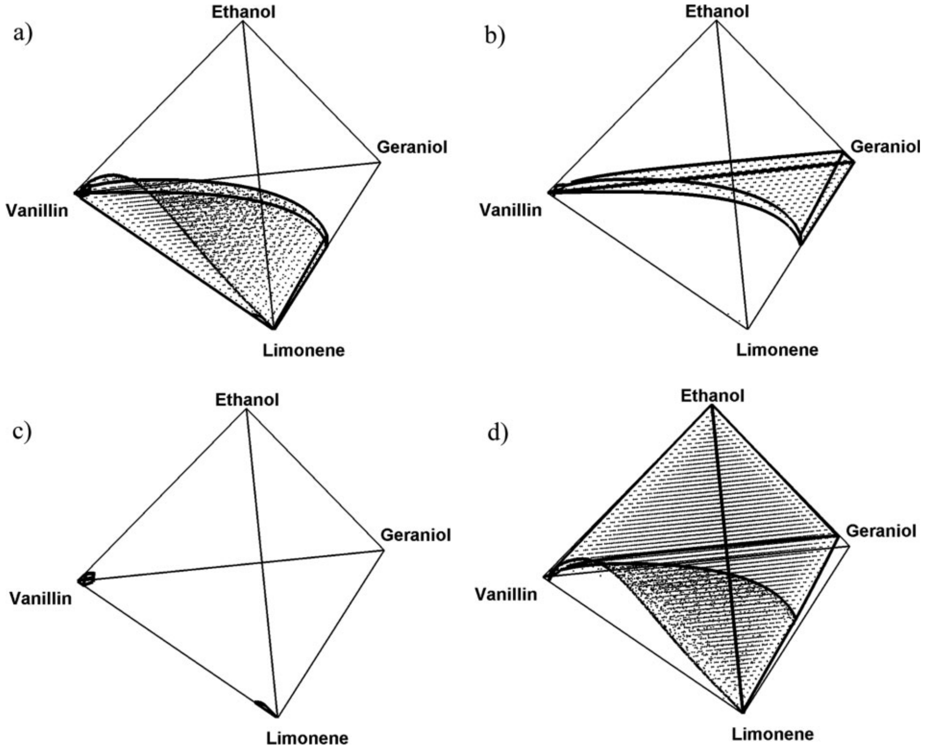

Figure 3. Perfumery fragrance volumes considering the Power Law model for the odor perception in system 1: (a) limonene, (b) geraniol, (c) vanillin, (d) ethanol.

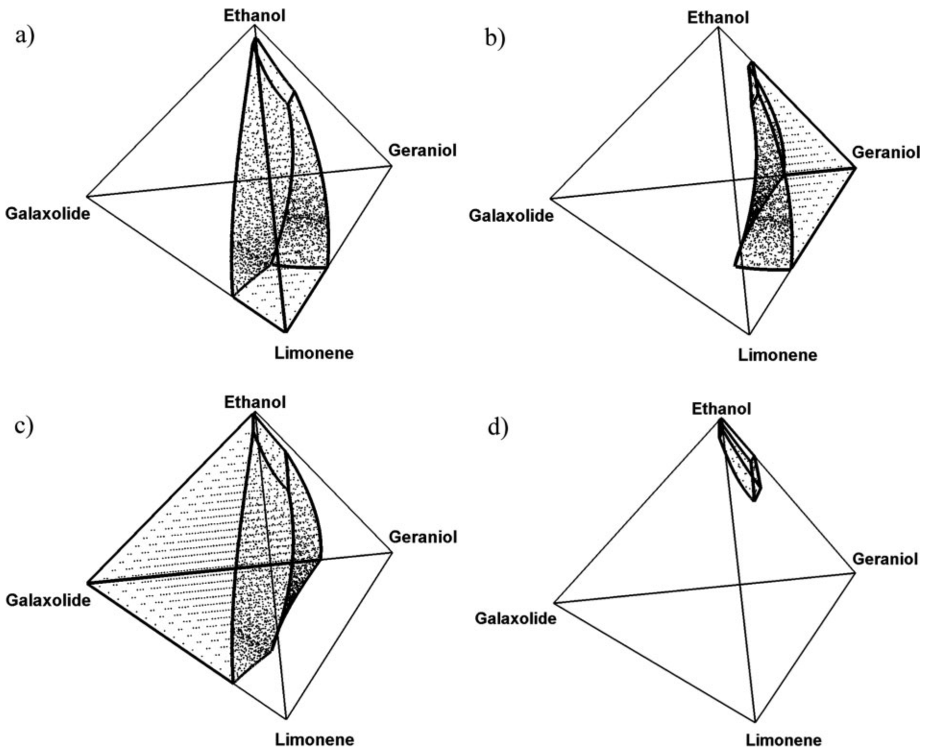

Figure 4. Perfumery fragrance volumes considering the OV model for the odor perception in system 2: (a) limonene, (b) geraniol, (c) galaxolide, (d) ethanol.

