A New Methodology for the Definition of Odor Zones in Perfumery Ternary Diagrams

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The new methodology called "Perfumery Ternary Diagram" helps perfumers in odor prediction, allowing a fast evaluation of the odor value in the headspace for all possible combinations of a non-ideal perfume liquid mixture with three fragrant components and one or more solvents. In this work, the determination of Perfumery Ternary Points *(PTP) and* Perfumery Binary Lines *(PBL) is described, allowing a complete definition of* Perfumery Ternary Diagram *(PTD) odor zones, without the need to calculate a large number of points inside the triangle region. The methodology of PTP and PBL determination was applied to the system: limonene, geraniol, vanillin, and ethanol. The effect of solvent—ethanol—on the odor zones, namely on the number of PTP and on the shape of the PBL was studied, as well as the effect of the non-idealities.* © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 2938–2948, 2006
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Introduction

One of the biggest challenges in perfumery today is the discovery of new fragrant molecules.[1,2] These new molecules can be isolated from natural products[3] like flower or animal extracts, or can be synthesized from known molecules.[4,5] Until the end of the nineteenth century, perfumers worked with a small number of materials, mainly naturals. The explosive growth of organic chemistry at the end of that century made numerous new fragrant molecules available to the perfumer, requiring a rational method of fragrance creation.[1] Nowadays, perfumers have more than 4000 raw materials that can be used in perfume formulations.

When a new molecule is discovered, and after the perfumery experts verify its potential for use in perfumes or colognes, a systematic analysis of its behavior in different solutions must be done.[6] It is known that a perfume is a complex non-ideal mixture of chemicals, having a wide range of physical and chemical properties, such as polarities, solubilities, volatilities, and odor strengths.

The typical matrix used in perfumery to dissolve the perfume materials is a mixture of ethanol and water. The behavior of these new molecules in different liquid matrices and liquid proportions is a tedious process, generally a trial-and-error approach to create the optimized mixture that has the desired smell. During the development of a perfume, the perfumer evaluates the mixture as it evaporates off a paper blotter.[7] As this fragranced mixture evaporates, it changes its character continuously once some components present in the initial mixture—mainly those with high volatility—have disappeared with time.

The prediction of the odor characteristic of the headspace above a liquid solution of three fragrant components in a liquid matrix constituted by one or more components was studied earlier by the authors.[8,9,10] They developed a methodology, called Perfumery Ternary Diagram, that allows a fast evaluation of the odor for any possible combination of the fragrant chemicals involved, avoiding in this way a long trial and error experimental procedure. However, a large number of points were necessary to be calculated in order to have a good defi-

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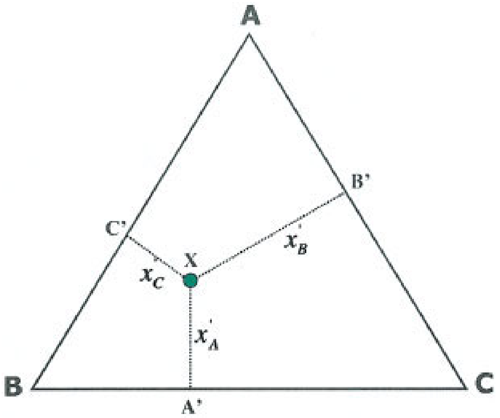


Figure 1. Ternary diagram scheme, representing one ternary mixture composition.

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

nition of the developed Perfumery Ternary Diagram (PTD) methodology.

In this work, a more systematic approach was developed, in order to define completely a Perfumery Ternary Diagram, by the determination of all the Perfumery Binary Lines, PBL, and Perfumery Ternary points, PTP, belonging to the triangle.

The Odor Value (OV) Concept

A perfume system consists of a complex fragrant liquid mixture and a corresponding air phase above it, the headspace, which we smell. In this work, it is considered that:

(i) The headspace is an ideal solution, since the components are highly diluted:

$$c_i^g = \frac{y_i M_i P}{RT} \tag{1}$$

where c_i^g is the concentration of component i in the headspace, y_i is the gas phase molar fraction of component i, P is the total gas phase pressure, M_i is the molecular weight of i**,** R is the ideal gas constant, and T is the absolute temperature.

(ii) The liquid is a non-ideal solution, and the headspace is in equilibrium with the liquid perfume mixture:

$$y_i = \gamma_i x_i \frac{P_i^{sat}}{P} \tag{2}$$

where y_i is the gas phase molar fraction of component i in the headspace in equilibrium with the liquid with composition x_i, γ_i is the activity coefficient of i in the liquid, and P_i^{sat} is the saturated vapor pressure of component i. In this work, values of γ_i were calculated using the UNIFAC method, which is based on molecular group contribution.[11] This method takes into account the contribution due to differences in molecular size and molecular shape—the combinatorial part—and the contribution due to molecular interactions—the residual part (see Appendix A).

The intensity of a fragrant component i is related with its odor value, OV_i, which is defined as[12]:

$$OV_i = \frac{c_i^g}{Thr_i} \tag{3}$$

where Thr_i is the threshold concentration of i in air.

Combining Eqs. 1-3, we get:

$$OV_i = \gamma_i x_i \left(\frac{P_i^{sat} M_i}{Thr_i}\right)\left(\frac{1}{RT}\right) \tag{4}$$

This equation relates the liquid perfume composition, x_i with the human sensory response of the evaporated perfume.

In this work it is considered that one component i**,** present in a liquid mixture of N fragrant components, is perceived strongly by the human nose when its odor value, OV_i, in the headspace above the liquid is higher than those of the other components.[13] However, it is important to notice that when one component A has a maximum odor value, $OV_{\mathrm{MAX}} = OV_A$, it will be more strongly perceived than the others that coexist in the mixture, but solutions with different values of $OV_{\mathrm{MAX}} = OV_A$ also have different smells.

Perfumery Ternary Diagrams

Consider a ternary liquid mixture, **A+B+C**, constituted by three chemical components having different volatilities, each one belonging to one type of fragrant notes, that is, **A** represents a top note, **B** a middle note, and **C** a base note. It is also considered that a certain amount of solvent, **S**, in this case ethanol, is added to the mixture, resulting this way in a quaternary mixture that will be called the *test perfume*.[8,9,10]

The amount of each component in any ternary perfume mixture—represented by the general point *X*—is given by its molar fraction: x_A, x_B, x_C, and x_S.

