Vapor–Liquid Equilibria Measurements of Bitter Orange Aroma Compounds Highly Diluted in Boiling Hydro-Alcoholic Solutions at 101.3 kPa

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ABSTRACT: In this work, experimental vapor–liquid equilibria (VLE) of water + ethanol + five aroma compound (two monoterpene hydrocarbons, α-pinene and D-limonene, and three oxygenated compounds, linalool, citral, and linalool oxide) mixtures were measured at boiling point at 101.3 kPa for ethanol molar fractions ranging from 0.0140 to 0.8389. The five aroma compounds were selected for their strong contribution to the aroma of the distillate of bitter orange essential oil. First, the thermodynamic consistency of the experimental VLE data was validated. Then the NRTL and Henry's law type models were tested to correlate the experimental data. Good agreement was obtained with both models to predict the phase equilibrium of the oxygenated compounds, and a better agreement was obtained with Henry's law type models for the monoterpene hydrocarbons in this kind of mixture.
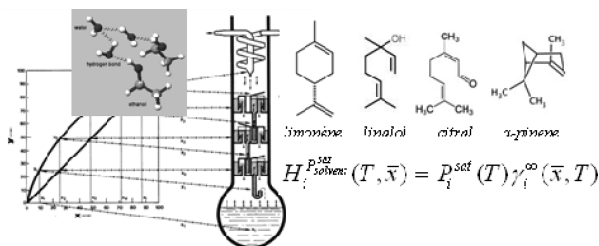
1. INTRODUCTION

Citrus essential oils are widely used as flavorings and fragrances in industries. Bitter orange essential oil is particularly used in the perfume and beverage industries. This essential oil contains numerous volatile compounds,[1] some belonging to monoterpene hydrocarbons with a percentage content from 97.3 % to 97.8 %, and some to oxygenated compounds in lower quantities between 1.8 % and 2.2 %. Volatile compounds of citrus essential oil are usually extracted from peels by alcoholic maceration and/or distillation processes.[2−9] The efficiency of the extraction mainly depends on the physicochemical properties of the volatile compounds in the process conditions.

The composition of the bitter orange (*Citrus aurantium* L.) macerate-distillate has been previously characterized by Deterre et al.[10] Twenty-four aroma volatile compounds were identified by gas chromatography (GC) coupled with olfactometry. Among them, we selected for this study the most olfactory impacting compounds: two monoterpene hydrocarbons, α-pinene and D-limonene, and three oxygenated compounds, linalool, citral (*E* and *Z* forms), and linalool oxide (*E* and *Z* forms). Oxygenated compounds contribute substantially to bitter orange flavor and fragrance due to their pleasant odor.[11,12]

For the maceration step, several works report liquid–liquid equilibrium data with ethanol and/or aroma compounds identified in bitter orange essential oil in hydro-alcoholic solution.[13−23] According to Chafer et al.,[17] limonene becomes soluble in an ethanol–water mixture with a molar fraction above 0.5. In the same way, Chafer et al.[18] showed that the linalool becomes soluble above 0.2 and Gramajo et al.[20] that citral becomes soluble above a molar fraction 0.21 for hydro-alcoholic mixture.

Distillation of alcoholic solution of essential oil is mainly carried out in batch distillation with or without a plate column. The ethanol concentration determines the relative volatility of aroma compounds of the essential oil. A better understanding of the behavior of the aroma compounds during distillation requires data on vapor–liquid equilibria (VLE). Unfortunately, studies are limited by the lack of VLE data for systems containing monoterpene hydrocarbons, oxygenated compounds, water, and ethanol at atmospheric pressure (101.3 kPa). Athès et al.[24] reported VLE data of 13 aroma compounds playing a

Table 1. Physico-Chemical Properties of the Compounds Studied in This Work: Molecular Weight (MW/g·mol⁻¹), Boiling Point (T_b/K), log of the Octanol/Water Partition Coefficient at T = 298.15 K (log K_{ow})

group	name	MW	$T_b{}^a$	log $K_{ow}{}^a$	supplier	purity (%)
alcohol	ethanol	46.07	351.15	−0.31 (exp)	Carlo Erba	≥ 99.8
terpene hydrocarbons	α-pinene	136.23	429.2	4.83	Aldrich	98
	D-limonene	136.23	449.2	4.57	Aldrich	97
oxygenated compounds	linalool	154.25	471.8	2.97	Aldrich	97
	citral	152.23	500.2	3.45	SAFC	≥ 96
	linalool oxide	170.25	461.2	2.43	Aldrich	≥ 97

[a]Reference 37.

role in the sensory quality of brandies. In this work, linalool is the one of the compounds which is also present in bitter orange distillate.