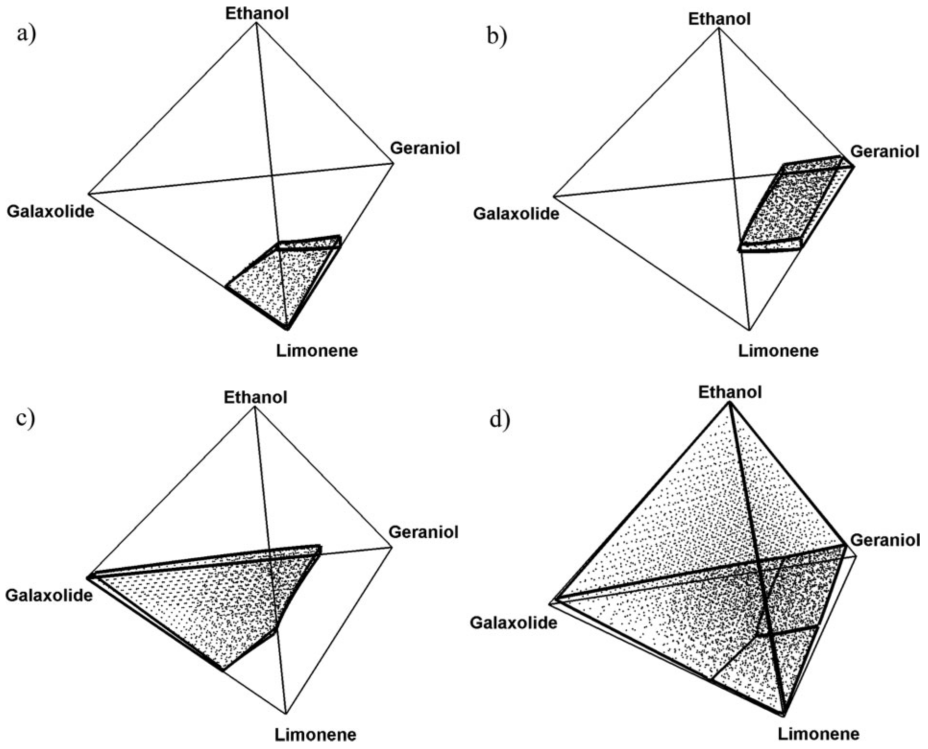

Figure 5. Perfumery fragrance volumes considering the Power Law model for the odor perception in system 2: (a) limonene, (b) geraniol, (c) galaxolide, (d) ethanol.

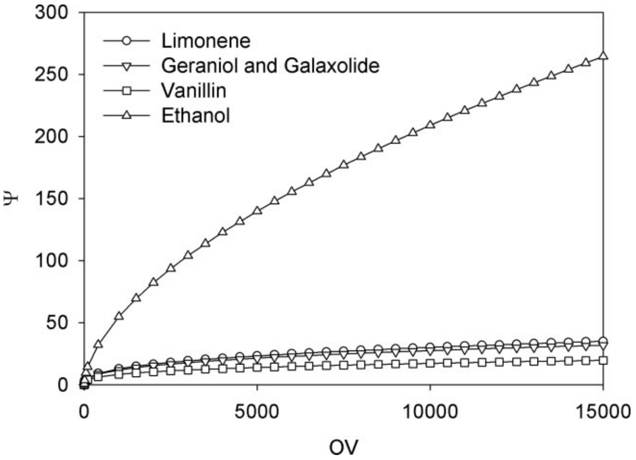

Figure 6. Effect of the exponent (*n*) on the odor intensity of the fragrant molecules.

when the power law is applied is higher than for the other components, thus sharply increasing its odor intensity. The curves for geraniol and galaxolide in Figure 6 are overlapped since they have the same exponent while vanillin, the less volatile component, has the lowest curve.[30] The truth is that perfumers generally follow a rule that says that a perfume should never smell to the alcohol solution, once it is not aesthetically pleasant for consumers. However, a perfume mixture is formulated with a wide number of odorant components (in the order of dozens) and is designed to be smelled and perceived differently with time and at different distances from the point of application. The effect of the diffusion of the perfume mixtures studied here and their odor intensity over time and away from the source will be seen ahead. Nevertheless, one of the major components widely used in commercial perfumes as a solvent is water, usually in a mixed solution of water/alcohol.[9,10] This way, it is important to understand the effect of the highly polar water molecules in a perfume mixture and how they will affect the odor intensity and character of the headspace above the fragrance solution.

The effect of water on fragrance mixtures

The effect of water in perfume mixtures was studied considering the same quaternary systems previously analyzed in this work and adding water as the fifth component in a fixed mole fraction. It is important to highlight that although water can not be smelled or perceived by the human nose, water

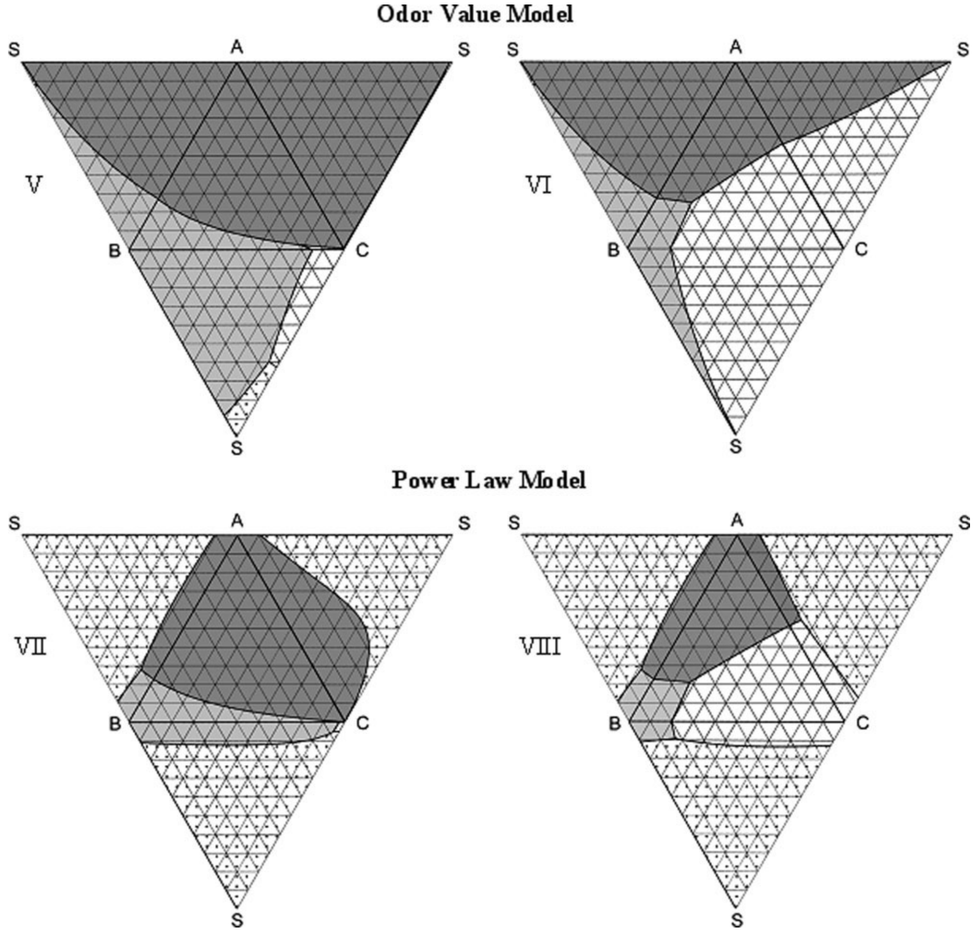

Figure 7. PTD® of the different pseudo-quaternary subsystems of the two quinary mixtures.