To simplify, this quaternary system is transformed into a ternary system, by recalculating the molar fractions for A, B, and C in a solvent free basis, resulting in the new fractions:

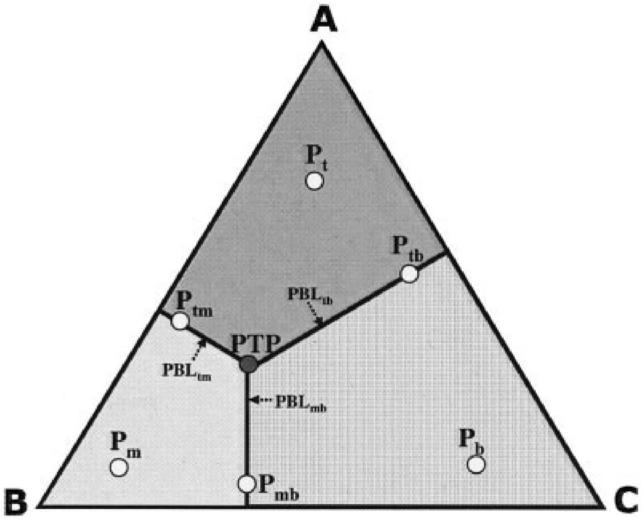


Figure 2. Scheme of a perfumery ternary diagram (PTD), showing the Perfumery Binary Lines (PBL) and Perfumery Ternary Points (PTP).

Table 1. Conditions for the Determination of Perfumery Ternary Points

Type I A + B + C $OV_A = OV_B = OV_C = OV_{\mathrm{MAX}}$	Type II A + B + S $OV_A = OV_B = OV_S = OV_{\mathrm{MAX}}$	Type III B + C + S $OV_B = OV_C = OV_S = OV_{\mathrm{MAX}}$	Type IV A + C + S $OV_A = OV_C = OV_S = OV_{\mathrm{MAX}}$
$\gamma_A x_A K_A^* = \gamma_B x_B K_B^*$ $\gamma_B x_B K_B^* = \gamma_C x_C K_C^*$ $x_A + x_B + x_C + x_S = 1$ x_S is known	$\gamma_A x_A K_A^* = \gamma_S x_S K_S^*$ $\gamma_B x_B K_B^* = \gamma_S x_S K_S^*$ $x_A + x_B + x_C + x_S = 1$ x_S is known	$\gamma_B x_B K_B^* = \gamma_S x_S K_S^*$ $\gamma_C x_C K_C^* = \gamma_S x_S K_S^*$ $x_A + x_B + x_C + x_S = 1$ x_S is known	$\gamma_A x_A K_A^* = \gamma_S x_S K_S^*$ $\gamma_C x_C K_C^* = \gamma_S x_S K_S^*$ $x_A + x_B + x_C + x_S = 1$ x_S is known

$$x'_A = \frac{x_A}{x_A + x_B + x_C},\ x'_B = \frac{x_B}{x_A + x_B + x_C} \text{ and } x'_C = \frac{x_C}{x_A + x_B + x_C}.$$

These three quantities are then represented in a ternary diagram,[6] as is shown in Figure 1.

Considering a general liquid mixture, which composition is represented by point X, the composition (solvent-free basis) of component A, x_A', is given by the distance $\overline{XA'}$, the composition of B, x_B', is given by the distance $\overline{XB'}$, and the composition of C, x_A', is given by the distance $\overline{XC'}$. It is considered that the mole fraction of the solvent, x_s, is known and constant for each ternary diagram. As can be seen, the ternary diagram represents all compositions that could be made experimentally using different quantities of A, B, and C, for a given quantity of ethanol, S.

Now, for each liquid perfume mixture, X (that is, each point in the ternary diagram), the correspondent odor value, OV_i, for each component in that mixture is calculated using Eq. 4.

After the calculation of all the individual odor values, for a given mixture the maximum odor value is calculated:

$$OV_{\mathrm{MAX}} = \max(OV_A, OV_B, OV_C, OV_S) \text{ for point } X \tag{5}$$

Then, we consider that, for each mixture X, we smell strongly the component that has the maximum OV. After the determination of the component that has the OV_{MAX} for a large number of points of the ternary diagram, we obtain as a result a *Perfumery Ternary Diagram* (PTD).

Table 2. Non-Linear Equation Systems Used for the Determination of Perfumery Ternary Points

Type I A + B + C	Type II A + B + S
$x_A = \dfrac{\dfrac{\gamma_B K_B^*}{\gamma_A K_A^*}(1 - x_S)}{\left(\dfrac{\gamma_B K_B^*}{\gamma_A K_A^*} + 1 + \dfrac{\gamma_B K_B^*}{\gamma_C K_C^*}\right)}$	$x_A = x_S \dfrac{\gamma_S K_S^*}{\gamma_A K_A^*}$
$x_B = \dfrac{(1 - x_S)}{\left(\dfrac{\gamma_B K_B^*}{\gamma_A K_A^*} + 1 + \dfrac{\gamma_B K_B^*}{\gamma_C K_C^*}\right)}$	$x_B = x_S \dfrac{\gamma_S K_S^*}{\gamma_B K_B^*}$
$x_C = \dfrac{\dfrac{\gamma_B K_B^*}{\gamma_C K_C^*}(1 - x_S)}{\left(\dfrac{\gamma_B K_B^*}{\gamma_A K_A^*} + 1 + \dfrac{\gamma_B K_B^*}{\gamma_C K_C^*}\right)}$	$x_C = 1 - x_A - x_B - x_S$
x_S is known	x_S is known

Type III B + C + S	Type IV A + C + S
$x_B = x_S \dfrac{\gamma_S K_S^*}{\gamma_B K_B^*}$	$x_A = x_S \dfrac{\gamma_S K_S^*}{\gamma_A K_A^*}$
$x_C = x_S \dfrac{\gamma_S K_S^*}{\gamma_C K_C^*}$	$x_C = x_S \dfrac{\gamma_S K_S^*}{\gamma_C K_C^*}$
$x_A = 1 - x_B - x_C - x_S$	$x_B = 1 - x_A - x_C - x_S$
x_S is known	x_S is known

Figure 2 shows an example of a Perfumery Ternary Diagram (PTD).[8,9,10] In this diagram three different areas can be distinguished, giving some highlight to the following typical composition points: P_t—We smell strongly the top note: $OV_{\mathrm{MAX}} = OV_A$ (dark shaded area);

P_m—We smell strongly the middle note: $OV_{\mathrm{MAX}} = OV_B$ (light shaded area);

P_b—We smell strongly the base note: $OV_{\mathrm{MAX}} = OV_C$ (dotted area).