We therefore decided to measure the VLE data of specific aroma compounds in hydro-alcoholic solutions at atmospheric pressure to understand their behaviors in the distillation process.

As aroma compounds are highly diluted and as ethanol may interfere with some gas chromatography analysis, measuring precisely VLE is a real challenge.[25] Many experimental methods are available, and a previous study[24] recommended for these aroma compounds the dynamic recirculation method (Gillespie-like recirculating still), originally proposed by Gillespie.[26] This choice is in accordance with recommendations by Raal and Muhlbauer[27] and Christensen.[28] For a vapor—liquid solution in thermodynamic equilibrium, temperature and pressure are the same in both phases.

The understanding of a distillation process involving aroma compounds and ethanol needs not only experimental data but also an accurate thermodynamic model to predict vapor—liquid data. Furthermore, thermodynamic models are required in view to use properly process simulation softwares. It is thus essential to select appropriate thermodynamic models with estimated parameters from experimental data. For systems containing aroma compounds different thermodynamic models may be used, as predictive models, such as the universal functional activity coefficient (UNIFAC) model,[29−33] or semipredictive models, such as the non-random two liquid (NRTL) model[34] and the universal quasi chemical model (UNIQUAC).[35,36]

The aim of this work is to measure volatilities of bitter orange aroma compounds. We therefore measured the VLE of systems containing five aroma compounds, water, and ethanol at 101.3 kPa with the recirculation method. We used these experimental data to propose a simple Henry's law based thermodynamic model.

2. INSTRUMENTAL SECTION

2.1. Aroma Compounds. The selected aroma compounds [α-pinene (CAS no. 80-56-8), D-limonene (CAS no. 5989-27-5), linalool (CAS no. 78-70-6), citral (CAS no. 5392-40-5), and linalool oxide (CAS no. 60047-17-8)] are known for their role in the sensory quality of orange and are listed in Table 1 with some of their physicochemical properties [molecular weight (MW/g·mol⁻¹), boiling point (T_b/K) at atmospheric pressure, and hydrophobicity constant at 298.15 K (log K_{ow})].[37]

2.2. Solution Preparation. To obtain different hydro-alcoholic mixtures, water (Milli-Q system, Millipore Waters, France) and absolute ethanol were precisely weighed. Nine solutions with different ethanol concentrations from 0.0140 to 0.8389 in molar fractions were prepared. Then, aroma compounds were introduced at infinite dilution, i.e., molar fractions lower than 10⁻⁴.[38] The monoterpene hydrocarbons were at 50 ppm (1.4·10⁻⁵ in molar fraction) and the oxygenated

compounds at 100 ppm (6.1·10⁻⁶ in molar fraction). Only the mass of each compound was considered (Mettler AE2405 scale accuracy of 0.0001 g for the aroma compounds and Sartorius LLP5200P scale accuracy of 0.01 g for ultrapure water and ethanol).

2.3. Experimental Determination of VLE. The equipment (Ladodest) used for the VLE measurements was purchased from Iludest, Germany. The detailed procedure is given in Athès et al.'s study.[24] A 35 mL mixture is heated and partially evaporated while the pressure is maintained at 101.3 kPa (accuracy of 0.1 kPa). The rising vapor transports fine droplets of boiling liquid. Then the liquid and vapor phases are separated and the status of equilibrium is reached when the vapor temperature is stable (accuracy of 0.02 K). Then after 30 min of equilibrium, the recycled liquid and the condensed vapor phases were sampled for analysis. Each hydro-alcoholic mixture underwent three runs in a row with the recirculation device, and 3 mL samples of both phases were collected for each run.

2.4. GC Analysis. The composition of the volatile compounds in the liquid and condensed-vapor phases was measured by GC through a direct liquid injection in a CPG Agilent 6890 (Agilent Technologies, Santa Clara, CA, U.S.A.) directly interfaced with a flame ionization detector (240 °C; H₂: 40 mL·min⁻¹; air: 450 mL·min⁻¹; makeup gas He: 45 mL·min⁻¹). A capillary fused silica apolar capillary DB-5 (5 % diphenyl/95 % dimethyl siloxane) column (30 m, 0.320 mm I.D., 0.5 μm film thickness) with a helium carrier gas (flow rate 1 mL·min⁻¹) was used for the analysis. Samples were injected by using a GERSTEL MPS2 autosampler (GERSTEL GmbH&Co. KG) with a syringe of 1.2 μL.