A: Top note (dark gray, limonene), B: middle note (light gray, geraniol), C: base note (white, V–VII: vanillin, VI–VIII: galaxolide), S: solvent (dotted, ethanol). Top diagrams simulated using the OV model (V–VI), bottom diagrams with Power Law model (VII–VIII). All systems include 45% water.

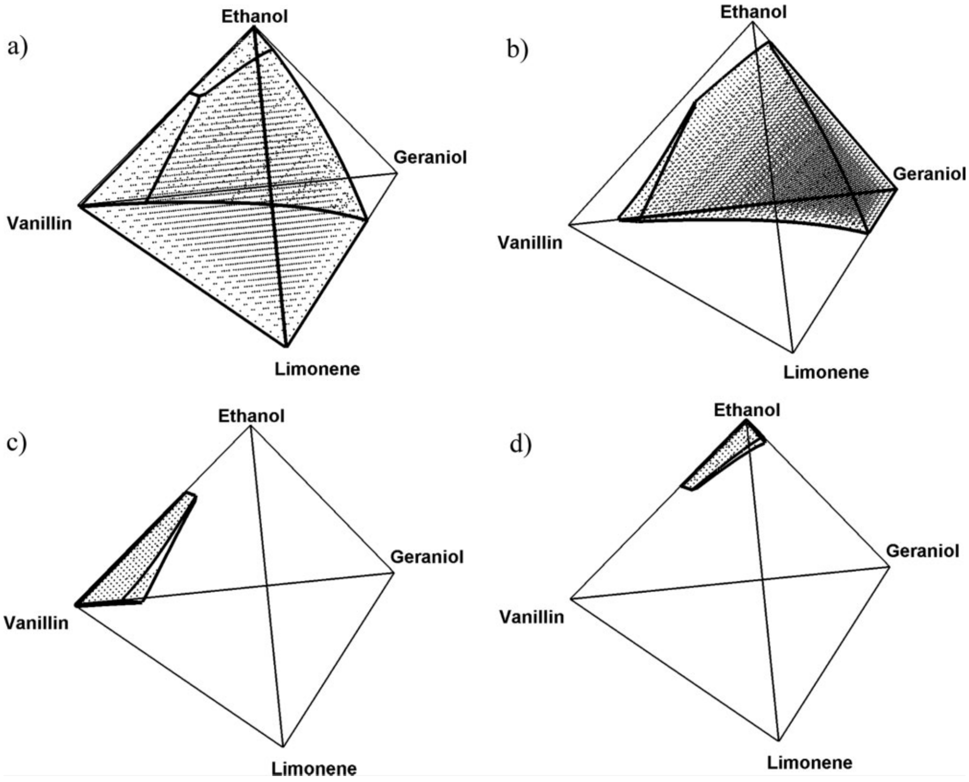

Figure 8. Perfumery fragrance volumes considering the OV model for the odor perception in system 3: (a) limonene, (b) geraniol, (c) vanillin, (d) ethanol.

molecules influence the molecular interactions in a perfume mixture. Two different quinary fragrance systems were studied as follows:

- System 3: limonene (A), geraniol (B), vanillin (C), ethanol (S), and water (S′).
- System 4: limonene (A), geraniol (B), galaxolide (C), ethanol (S), and water (S′).

The selected mole fraction of water ($x_{S'}$) was considered to be equal to 45% of the solution. In the formulation of fine fragrances this corresponds to the case of after shaves or splash colognes as mentioned earlier.[9] The results showing the odor distribution for these quinary systems are presented in Figure 7 for the pseudo-quaternary subsystems that constitute the quinary one. The whole distribution of the odor character for these two quinary mixtures can be shown using the PQD for the different odor intensity models as presented in Figures 8–11.

When considering the OV model alone to account for the odor intensity it is possible to compare from Figures 1 (I–II) and 7 (V–VI) that in both perfume systems the presence of water molecules induces a larger odor zone for the top note (limonene). This can be explained by the fact that when including water in the system the average polarity of the mixture increases, and so tends to push out of the solution the less polar component, limonene.[9,56] This effect was previously seen in an experimental study where the activity coefficients (γ_i) of three fragrant components were measured in three different media (aqueous surfactant, diethyl phthalate and water). The authors shown that for the case of limonene the activity coefficients in water were two or three orders of magnitude higher than in other solvent media. In the same way, the ethanol odor zones seem to be significantly reduced probably due to the strong water–ethanol interactions (hydrogen bonding) which retain ethanol in the liquid phase. The same effect of the presence of water molecules in the perfume composition is seen when the Power Law model is considered, since these effects are independent of the sensory model selected. Comparing Figures 1 (III–IV) and 7 (VII–VIII), it is slightly perceptible that the ethanol odor zone is reduced, though this effect is far less evident than in the OV model. The effect of water molecules in quinary perfume mixtures can also be seen through the odor volumes represented in the PQDs for the different fragrant species (Figures 8–11). In fact, various molecules may mix and dissolve in each other when they have similar polarities. In the case of water and ethanol, this is the situation. The —OH group of ethanol is polar and hydrogen may bond to an oxygen of a water molecule. These bindings are strong and can have a fixative effect on ethanol so that it is not strongly perceived (as it is desirable from the perfumery viewpoint). This water–ethanol effect has already been reported to the light of perfumery, mainly as an empiric verification but nothing has been proved at the molecular level.[9] Although water has shown to have a retention effect on ethanol for the quinary mixtures studied here, it is important to note that in the formulation of a real perfume a large number of fragrant species is involved, and some can (e.g., base notes) also have a strong fixative effect.[12,13]