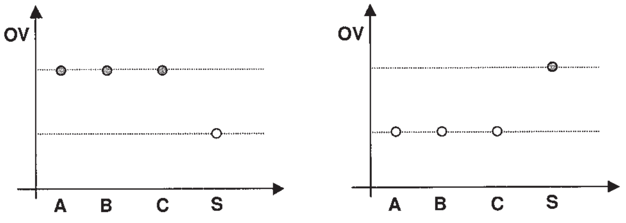
There can exist also points for which we smell strongly the solvent: $OV_{\mathrm{MAX}} = OV_s$. These points are referred to as P_s.

There are characteristic lines designated in this work by *Perfumery Binary Lines* (PBL) separating the areas defined above: PBL_{tm} separates the areas where we smell the top note and the middle note, PBL_{tb} separates the areas of the top note and the base note, and PBL_{mb} separates the areas of the middle note and the base note.[8]

A characteristic point P_{tm} in the line PBL_{tm} represents a composition in which the odor value of the top note is equal to the odor value of the middle note; it is difficult to recognize both notes. The same happens to the composition defined by point P_{tb} (odor value of the top note is equal to the odor value of the base note) and by point P_{mb} (odor value of the middle note is equal to the odor value of the base note).

There is a particular point in the diagram where the top, middle, and base notes have the same odor value. The odor of the corresponding mixture is different from the individual components because none can be distinguished separately once they have equal intensities. We call this point a *Perfumery Ternary Point* (PTP).[8]

Sometimes, there are also points for which the strongest smell is that of the solvent: $OV_{\mathrm{MAX}} = OV_S$. This situation



(a) PTP (b) TP

Figure 3. Graphical representation of a (a) Perfumery Ternary Point (PTP) and (b) Ternary Point (TP).

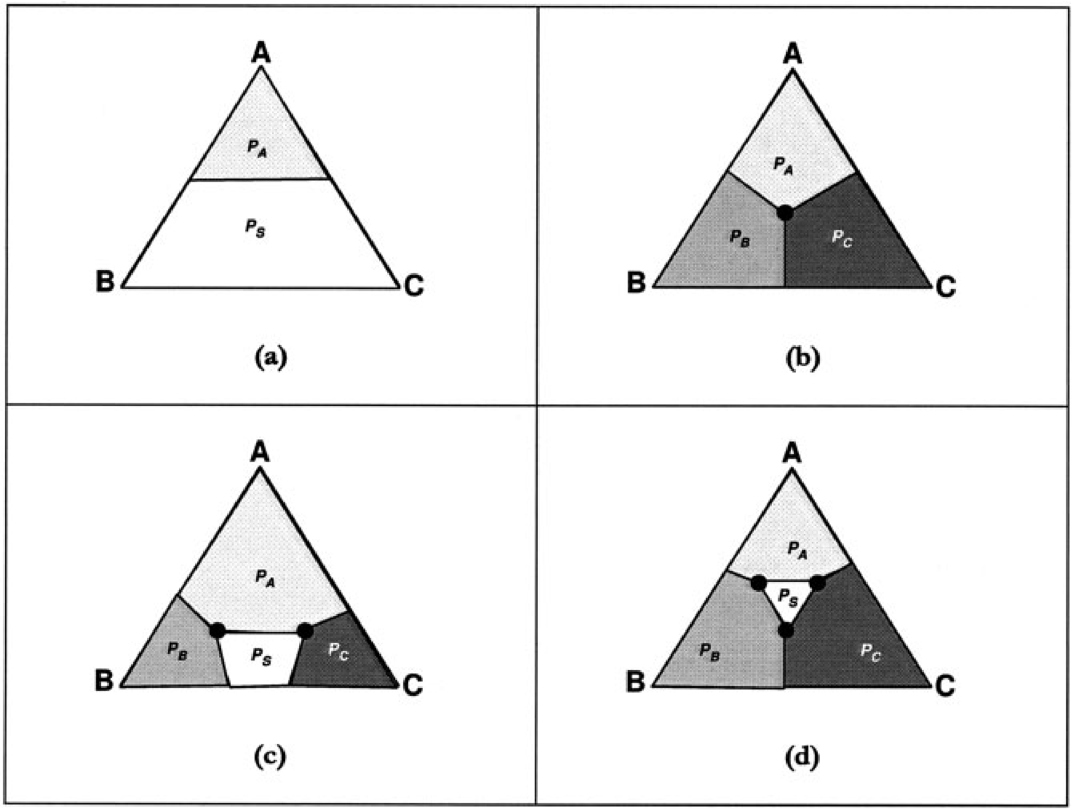


Figure 4. Perfumery Ternary Diagrams (PTD) having different numbers of Perfumery Ternary Points (PTP).
(a) 0 PTP, (b) 1 PTP, (c) 2 PTP, and (d) 3 PTP.

happens generally for mixtures having a high content of solvent, as will be seen below. In these cases, there can also exist Perfumery Binary Lines (PBL) between one fragrant component and the solvent and Perfumery Ternary Points (PTP) between two fragrant components and the solvent.

In this work, each point inside the perfumery ternary diagram represents one perfume liquid composition in equilibrium with its corresponding headspace.

Calculation of Perfumery Binary Lines and Perfumery Ternary Points

The following procedure will show the methodology to calculate Perfumery Binary Lines and Perfumery Ternary Points, without the need to calculate a large number of points belonging to the Perfumery Ternary Diagram. Equation 4 can be represented by:

$$OV_i = \gamma_i x_i K_i \tag{6}$$

where $K_i = c_i^{sat}/Thr_i$ being $c_i^{sat} = P_i^{sat} M_i/RT$ (c_i^{sat} is the concentration of saturated component i in the ideal gas phase—partial density of i—and it is constant for a given temperature, T).

The values of K_i are then normalized by the sum of the K_i of all the N components, K_T :

$$K_i^* = \frac{K_i}{K_T} = \frac{K_i}{\sum_{c=1}^{N} K_i}, \text{ where } 0 < K_i^* < 1 \tag{7}$$

K_T is constant for each perfume mixture.

Using this normalization, Eq. 7 becomes:

$$OV_i = \gamma_i x_i K_i^* K_T \tag{8}$$

Determination of Perfumery Ternary Points

We consider that there exists a Perfumery Ternary Point (PTP) between the three components i, j, and k when:

$$OV_i = OV_j = OV_k = OV_{\text{MAX}}, (i, j, k = A, B, C, S) \tag{9}$$

Again, substituting Eq. 8 into Eq. 9:

$$\gamma_i x_i K_i^* = \gamma_j x_j K_j^* = \gamma_k x_k K_k^*, \ (i, j, k = A, B, C, S) \tag{10}$$

leads to the condition to find the Perfumery Ternary Points (PTP).