The temperature program for the aroma compounds was as follows: initial temperature of 90 °C raised at 4 °C·min⁻¹ to 180 °C and then raised at 40 °C·min⁻¹ to 240 °C, giving a total running time of 24 min. A sample volume of 1 μL was injected in splitless mode. For the ethanol, the temperature program was as follows: initial temperature of 50 °C, hold 1 min, raised at 5 °C·min⁻¹ to 75 °C, and then raised at 30 °C·min⁻¹ to 160 °C, giving a total running time of 8 min. A sample volume of 1 μL was injected in split mode (split ratio 1:80). The software MSD ChemStation Data Analysis (Rev D) from Agilent was used to record general operations and data acquisition of the results.

The six compounds (except water) were quantified by the internal standard technique through the construction of calibration curves. The internal standards were 1-hexanol (CAS no. 111-27-3 from Aldrich with 98 % of purity) diluted in absolute ethanol (CAS no. 64-17-5 from Carlo Erba with ≥ 99.8 % of purity) for α-pinene and D-limonene, 1-nonanol (CAS no. 143-08-8 from Ega-Chemie with 97−98 % of purity) diluted in absolute ethanol for linalool oxide, linalool, and citral, and 1-butanol (CAS no. 71-36-8 from Carlo Erba with 99.99 % of purity) diluted in 1-propanol (CAS no. 71-23-8 from Carlo

Table 2. Experimental Mass Fractions of Ethanol and Terpene Hydrocarbons in the Liquid (w/w) and Vapor (w/w) Phases at Equilibrium and Experimental Temperatures of the System, over Three Runs