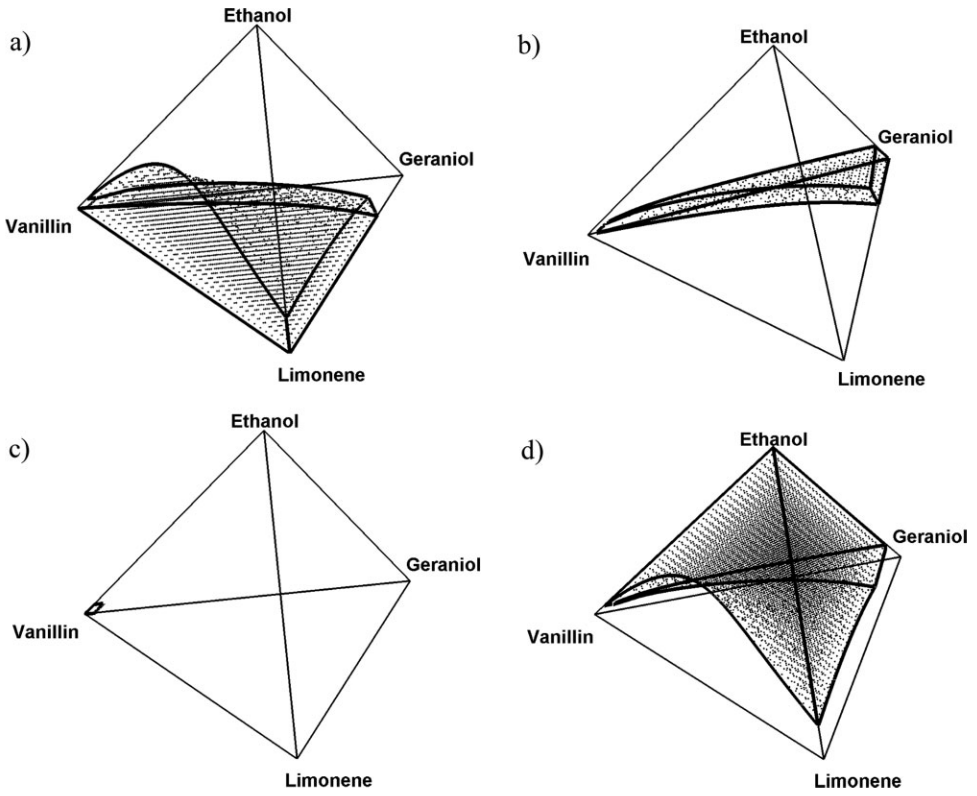

Figure 9. Perfumery fragrance volumes considering the Power Law model for the odor perception in system 3: (a) limonene, (b) geraniol, (c) vanillin, (d) ethanol.

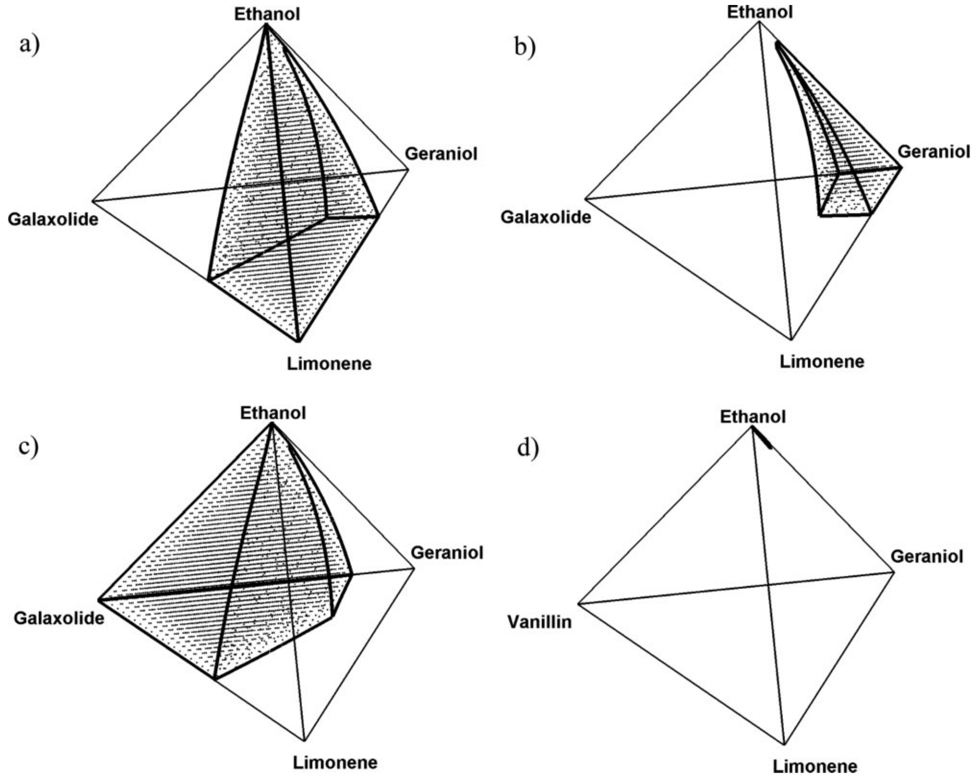

Figure 10. Perfumery fragrance volumes considering the OV model for the odor perception in system 4: (a) limonene, (b) geraniol, (c) galaxolide, (d) ethanol.