As the system is constituted by four components (three fragrant notes and the solvent), four combinations of PTP are possible: A+B+C, A+B+S, B+C+S, and A+C+S. The conditions that have to be met for each one of these points are

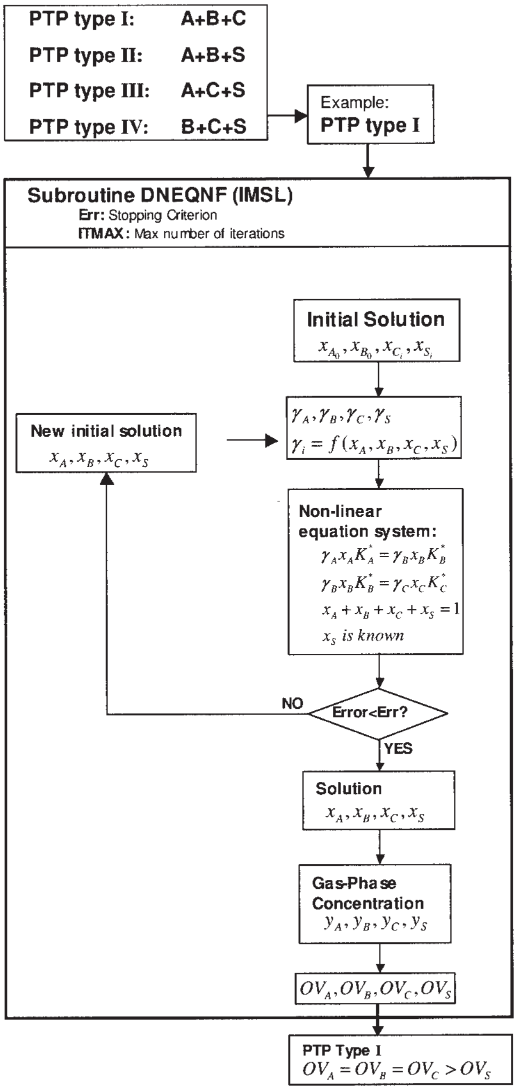


Figure 5. Iterative method used to make the determination of the Perfumery Ternary Points (PTP).

shown in Table 1. The corresponding equations that are used to determine their compositions are shown in Table 2.

There are also points in the Perfumery Ternary Diagram (PTD) where $OV_i = OV_j = OV_k < OV_{\text{MAX}}$ $(i,j,k = A,B,C,S)$, called simply Ternary Points (TP). These points are mathematical solutions obtained by solving the system of equations shown in Table 2. However, they represent points for which the strongest smell is due to the component l, meaning that $OV_{\text{MAX}} = OV_l$ $(l = A,B,C,S)$ (see Figure 3). For example, if $OV_A = OV_B = OV_C < OV_{\text{MAX}}$, the dominant smell is that of S, since $OV_{\text{MAX}} = OV_S$ (Figure 3b). In this case, there is only a Ternary Point (TP) and no PTP.

Figure 4 shows all the possible situations that can be obtained after the resolution of each system shown in Table 2, namely, the Perfumery Ternary Diagram (PTD) can have: 0, 1, 2, or 3 PTP (Figures 4a-d). Each region separated by a PBL is designated by $P_{x,}$ where all the points in that space have $OV_{\text{MAX}} = OV_x$.

All the Perfumery Ternary points (PTP) and Ternary Points (TP) can be calculated by solving each system of non-linear equations represented in Table 2, where the activity coefficient of each component, γ_i, is a function of all N components in the liquid mixture, $\gamma_i = f\,(x_j, j = 1,N)$, when non-ideal liquid mixtures are considered.

Figure 5 shows the algorithm developed in this work in order to make the determination of each PTP of a single Perfumery Ternary Diagram, PTD.

The system of non-linear equations was solved using a modification of Powell's hybrid algorithm and a finite-difference approximation to the Jacobian.[14,15]

Determination of Perfumery Binary Lines

For a fixed quantity of solvent, a Perfumery Binary Line (PBL) represents a line in which all points satisfy the following condition:

$$OV_i = OV_j = OV_{\text{MAX}}, \; (i, j = A, B, C, S) \tag{11}$$

Substituting Eq. 8 into Eq. 11, we obtain:

$$\gamma_i x_i K_i^* = \gamma_j x_j K_j^*, \; (i, j = A, B, C, S) \tag{12}$$

which is used for the determination of the Perfumery Binary Line (PBL) between components i and j.

As the system is constituted by four components (three fragrant notes and the solvent), six combinations of Perfumery Binary Lines, PBL, are possible: $A+B$, $B+C$, $A+C$, $A+S$, $B+S$, and $C+S$. The conditions that have to be met for each one of these points are shown in Table 3. The corresponding

Table 3. Conditions for the Determination of Perfumery Binary Lines

Type I A + B $OV_A = OV_B = OV_{\text{MAX}}$	Type II B + C $OV_B = OV_C = OV_{\text{MAX}}$	Type III A + C $OV_A = OV_C = OV_{\text{MAX}}$
$\gamma_A x_A K_A^* = \gamma_B x_B K_B^*$ $x_A + x_B + x_C + x_S = 1$ $0 \leq x_C \leq 1$ x_S is known	$\gamma_B x_B K_B^* = \gamma_C x_C K_C^*$ $x_A + x_B + x_C + x_S = 1$ $0 \leq x_A \leq 1$ x_S is known	$\gamma_A x_A K_A^* = \gamma_C x_C K_C^*$ $x_A + x_B + x_C + x_S = 1$ $0 \leq x_B \leq 1$ x_S is known
Type IV A + S $OV_A = OV_S = OV_{\text{MAX}}$	Type V B + S $OV_B = OV_B = OV_{\text{MAX}}$	Type VI C + S $OV_C = OV_B = OV_{\text{MAX}}$
$\gamma_A x_A K_A^* = \gamma_S x_S K_S^*$ $x_A + x_B + x_C + x_S = 1$ $0 \leq x_C \leq 1$ x_S is known	$\gamma_B x_B K_B^* = \gamma_S x_S K_S^*$ $x_A + x_B + x_C + x_S = 1$ $0 \leq x_A \leq 1$ x_S is known	$\gamma_C x_C K_C^* = \gamma_S x_S K_S^*$ $x_A + x_B + x_C + x_S = 1$ $0 \leq x_B \leq 1$ x_S is known

Table 4. Non-Linear Equation Systems Used for the Determination of Perfumery Binary Lines