T/°C	ethanol liquid	ethanol vapor	α-pinene liquid	α-pinene vapor	D-limonene liquid	D-limonene vapor
96.8	0.0301 ± 0.0006	0.1994 ± 0.0006				
96.8	0.0277 ± 0.0004	0.1991 ± 0.0012				
97.0	0.0255 ± <0.0001	0.1930 ± 0.0007				
89.1	0.1318 ± 0.0016	0.5741 ± 0.0103		$3.73 \cdot 10^{-6}$ ± $1.04 \cdot 10^{-6}$		$1.24 \cdot 10^{-5}$ ± $2.37 \cdot 10^{-6}$
89.2	0.1322 ± 0.0026	0.5580 ± 0.0029		$8.24 \cdot 10^{-6}$ ± $1.94 \cdot 10^{-6}$		$2.23 \cdot 10^{-5}$ ± $2.24 \cdot 10^{-6}$
89.0	0.1441 ± 0.0157	0.5970 ± 0.0205		$3.52 \cdot 10^{-6}$ ± $0.36 \cdot 10^{-6}$		$1.79 \cdot 10^{-5}$ ± $1.76 \cdot 10^{-6}$
86.1	0.2174 ± 0.0039	0.6977 ± 0.0105		$1.82 \cdot 10^{-5}$ ± $1.25 \cdot 10^{-6}$		$5.96 \cdot 10^{-5}$ ± $0.11 \cdot 10^{-6}$
86.0	0.2228 ± 0.0002	0.6988 ± 0.0092		$2.39 \cdot 10^{-5}$ ± $1.92 \cdot 10^{-6}$		$6.46 \cdot 10^{-5}$ ± $8.63 \cdot 10^{-6}$
86.0	0.2280 ± 0.0015	0.7811 ± 0.0053		$2.20 \cdot 10^{-5}$ ± $1.79 \cdot 10^{-6}$		$7.91 \cdot 10^{-5}$ ± $1.75 \cdot 10^{-6}$
84.6	0.2854 ± 0.0022	0.7076 ± 0.0050		$1.03 \cdot 10^{-5}$ ± $6.14 \cdot 10^{-7}$		$1.11 \cdot 10^{-4}$ ± $20.30 \cdot 10^{-6}$
84.5	0.2880 ± 0.0012	0.7033 ± 0.0070		$0.91 \cdot 10^{-5}$ ± $0.32 \cdot 10^{-7}$		$1.09 \cdot 10^{-4}$ ± $5.36 \cdot 10^{-6}$
84.4	0.2130 ± 0.0017	0.7118 ± 0.0049		$2.88 \cdot 10^{-5}$ ± $6.00 \cdot 10^{-7}$		$0.68 \cdot 10^{-4}$ ± $1.82 \cdot 10^{-6}$
83.1	0.3889 ± 0.0080	0.7642 ± 0.0073	$3.28 \cdot 10^{-6}$ ± $1.34 \cdot 10^{-7}$	$2.06 \cdot 10^{-4}$ ± $3.65 \cdot 10^{-6}$	$0.82 \cdot 10^{-5}$ ± $0.37 \cdot 10^{-6}$	$2.51 \cdot 10^{-4}$ ± $0.92 \cdot 10^{-5}$
82.9	0.3995 ± 0.0034	0.7592 ± 0.0073	$14.00 \cdot 10^{-6}$ ± $21.80 \cdot 10^{-7}$	$3.71 \cdot 10^{-4}$ ± $1.51 \cdot 10^{-6}$	$2.36 \cdot 10^{-5}$ ± $0.93 \cdot 10^{-6}$	$3.76 \cdot 10^{-4}$ ± $1.54 \cdot 10^{-5}$
82.9	0.4021 ± 0.0075	0.7607 ± 0.0028	$8.21 \cdot 10^{-6}$ ± $0.46 \cdot 10^{-7}$	$1.91 \cdot 10^{-4}$ ± $7.90 \cdot 10^{-6}$	$2.56 \cdot 10^{-5}$ ± $2.22 \cdot 10^{-6}$	$2.25 \cdot 10^{-4}$ ± $1.02 \cdot 10^{-5}$
82.6	0.5152 ± 0.0040	0.7574 ± 0.0132	$0.84 \cdot 10^{-5}$ ± $2.04 \cdot 10^{-7}$	$1.13 \cdot 10^{-4}$ ± $2.75 \cdot 10^{-6}$	$0.92 \cdot 10^{-5}$ ± $0.21 \cdot 10^{-6}$	$1.11 \cdot 10^{-4}$ ± $2.68 \cdot 10^{-6}$
81.6	0.5152 ± 0.0039	0.7897 ± 0.0004	$1.12 \cdot 10^{-5}$ ± $10.50 \cdot 10^{-7}$	$2.64 \cdot 10^{-4}$ ± $6.29 \cdot 10^{-6}$	$2.19 \cdot 10^{-5}$ ± $2.25 \cdot 10^{-6}$	$2.20 \cdot 10^{-4}$ ± $4.07 \cdot 10^{-6}$
81.5	0.5287 ± 0.0029	0.7916 ± 0.0078	$1.54 \cdot 10^{-5}$ ± $8.60 \cdot 10^{-7}$	$2.98 \cdot 10^{-4}$ ± $7.47 \cdot 10^{-6}$	$2.66 \cdot 10^{-5}$ ± $1.33 \cdot 10^{-6}$	$2.50 \cdot 10^{-4}$ ± $7.68 \cdot 10^{-6}$
80.6	0.6243 ± 0.0024	0.8140 ± 0.0165	$3.18 \cdot 10^{-5}$ ± $2.06 \cdot 10^{-6}$	$2.85 \cdot 10^{-4}$ ± $1.68 \cdot 10^{-5}$	$3.72 \cdot 10^{-5}$ ± $1.93 \cdot 10^{-6}$	$1.57 \cdot 10^{-4}$ ± $9.37 \cdot 10^{-6}$
80.6	0.6508 ± 0.0157	0.8305 ± 0.0083	$3.44 \cdot 10^{-5}$ ± $0.55 \cdot 10^{-6}$	$2.70 \cdot 10^{-4}$ ± $1.17 \cdot 10^{-5}$	$3.61 \cdot 10^{-5}$ ± $1.28 \cdot 10^{-6}$	$1.55 \cdot 10^{-4}$ ± $6.36 \cdot 10^{-6}$
80.7	0.6165 ± 0.0060	0.8386 ± 0.0090	$3.00 \cdot 10^{-5}$ ± $1.93 \cdot 10^{-6}$	$2.35 \cdot 10^{-4}$ ± $0.47 \cdot 10^{-5}$	$2.56 \cdot 10^{-5}$ ± $1.03 \cdot 10^{-6}$	$1.14 \cdot 10^{-4}$ ± $0.32 \cdot 10^{-6}$
79.7	0.7474 ± 0.0062	0.8470 ± 0.0093	$3.54 \cdot 10^{-5}$ ± $1.81 \cdot 10^{-7}$	$1.53 \cdot 10^{-4}$ ± $2.05 \cdot 10^{-6}$	$3.88 \cdot 10^{-5}$ ± $4.64 \cdot 10^{-7}$	$8.11 \cdot 10^{-5}$ ± $12.00 \cdot 10^{-7}$
79.6	0.7533 ± 0.0073	0.8586 ± 0.0077	$2.49 \cdot 10^{-5}$ ± $4.57 \cdot 10^{-7}$	$1.25 \cdot 10^{-4}$ ± $7.87 \cdot 10^{-6}$	$3.17 \cdot 10^{-5}$ ± $17.20 \cdot 10^{-7}$	$7.69 \cdot 10^{-5}$ ± $2.10 \cdot 10^{-7}$
79.6	0.7587 ± 0.0181	0.8290 ±0.0036	$3.75 \cdot 10^{-5}$ ± $8.43 \cdot 10^{-7}$	$1.94 \cdot 10^{-4}$ ± $9.07 \cdot 10^{-6}$	$3.80 \cdot 10^{-5}$ ± $4.27 \cdot 10^{-7}$	$8.42 \cdot 10^{-5}$ ± $9.79 \cdot 10^{-7}$
78.2	0.9610 ± 0.0123	0.9414 ± 0.0040	$6.83 \cdot 10^{-5}$ ± $3.79 \cdot 10^{-6}$	$8.45 \cdot 10^{-5}$ ± $7.79 \cdot 10^{-7}$	$5.85 \cdot 10^{-5}$ ± $1.46 \cdot 10^{-6}$	$3.20 \cdot 10^{-5}$ ± $0.26 \cdot 10^{-6}$
78.2	0.9552 ± 0.0098	0.9656 ± 0.0068	$6.21 \cdot 10^{-5}$ ± $2.29 \cdot 10^{-6}$	$8.10 \cdot 10^{-5}$ ± $34.70 \cdot 10^{-7}$	$5.51 \cdot 10^{-5}$ ± $0.97 \cdot 10^{-6}$	$3.40 \cdot 10^{-5}$ ± $2.79 \cdot 10^{-6}$
78.3	0.9497 ± 0.0128	0.9536 ± 0.0050	$6.32 \cdot 10^{-5}$ ± $0.79 \cdot 10^{-6}$	$8.93 \cdot 10^{-5}$ ± $2.16 \cdot 10^{-7}$	$5.72 \cdot 10^{-5}$ ± $2.10 \cdot 10^{-6}$	$3.54 \cdot 10^{-5}$ ± $1.14 \cdot 10^{-6}$