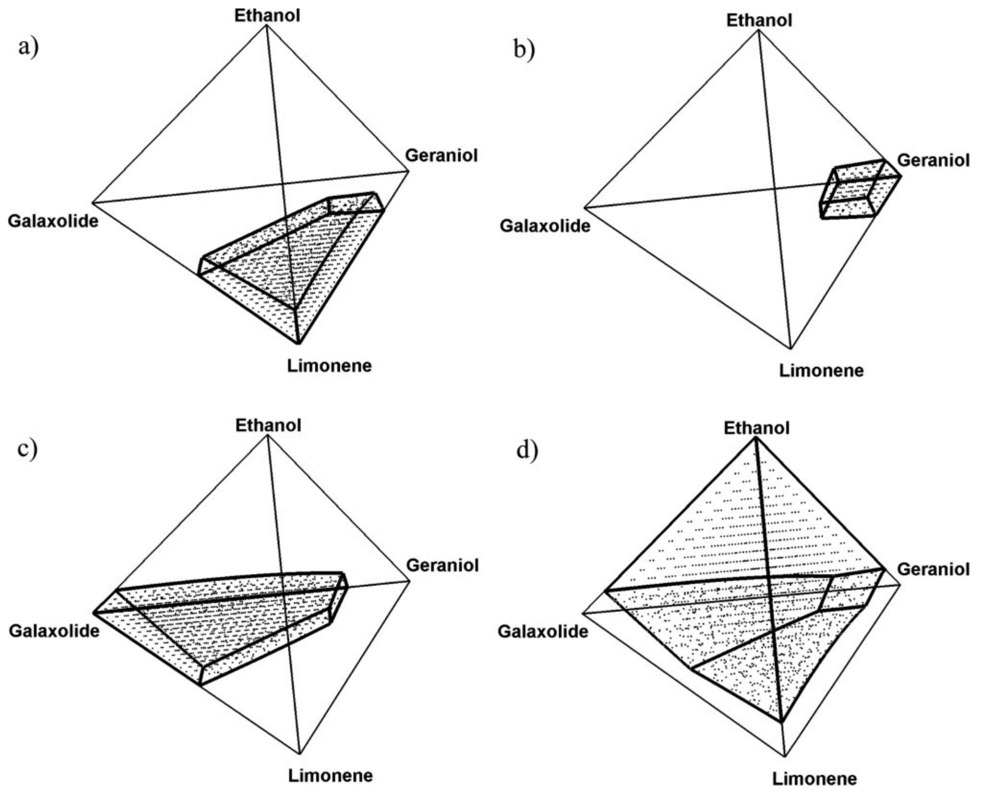

Figure 11. Perfumery fragrance volumes considering the Power Law model for the odor perception in system 4: (a) limonene, (b) geraniol, (c) galaxolide, (d) ethanol.

Diffusion of quaternary fragrance mixtures

As seen before, the use of different odor intensity models affects the prediction of the odor character of fragrance mixtures in the first moments after the application of a perfume. However, it is important to see how these models will affect or not the performance of the perfume mixtures over time and distance. Perfumes and fragranced products are designed to be used over time and it is desirable that its smell diffuses over the surrounding space with time. Therefore, the question here is whether the use of one model or another will influence the odor perception/performance of fragrance mixtures over time and distance.

This way, a diffusion model was applied to the perfume mixtures studied in this work to simulate the evaporation and diffusion processes of quaternary mixtures. This model simulates a physical system with a small volume of a liquid perfume mixture evaporating over time (t) and diffusing upward (z) through the gas phase above it (headspace). The odor profiles obtained for the diffusion simulations for perfume system 1, using both odor intensity models, for some initial mixture composition (see Table 3) are shown in Figure 12.

The odor profiles presented in Figure 12 show that despite the first odor impression is different using the OV or the Power Law model (as seen before in the PQDs), after some time of evaporation the dominant smell is that of component B (geraniol) for both cases. The fact is that as seen in Table 3 for this initial composition of the perfume mixture it takes nearly 80 s until the odor intensity of component B becomes

Table 3. Comparison of the OV and Power Law Models at Different Times During Evaporation, for Perfumery Systems 1 and 2

		Mole Fractions				OV				Power Law			
	Time (s)	x_A	x_B	x_C	x_S	OV_A	OV_B	OV_C	OV_S	ψ_A	ψ_B	ψ_C	ψ_S
System 1—Mixture P1													
$P1_{initial}$	0.0	0.120	0.120	0.060	0.700	**2947**	840	343	1862	19	11	6	**79**
$P1_A$	14.4	0.288	0.391	0.196	0.125	**3246**	2396	3237	365	20	16	12	**31**
$P1_B$	72.1	0.192	0.497	0.250	0.061	2476	3108	**3614**	156	18	18	13	**19**
$P1_C$	198.4	0.110	0.565	0.286	0.039	1612	**3653**	3646	94	15	**19**	13	14
System 2—Mixture P1													
$P1_{initial}$	0.0	0.120	0.120	0.060	0.700	2142	764	**2559**	2038	17	11	17	**83**
$P1_A$	14.4	0.332	0.401	0.201	0.067	2089	3337	**3421**	361	17	19	19	**30**
$P1_B$	72.1	0.274	0.463	0.233	0.030	1730	3837	**4032**	156	16	19	**20**	19
$P1_C$	198.4	0.207	0.514	0.260	0.019	1340	4155	**4640**	94	14	20	**21**	14

Values in bold represent maximum odor intensity.

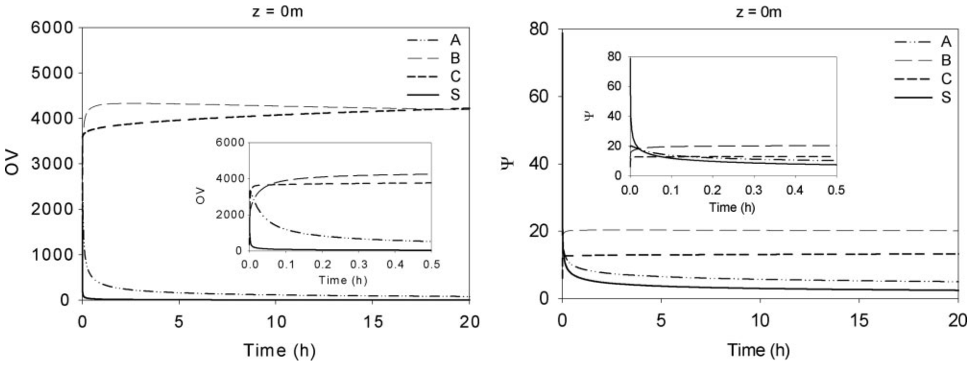

Figure 12. Comparison of the odor profiles for perfume mixture P1 of the quaternary system 1, using the OV (left) and the Power Law (right) as odor intensity models.