Type I A + B	Type II B + C	Type III A + C
$x_B = \dfrac{(1-x_C-x_S)\dfrac{\gamma_A K_A^*}{\gamma_B K_B^*}}{1+\dfrac{\gamma_A K_A^*}{\gamma_B K_B^*}}$	$x_B = \dfrac{(1-x_A-x_S)\dfrac{\gamma_B K_B^*}{\gamma_C K_C^*}}{1+\dfrac{\gamma_B K_B^*}{\gamma_C K_C^*}}$	$x_C = \dfrac{(1-x_B-x_S)\dfrac{\gamma_A K_A^*}{\gamma_C K_C^*}}{1+\dfrac{\gamma_A K_A^*}{\gamma_C K_C^*}}$
$x_A = \dfrac{(1-x_C-x_S)}{1+\dfrac{\gamma_A K_A^*}{\gamma_B K_B^*}}$	$x_C = \dfrac{(1-x_A-x_S)}{1+\dfrac{\gamma_B K_B^*}{\gamma_C K_C^*}}$	$x_A = \dfrac{(1-x_B-x_S)}{1+\dfrac{\gamma_A K_A^*}{\gamma_C K_C^*}}$
$0 \leq x_C \leq 1$	$0 \leq x_A \leq 1$	$0 \leq x_B \leq 1$
x_S is known	x_S is known	x_S is known
Type IV A + S	Type V B + S	Type VI C + S
$x_B = 1 - x_C - x_S\left(1-\dfrac{\gamma_S K_S^*}{\gamma_A K_A^*}\right)$	$x_C = 1 - x_A - x_S\left(1-\dfrac{\gamma_S K_S^*}{\gamma_B K_B^*}\right)$	$x_A = 1 - x_B - x_S\left(1-\dfrac{\gamma_S K_S^*}{\gamma_C K_C^*}\right)$
$0 \leq x_C \leq 1$	$0 \leq x_A \leq 1$	$0 \leq x_B \leq 1$
x_S is known	x_S is known	x_S is known

equations that are used to determine their compositions are shown in Table 4.

There are also points in the Perfumery Ternary Diagram (PTD) where $OV_i = OV_j < OV_{\mathrm{MAX}}$ ($i,j,k = A,B,C,S$). These solutions will be neglected in this work.

Figure 6 shows all the possible types of PBL that can be obtained after the resolution of each system shown in Table 4. The Perfumery Ternary Diagram (PTD) can have PBL connecting: (i) two sides of the triangle (Figure 6a), (ii) one side of the triangle and one PTP (Figure 6b), and (iii) two PTP (Figure 6c). There are also situations where there are no PBL, as will be seen below.

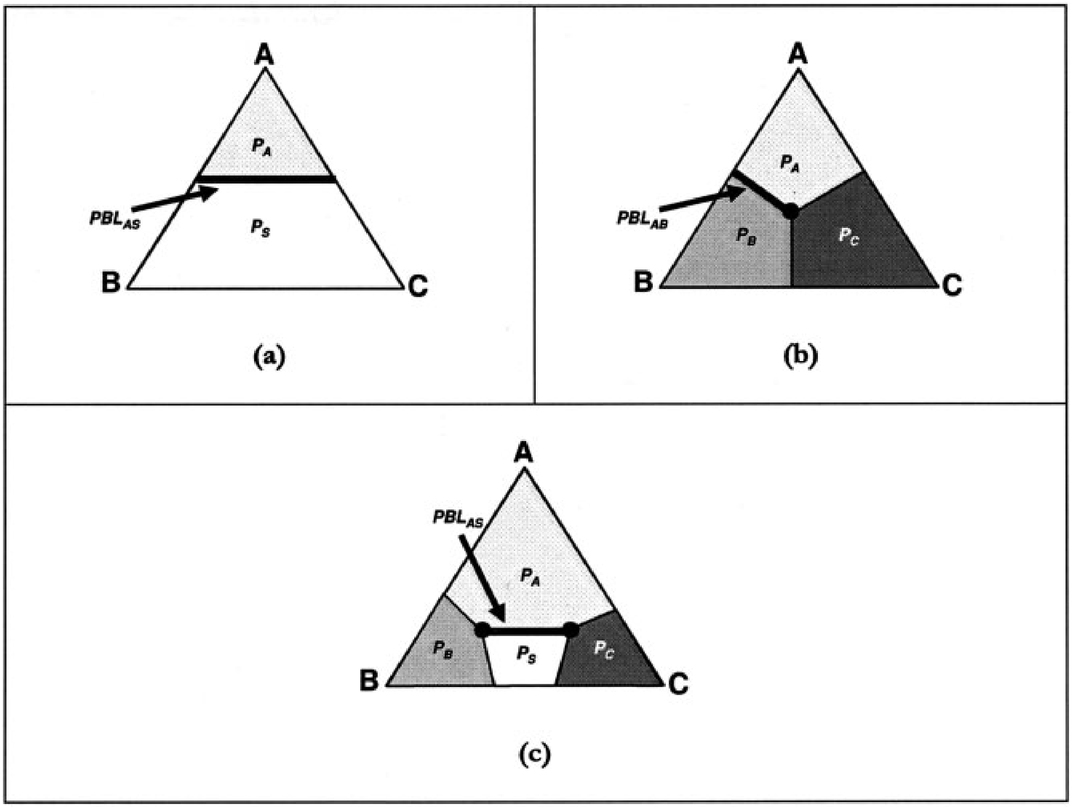


Figure 6. Perfumery ternary diagrams (PTD) having different types of Perfumery Binary Lines (PBL).

(a) PBL connected to two different edges, (b) PBL connects one edge and one PTP, and (c) PBL connects two different PTP.