Erba with 99.5 % of purity) for ethanol. All internal standards were chromatographic grade. Calibration curves were constructed with pure compounds diluted in ethanol (aroma compounds) or 1-propanol (ethanol) using six points of calibration, each point analyzed in triplicate. Their respective range concentrations are α-pinene ($0.002-0.139$ mg·g^{-1} of solution), D-limonene ($0.002-0.113$ mg·g^{-1} of solution), linalool ($0.005-0.310$ mg·g^{-1} of solution), citral ($0.005-0.308$ mg·g^{-1} of solution), linalool oxide ($0.005-0.313$ mg·g^{-1} of solution), and ethanol ($0.064-81.431$ mg·g^{-1} of solution). The quantification limit values are ($0.007, 0.005, 0.007, 0.019$, and 0.020) mg·g^{-1} for α-pinene, D-limonene, linalool, linalool oxide, and citral, respectively.

Sample preparations depended on the compound to quantify. For the aroma compounds, solutions of 0.9 mL of sample and 0.1 mL of internal standards were prepared. For the ethanol, solutions of 0.1 mL of sample, 0.1 mL of internal standard, and 0.8 mL of 1-propanol were prepared. For the latter solution, samples had previously been diluted to decrease the ethanol concentration to 40 mg·g^{-1} (0.0159 molar fraction).

Each sample collected at equilibrium was injected in GC in triplicate. All concentrations were expressed in mass fraction. Dispersion on experimental data can be evaluated by calculating a coefficient of variation (standard deviation/average value) based on repetitions of sample injections on GC. The coefficient of variation is ranging between 0.5 % to 11 % at most for those GC analyses. The mass fraction of water was determined by difference.