higher than the solvent when the Power Law model is used and some 200 s when the OV model is considered. So at this point will it make sense to say that the odor prediction done by the Power Law invalidates the previous one using the OV model? In fact, both odor intensity models give similar odor profiles with time, except for short times after the evaporation process has started. An example of this case might be seen when one sprays a perfume in paper test blotter, fans it and then smells it after a few seconds. The typical initial impression would be that of the top notes, and it is undesirable that the alcohol solution might be perceived at this point. Nevertheless, in this particular experimental case, we would be introducing convection flows by first agitating the paper test in the air, and so speeding up the evaporating process. In our diffusion model, no convection is considered, only the simple diffusion process which turns the evaporation slower than in a traditional real case. Additionally, it is important to note that the high predicted impact of ethanol (with the Power Law model) can be decreased by introducing water in the solution as will be seen ahead or by a fixative odorant that has the capacity to retain in the liquid the more polar components (as it is often done in perfume formulation).

The results obtained by simulation using both the odor intensity models can be seen to the light of the PTD®, if they are plotted as a function of the time as seen in Figure 13 for some selected times of Table 3.

The PTDs simulated at different times during the evaporation and diffusion process show significant differences in the odor zones over time and, additionally, also present differences depending on the odor intensity model used. These PTDs represent only the initial times after the application of the perfume mixture, when the evaporation of ethanol is higher and thus more evident on the PTD® of the right side of Figure 13 due to the exponent for this component. However, after ~3 min and for a long period of time both odor intensity models predict that component B (geraniol) will be the most strongly perceived. There is therefore a slight difference between the models for the prediction of the odor intensity for short times after the evaporation has started but then they tend to be similar in odor character.

For the case of perfume system 2, where a different base note is used (galaxolide), it is possible to compare in Figure 14 the odor profiles using the OV and the Power Law models, for some initial mixture composition (Table 3).

The similarities in the odor profiles of this perfume quaternary system are visible for times over 3 min, as seen in Table 3, where after this time the base note galaxolide dominates the odor character, followed by the middle note (geraniol) and top note (limonene). At initial times after the perfume has started to evaporate there are some differences in the prediction of the odor character with the two models. As in the case of system 1, the alcohol (ethanol) is strongly perceived and dominates the first impact when the Power Law is used, while galaxolide is more strongly perceived when the OV model is applied.

As long as the evaporation takes place the odorant molecules will diffuse into the surrounding air above the liquid. Additionally, since the liquid composition is changing and the fragrant molecules have different rates of evaporation and diffusion the odor character evolves with time and distance. Taking into account this effect between the composition in the liquid perfume mixture and the odor character perceived by the human nose, it is possible to represent evaporation lines in the PQD. In Figure 15 the evaporation paths of some perfume mixtures are shown considering the Power Law model only for some initial mixture compositions: P1 ($x_A = 0.120$, $x_B = 0.120$, $x_C = 0.060$, $x_S = 0.700$); P2 ($x_A = 0.234$, $x_B = 0.060$, $x_C = 0.006$, $x_S = 0.700$); and P3 ($x_A = 0.200$, $x_B = 0.100$, $x_C = 0.200$, $x_S = 0.500$).

The evaporation lines represent the evolution of the perfume mixture composition in the liquid interlinked with the representation of the odor character in the gas phase. Over the time of the dual process of evaporation and diffusion, the evaporation lines cross different odor volumes in the PQD (Figure 15). This means that the dominant smell is changing as the liquid composition changes too. It is possible to see that these evaporation paths are shape depending on the initial mixture concentration, though all follow the same trend: initially, a step curve due to the fast evaporation of ethanol; then the evaporation lines approximate the geraniol-vanillin binary edge, once the top note (limonene) is very volatile; and, finally, at the end they tend to the vertex of the base note (vanillin or galaxolide) since it is the fragrant species that lasts longer.

Diffusion of quinary fragrance mixtures

In order to come close to a real perfume formulation it would be necessary to include several components (fragrances