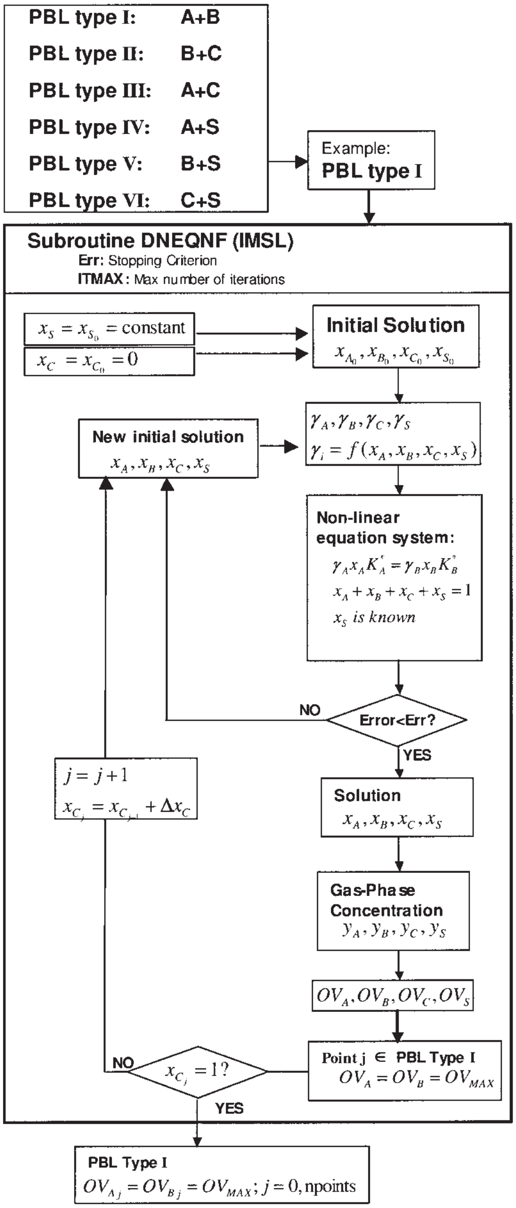


Figure 7. Iterative method used to make the determination of the Perfumery Binary Lines (PBL).

Again, all the PBL can be determined by solving each system of non-linear equations represented in Table 4, using the same numerical method used for the determination of the PTP described above.

Figure 7 shows the algorithm developed in this work in order to make the determination of each PBL.

Results

The methodology developed in this work for the determination of the Perfumery Ternary Points (PTP) and Perfumery Binary Lines (PBL) was applied to the following system: (A) limonene, (B) geraniol, (C) vanillin, and S (ethanol).

Table 5 shows the physical parameters of each component i, namely: molecular weight, M_{Wi}, vapor pressure, P_{Vi}, and odor threshold, Thr_i, used for the determination of the values of K_i^*. Table 6 shows the list of UNIFAC groups and subgroups[11] and their respective numbers existing in each molecule used in this article.

Table 5. Physical Properties for Each Component of the Case Study Perfume Mixture

	Name	M_{Wi} (g/mol)	$P_{Vi}^{\dagger}$(Pa)	$Thr_i^{\dagger}$(g/m3)	K_i^*
A	Limonene	136.2	20.5×10^1	2.45×10^{-3}	0.24
B	Geraniol	154.3	26.7×10^{-1}	2.48×10^{-5}	0.35
C	Vanillin	152.2	16.0×10^{-3}	1.87×10^{-7}	0.28
S	Ethanol	46.0	72.7×10^2	5.53×10^{-2}	0.13

†From literature.[12]

The PTP and PBL were calculated for the following constant mole fractions of solvent: x_s =0.3, 0.6, 0.7, and 0.9 (Figures 8 and 9).

Figure 8 shows the effect of the ethanol content on the shape of the corresponding PTD, namely, the shape and number of their Perfumery Binary Lines (PBL): ▬; Perfumery Ternary Points (PTP): ◍; and Ternary points (TP): ○, respectively. Table 7 shows the mole fractions of each PTP and TP and the corresponding odor values for each component.

Each PTP is a cross point of three PBL. The other points represented in each triangle are the Ternary points (TP). Table 6 shows the corresponding values of molar fraction for each PTP and TP, as well as the odor values for each component in each PTP/TP.

In Figure 8a, three well-separated regions can be observed. Each region corresponds to points where the maximum odor value is that of: (A) limonene: $OV_{\text{MAX}} = OV_A$; (B) geraniol: $OV_{\text{MAX}} = OV_B$; and (C) vanillin: $OV_{\text{MAX}} = OV_C$. There is only one PTP, of type I: A+B+C. All three PBL are connected between one side of the triangle and that PTP.

In Figure 8b, a new region appears, for which the maximum odor value is that of ethanol (S): $OV_{\text{MAX}} = OV_S$. This

Table 6. Number of UNIFAC Groups and Subgroups Present in Each Molecule of the Case Study Perfume Mixture

Molecule (i)	Subgroup	UNIFAC Subgroup Number[11]	UNIFAC Group Number[11]	Number of Subgroups in the Molecule (i)
Limonene	CH_3	1	1	2
	CH_2	2	1	3
	CH	3	1	1
	CH = C	8	2	1
	CH_2 = C	7	2	1
Geraniol	CH_3	1	1	4
	CH_2	2	1	2
	CH = C	8	2	2
	OH	15	5	1
Vanillin	ACH	10	3	3
	AC	11	3	2
	ACOH	18	8	1
	CHO	21	10	1
	CH_3O	25	13	1
Ethanol	CH_3	1	1	1
	CH_2	2	1	1
	OH	15	5	1