3. RESULTS

3.1. Vapor–Liquid Equilibria Data. The temperature and mass fraction measurements of the liquid and vapor phases are given in Tables 2 and 3. We present the data obtained from the three runs in the Labodest separately to highlight the value variations at equilibrium. For each sample, standard deviation is indicated. Molar fractions (Table 4) were deduced from mass fractions.

With the mixture containing the highest ethanol concentration (0.8389 in molar fraction), the liquid molar fraction of ethanol $x_{Ethanol}$ of the first run is 0.9068 and the vapor molar fraction $y_{Ethanol}$ of the second run is 0.9166. These two values are greater than the azeotrope value (0.8943[39]) at atmospheric pressure. The value differences are probably due to (1) the dilutions made to prepare the sample for the GC analysis and (2) the uncertainty in the GC analysis to measure the ethanol content.

Absence of aroma compounds data means that they are not detected in the phases at these temperatures. Molar fractions of aroma compounds and their sums correspond to infinite dilution ($\leq 10^{-4}$). This observation is important for the choice of the thermodynamic model.

3.2. Data Treatment: Thermodynamic Validation.
3.2.1. Theory. At equilibrium, the vapor (eq 1) and liquid (eq 2) fugacities f_i^V/Pa and f_i^L/Pa are equal, by assuming that the vapor phase behavior is a perfect gas.

$$f_i^V (y_i, P) = y_i P \tag{1}$$

Table 3. Experimental Mass Fractions of the Oxygenated Compounds in the Liquid (w/w) and Vapor (w/w) Phases at Equilibrium and Experimental Temperatures of the System, over Three Runs