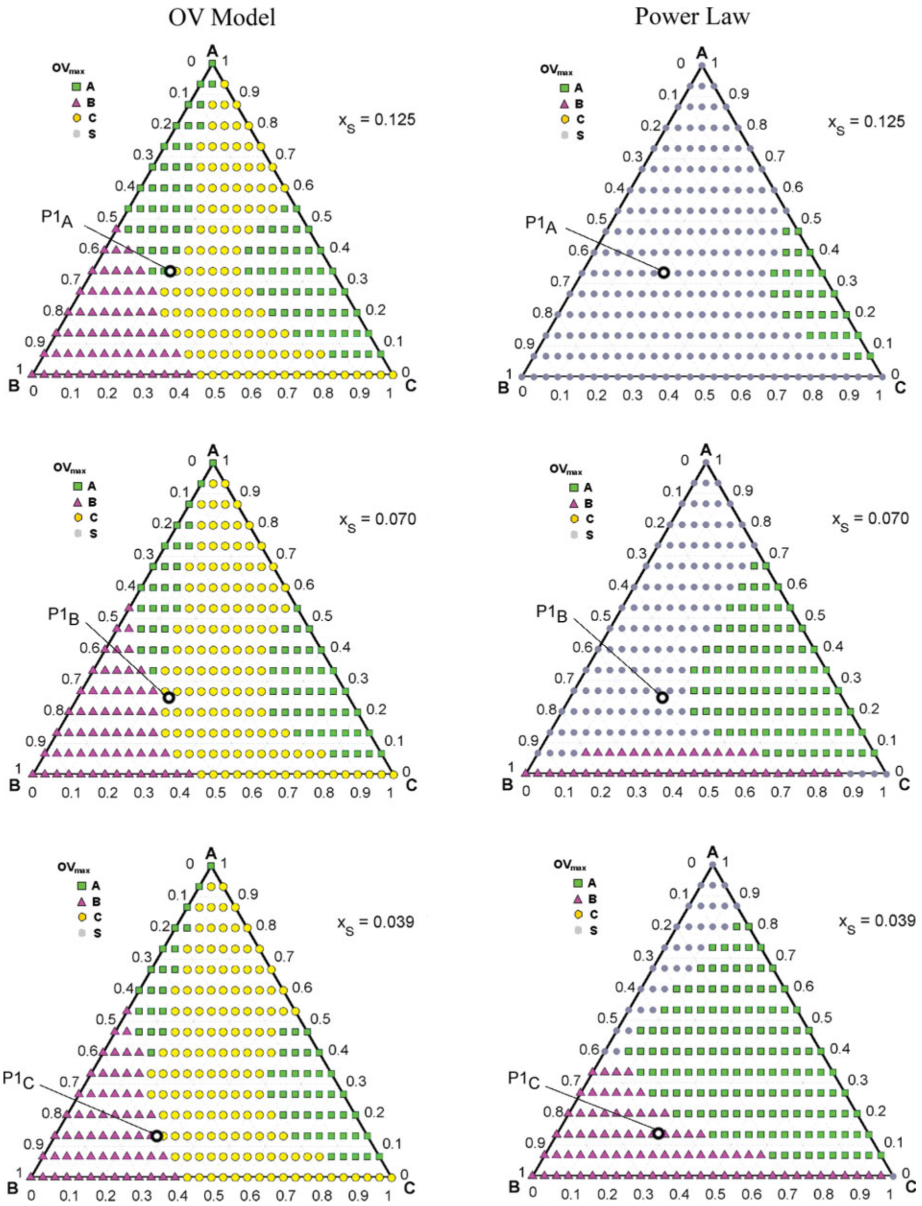

Figure 13. PTD® of perfume system 1, using the OV model (left) and the Power Law (right) at different times after application.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

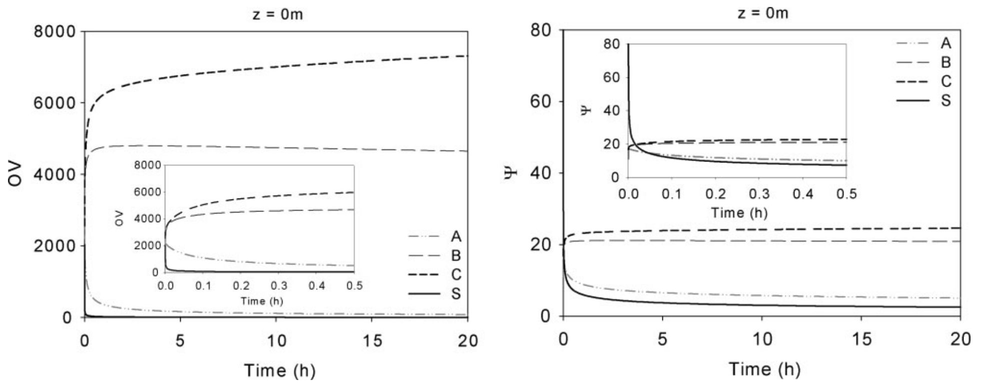

Figure 14. Comparison of the odor profiles for perfume mixture P1 of the quaternary system 2, using the OV (left) and the Power Law (right) as odor intensity models.

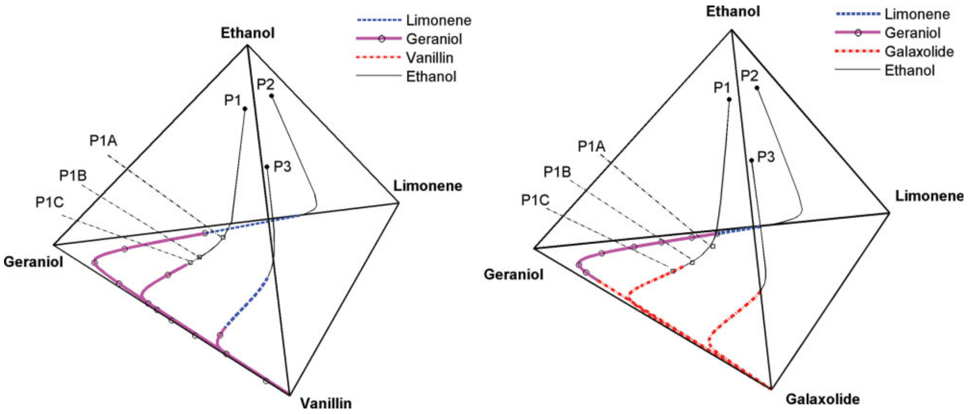

Figure 15. Perfumery evaporation lines plotted in the PQD for the quaternary system 1 (left) and system 2 (right) with different initial mixture compositions.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

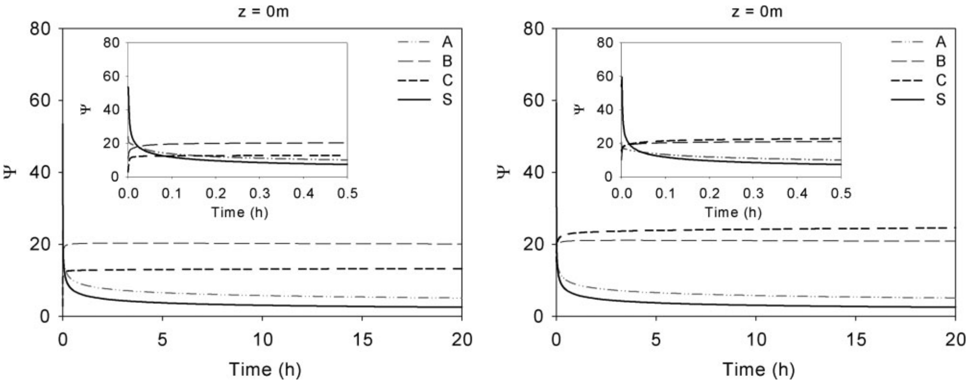

Figure 16. Evaporation profiles of the quinary mixtures of system 1 (left) and system 2 (right) using the Power Law model.