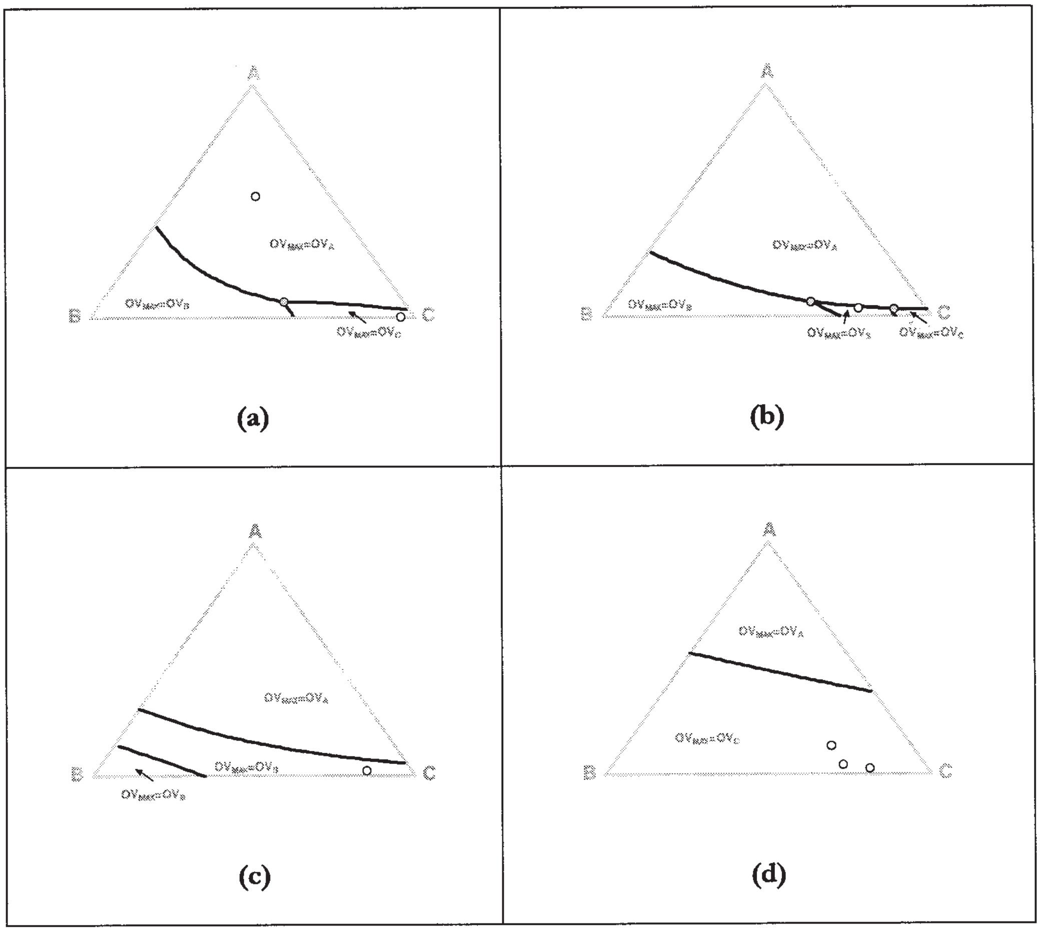


Figure 8. Perfumery Ternary Diagrams (PTD) with the corresponding Perfumery Ternary Points (PTP): ◍; Ternary Points (TP): ○; and Perfumery Binary Lines (PBL): —; considering non-ideal liquid solutions.

(a) $x_s = 0.3$, (b) $x_s = 0.6$, (c) $x_s = 0.7$, and (d) $x_s = 0.9$. (A) limonene; (B) geraniol; (C) vanillin; (S) ethanol.

change had created two different PTP: one PTP Type II and one PTP Type IV. Notice that this new region appeared instead of the region where $OV_{\text{MAX}} = OV_C$. This happened because vanillin is the less volatile component, so, increasing the quantity of ethanol increases also its odor value and it becomes in some parts of the triangle, higher than that of vanillin.

In Figure 8c, ($x_s = 0.7$) there are no points for which the maximum odor value is that of vanillin. The area where ethanol has a maximum odor value has increased. In this case, there are no PTP.

Finally, Figure 8d shows that, for $x_s = 0.9$, there are only points where $OV_{\text{MAX}} = OV_A$ and $OV_{\text{MAX}} = OV_S$. There exists only one PBL connecting two sides of the triangle. Once all the solutions represented by the Perfumery Ternary Diagram are very diluted, it can be seen that this PBL is almost a straight line, as would be expected for ideal solutions.

So, for comparison, the same methodology was applied to the case where ideal liquid solutions were considered. For this assumption, the constant mole fractions of solvent used were also: $x_s = 0.3$, 0.6, 0.7, and 0.9. Again, Table 8 shows the mole fractions of each PTP and TP and the corresponding odor values for each component for this case. Figure 9 shows the corresponding Perfumery Ternary Diagrams, together with the Perfumery Ternary points (PTP) and the linear Perfumery Binary Lines (PBL). Here, the PBL are straight lines, because the system of equations present in Table 4 for the ideal case ($\gamma_I = 1$) is a linear system. When compared to the results obtained for non-ideal solutions, it is seen that such an assumption results in distorted values compared to the real ones.

Conclusions

A complete definition of any Perfumery Ternary Diagram (PTD) was developed in this work, based on the determination of Perfumery Binary Lines (PBL) and Perfumery Ternary points (PTP). The method was based on the solution of several non-linear systems of equations, using a modification of Powell's hybrid algorithm and a finite-difference approximation to the Jacobian.

This methodology was applied to the system: limonene + geraniol + vanillin+ethanol. The results obtained for non-ideal solutions were compared with those obtained for ideal solutions, and large differences in the PTD shape were obtained, namely, in the number of Perfumery Ternary points (PTP) and on the shape of the Perfumery Binary Lines (PBL).

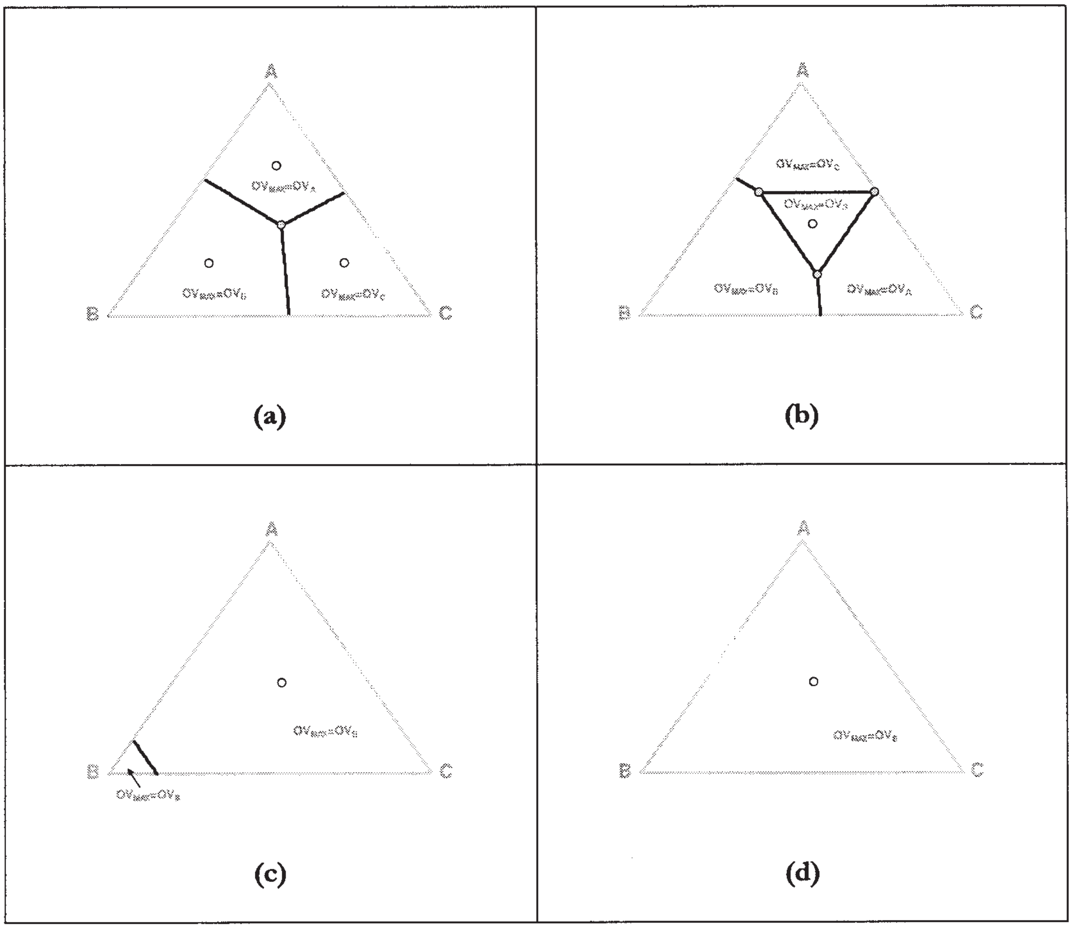


Figure 9. Perfumery Ternary Diagrams (PTD) with the corresponding Perfumery Ternary Points (PTP): ◍; Ternary Points (TP): ○; and Perfumery Binary Lines (PBL): ▬; considering ideal liquid solutions.

(a) $x_s = 0.3$, (b) $x_s = 0.6$, (c) $x_s = 0.7$, and (d) $x_s = 0.9$. (A) limonene; (B) geraniol; (C) vanillin; (S) ethanol.

Table 7. Composition of Perfumery Ternary Points (PTP) and Ternary Points (TP), Obtained for the Case Study System, Considering Non-Ideal Liquid Solutions

30% Ethanol

TP or PTP?		x_A	x_B	x_C	x_S	OV_A	OV_B	OV_C	OV_S
PTP	A+B+C	0.047	0.258	0.396	0.300	1382.0	1382.0	1382.0	410.5
TP	A+B+S	0.002	0.029	0.669	0.300	249.3	249.3	2680.0	249.3
TP	B+C+S	0.364	0.160	0.176	0.300	4181.0	731.5	731.5	731.5

60% Ethanol

TP or PTP?		x_A	x_B	x_C	x_S	OV_A	OV_B	OV_C	OV_S
TP	A+B+C	0.013	0.086	0.321	0.580	711.9	711.9	711.9	936.1
PTP	A+B+S	0.026	0.140	0.254	0.580	1043.0	1043.0	481.4	1043.0
PTP	A+C+S	0.013	0.041	0.366	0.580	878.9	376.3	878.9	878.9

70% Ethanol

TP or PTP?		x_A	x_B	x_C	x_S	OV_A	OV_B	OV_C	OV_S
TP	A+B+C	0.006	0.042	0.252	0.700	408.1	408.1	408.1	1275.0

90% Ethanol

TP or PTP?		x_A	x_B	x_C	x_S	OV_A	OV_B	OV_C	OV_S
TP	A+B+C	0.001	0.004	0.095	0.900	50.3	50.3	50.3	2047.0

Table 8. Composition of Perfumery Ternary Points (PTP) and Ternary Points (TP), Obtained for the Case Study System, Considering Ideal Liquid Solutions

30% Ethanol

TP or PTP?		x_A	x_B	x_C	x_S	OV_A	OV_B	OV_C	OV_S
PTP	A+B+C	0.273	0.188	0.239	0.300	1258.0	1258.0	1258.0	731.7
TP	A+B+S	0.159	0.109	0.432	0.300	731.7	731.7	2273.0	731.7
TP	B+C+S	0.452	0.109	0.139	0.300	2080.0	731.7	731.7	731.7
TP	A+C+S	0.159	0.402	0.139	0.300	731.7	2692.0	731.7	731.7

60% Ethanol

TP or PTP?		x_A	x_B	x_C	x_S	OV_A	OV_B	OV_C	OV_S
TP	A+B+C	0.195	0.134	0.171	0.500	898.5	898.5	898.5	1220.0
PTP	A+B+S	0.265	0.182	0.053	0.500	1220.0	1220.0	279.2	1220.0
PTP	B+C+S	0.086	0.182	0.232	0.500	396.8	1220.0	1220.0	1220.0
PTP	A+C+S	0.265	0.003	0.232	0.500	1220.0	23.2	1220.0	1220.0

70% Ethanol

TP or PTP?		x_A	x_B	x_C	x_S	OV_A	OV_B	OV_C	OV_S
TP	A+B+C	0.117	0.081	0.102	0.700	539.1	539.1	539.1	1707.0

90% Ethanol

TP or PTP?		x_A	x_B	x_C	x_S	OV_A	OV_B	OV_C	OV_S
TP	A+B+C	0.039	0.027	0.034	0.900	179.7	179.7	179.7	2195.0

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Appendix: Calculation of the Activity Coefficients Using the UNIFAC Method

In this work, values of activity coefficients, $\gamma_{i,}$ were calculated using the UNIFAC method, which is based on molecular group contribution for multi-component mixtures.[11] This method takes into account the contribution due to differences in molecular size and shape—the combinatorial part (C)—and the contribution due to molecular interactions—the residual part (R)—in the following way:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{A1}$$

Determination of the combinatorial part

The combinatorial part is calculated using the following equation:

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + 5q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \tag{A2}$$

where

$$l_i = 5(r_i - q_i) - (r_i - 1),\ \theta_i = \frac{q_i x_i}{\sum_j q_j x_j},\ \phi_i = \frac{r_i x_i}{\sum_j r_j x_j}$$

Parameters r_i and q_i are calculated for each molecule as the sum of the group volume and area parameters, Rj and Qj, as follows:[11]

$$r_i = \sum_j \nu_j^{(i)} R_j \text{ and } q_i = \sum_j \nu_j^{(i)} Q_j$$

where $\nu_j^{(i)}$is the number of groups of type j in molecule i (see Table 6).

Determination of the residual part

The residual part is calculated using the following equation:

$$\ln \gamma_i^R = \sum_{\substack{k \\ all\ groups}} \nu_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \tag{A3}$$

where Γ_k is the group residual activity coefficient and $\Gamma_k^{(i)}$ is the residual activity coefficient of group k in a reference solution containing only molecules of type i.

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_m \theta_m \psi_{mk} \right) - \sum_m \frac{\theta_m \psi_{km}}{\theta_n \psi_{nm}} \right] \qquad \text{(A4)}$$

Equation A4 also holds for $\Gamma_k^{(i)}$. In this equation, θ_m is the area fraction of group m, and the sum is over all different groups, this way:

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n}$$

where X_m is the mole fraction of group m in the mixture. The group interaction parameter ψ_{mn} is given by:

$$\psi_{mn} = \exp\left(-\frac{a_{mn}}{RT} \right)$$

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