and others) in the formulation process. One of the most important constituents of perfume mixtures is water, which we have included here in this work. The effect of water in the initial odor impact has already been presented. The next question to be addressed is if water has different or similar effects when the evaporation and diffusion processes are taken together into account. For the purpose of this study, the effect of water in perfume diffusion was analyzed for the quinary systems 3 and 4. The number of moles in the initial quinary mixture was kept the same of the quaternary ones, for all the fragrances and the ethanol. This way, the quantity of matter in the quinary systems is higher than 1 mmol, since water was included in a mole fraction of 45%. For comparison purposes, the mole fractions in a water free basis remain the same in the quinary and in the quaternary systems. The initial mixture composition is given by: $x_A = 0.066$, $x_B = 0.066$, $x_C = 0.033$, $x_{EtOH} = 0.385$, $x_{H_2O} = 0.45$. In Figure 16 the evaporation profiles of two quinary perfume mixtures are presented considering the Power Law as the odor intensity model. Table 4 shows some compositions of the mixture and

Table 4. Odor Intensity Values Using the Power Law Model at Different Times During Evaporation for the Quinary Mixtures 3 and 4

		Mole Fractions					Power Law				
	Time (s)	x_A	x_B	x_C	x_S	x_{H_2O}	ψ_A	ψ_B	ψ_C	ψ_S	ψ_{H_2O}
System 3—Mixture P1											
$P1_{initial}$	0.0	0.066	0.066	0.033	0.385	0.450	24	11	3	**53**	–
$P1_A$	14.4	0.233	0.331	0.166	0.145	0.125	20	16	10	**32**	–
$P1_B$	72.1	0.173	0.466	0.234	0.063	0.064	18	18	12	**19**	–
$P1_C$	198.4	0.103	0.541	0.273	0.040	0.044	15	**19**	12	14	–
System 4—Mixture P1											
$P1_{initial}$	0.0	0.066	0.066	0.033	0.385	0.450	21	10	16	**54**	–
$P1_A$	14.4	0.301	0.368	0.184	0.078	0.069	17	18	18	**32**	–
$P1_B$	72.1	0.262	0.448	0.225	0.032	0.033	16	19	**20**	19	–
$P1_C$	198.4	0.201	0.503	0.254	0.020	0.023	14	20	**21**	14	–

Values in bold represent maximum odor intensity.

its predicted odor intensity at different times during the evaporation process.

When a comparison is made between the quaternary (Table 3) and the quinary mixtures (Table 4) for the Power Law model, it is possible to see that in the latter ethanol is less dominant when water is included in the formulation of the perfume. In fact, the simulations for the odor intensity have shown that both quaternary systems 1 and 2, exhibit higher initial odor intensity for ethanol than in the quinary systems (3 and 4) where water is included. Thus, it can be seen that water has a retention effect on ethanol, preventing its faster evaporation from the liquid mixture and reducing its high initial odor intensity. The presence of water in the perfume formulation showed another effect on the release of the fragrances by increasing the odor intensity of limonene. This is due to the fact that incorporating water in the solution increases its polarity, thus pushing out of the solution the nonpolar top note, limonene. It is important to highlight that although ethanol evidences a high odor impact (in the first moments), which is not expected from the point of view of a perfumer, we are considering here in only diffusion effects (free of convection). Moreover, the perfume systems considered were for quaternary and quinary mixtures only, while commercial perfumes have a greater number of constituents some of which may have greater or lesser effect on the retention or release of others.

Conclusions

The comparison of two psychophysical intensity models to account for the odor perception of fragrance mixtures has shown differences in the prediction of the odor character for initial times after application of the perfume. The Power Law model predicted that ethanol was more strongly perceived than the OV model, for the beginning of the evaporation of the perfume, due to its large exponent. However, the end-use of perfume products is that they have high performance over time (long lastingness) and it was proven that when evaporation and diffusion effects were considered, the two odor intensity models tend to get the same odor character after some time of the processes.

The incorporation of water in the perfume formulation has shown two interesting phenomena that are supported by experimental evidences from perfumery: (i) nonpolar fragrances, especially limonene, tend to be pushed out of the solution and thus are more strongly perceived by the nose; (ii) water molecules have a retention effect on more polar components like ethanol, preventing it to evaporate faster and limiting its initial impression. The predictions of the odor intensity and character with water molecules in solution have shown that the use of water in perfumes is not only ruled by the cost factor but also by the odor performance and impact of the perfume.

The evaporation paths for different perfume mixtures presented with the PQD methodology show that the odor character (the dominant note) is evolving over time as the evaporation of the perfume goes on. These evaporation lines showed that in the evaporation and diffusion of a perfume mixture there can be seen two stages: first the rapid evaporation of ethanol and water as seen by the steepest descent curvatures, and then the evaporation of the fragrance components.

In brief, the comparison of the two psychophysical models for odor intensity showed slight differences for short times but similar predictions after that, thus concluding that the universality of a psychophysical law definitely established for perceptual continua and sensory perception must be continually tested in quest of possible exceptions.

Acknowledgments

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Notation

M_i = molecular mass of component *i*, g/mol
γ_i = activity coefficient of component *i* in the solution
Thr = concentration threshold value in air, g/m^3
C_i^{g} = concentration of species *i* in the vapor phase, g/m^3
$D_{i,\mathrm{air}}$ = diffusion coefficient of component *i* in the gas phase, m^2/h
x_i = mole fraction of component *i* in solution
x_{i_0} = initial mole fraction of component *i* in solution
n_i = number of moles of component *i* in the liquid phase, mol
n_T = total number of moles, mol
y_i = mole fraction of species *i* in the gas phase
y_{i_0} = initial mole fraction of species *i* in the gas phase
A_{lg} = area of liquid–gas interface, m^2
P = total pressure in the gas phase, Pa
P_i^{sat} = saturated vapor pressure, Pa
R = ideal gas constant
T = temperature, K
t = time variable
z = space variable

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