$T/°C$	linalool liquid	linalool vapor	citral (Z and E) liquid	citral (Z and E) vapor	linalool oxide (Z and E) liquid	linalool oxide (Z and E) vapor
96.8	$1.40\cdot10^{-5} \pm 0.32\cdot10^{-6}$	$1.39\cdot10^{-3} \pm 8.55\cdot10^{-5}$	$2.35\cdot10^{-5} \pm 3.28\cdot10^{-6}$	$1.34\cdot10^{-3} \pm 6.57\cdot10^{-5}$	$6.34\cdot10^{-5} \pm 2.07\cdot10^{-6}$	$1.72\cdot10^{-3} \pm 8.39\cdot10^{-5}$
96.8	$1.56\cdot10^{-5} \pm 1.68\cdot10^{-6}$	$1.25\cdot10^{-3} \pm 3.80\cdot10^{-5}$	$2.43\cdot10^{-5} \pm 3.52\cdot10^{-6}$	$1.14\cdot10^{-3} \pm 3.38\cdot10^{-5}$	$7.26\cdot10^{-5} \pm 9.07\cdot10^{-7}$	$1.35\cdot10^{-3} \pm 4.30\cdot10^{-5}$
97.0	$1.30\cdot10^{-5} \pm 2.09\cdot10^{-6}$	$1.31\cdot10^{-3} \pm 7.95\cdot10^{-5}$	$2.41\cdot10^{-5} \pm 1.33\cdot10^{-6}$	$1.30\cdot10^{-3} \pm 4.35\cdot10^{-5}$	$6.26\cdot10^{-5} \pm 5.78\cdot10^{-6}$	$1.59\cdot10^{-3} \pm 3.44\cdot10^{-5}$
89.1	$1.93\cdot10^{-4} \pm 9.62\cdot10^{-6}$	$1.63\cdot10^{-3} \pm 9.07\cdot10^{-5}$	$2.00\cdot10^{-4} \pm 1.73\cdot10^{-5}$	$1.04\cdot10^{-3} \pm 4.46\cdot10^{-5}$	$2.70\cdot10^{-4} \pm 2.20\cdot10^{-5}$	$7.53\cdot10^{-4} \pm 3.76\cdot10^{-5}$
89.2	$1.62\cdot10^{-4} \pm 16.60\cdot10^{-6}$	$1.27\cdot10^{-3} \pm 13.60\cdot10^{-5}$	$1.60\cdot10^{-4} \pm 1.25\cdot10^{-5}$	$6.98\cdot10^{-4} \pm 0.39\cdot10^{-5}$	$2.02\cdot10^{-4} \pm 1.01\cdot10^{-5}$	$5.17\cdot10^{-4} \pm 5.43\cdot10^{-5}$
89.0	$1.26\cdot10^{-4} \pm 4.66\cdot10^{-6}$	$1.30\cdot10^{-3} \pm 7.59\cdot10^{-5}$	$1.14\cdot10^{-4} \pm 0.21\cdot10^{-5}$	$6.36\cdot10^{-4} \pm 1.89\cdot10^{-5}$	$1.45\cdot10^{-4} \pm 0.69\cdot10^{-5}$	$4.46\cdot10^{-4} \pm 1.23\cdot10^{-5}$
86.1	$8.61\cdot10^{-5} \pm 0.24\cdot10^{-6}$	$4.16\cdot10^{-4} \pm 1.45\cdot10^{-5}$	$1.01\cdot10^{-4} \pm 0.54\cdot10^{-5}$	$1.85\cdot10^{-4} \pm 1.34\cdot10^{-5}$	$1.31\cdot10^{-4} \pm 0.59\cdot10^{-5}$	$1.48\cdot10^{-4} \pm 0.59\cdot10^{-5}$
86.0	$9.76\cdot10^{-5} \pm 8.72\cdot10^{-6}$	$4.28\cdot10^{-4} \pm 2.87\cdot10^{-5}$	$1.03\cdot10^{-4} \pm 2.25\cdot10^{-5}$	$1.87\cdot10^{-4} \pm 1.16\cdot10^{-5}$	$1.20\cdot10^{-4} \pm 1.78\cdot10^{-5}$	$1.53\cdot10^{-4} \pm 1.12\cdot10^{-5}$
86.0	$10.80\cdot10^{-5} \pm 5.34\cdot10^{-6}$	$4.27\cdot10^{-4} \pm 2.83\cdot10^{-5}$	$1.06\cdot10^{-4} \pm 1.59\cdot10^{-5}$	$2.01\cdot10^{-4} \pm 2.18\cdot10^{-5}$	$1.30\cdot10^{-4} \pm 1.94\cdot10^{-5}$	$1.61\cdot10^{-4} \pm 2.12\cdot10^{-5}$
84.6	$1.57\cdot10^{-4} \pm 3.14\cdot10^{-5}$	$3.47\cdot10^{-4} \pm 1.42\cdot10^{-5}$	$1.50\cdot10^{-4} \pm 16.50\cdot10^{-6}$	$1.67\cdot10^{-4} \pm 6.05\cdot10^{-6}$	$1.57\cdot10^{-4} \pm 2.58\cdot10^{-5}$	$1.37\cdot10^{-4} \pm 4.43\cdot10^{-6}$
84.5	$1.27\cdot10^{-4} \pm 0.56\cdot10^{-5}$	$2.44\cdot10^{-4} \pm 0.43\cdot10^{-5}$	$1.47\cdot10^{-4} \pm 8.88\cdot10^{-6}$	$1.17\cdot10^{-4} \pm 2.76\cdot10^{-6}$	$1.68\cdot10^{-4} \pm 0.72\cdot10^{-5}$	$1.16\cdot10^{-4} \pm 15.80\cdot10^{-6}$
84.4	$1.28\cdot10^{-4} \pm 2.68\cdot10^{-5}$	$1.99\cdot10^{-4} \pm 1.12\cdot10^{-5}$	$1.19\cdot10^{-4} \pm 6.55\cdot10^{-6}$	$9.03\cdot10^{-5} \pm 1.06\cdot10^{-6}$	$1.51\cdot10^{-4} \pm 1.54\cdot10^{-5}$	$0.86\cdot10^{-4} \pm 1.65\cdot10^{-6}$
83.1	$1.27\cdot10^{-4} \pm 12.30\cdot10^{-6}$	$12.40\cdot10^{-5} \pm 21.40\cdot10^{-6}$	$1.29\cdot10^{-4} \pm 1.52\cdot10^{-5}$	$4.82\cdot10^{-5} \pm 9.46\cdot10^{-8}$	$1.39\cdot10^{-4} \pm 11.60\cdot10^{-6}$	$7.21\cdot10^{-5} \pm 3.71\cdot10^{-6}$
82.9	$4.40\cdot10^{-4} \pm 5.90\cdot10^{-6}$	$7.32\cdot10^{-5} \pm 6.46\cdot10^{-6}$	$4.30\cdot10^{-4} \pm 1.24\cdot10^{-5}$	$3.06\cdot10^{-5} \pm 5.19\cdot10^{-6}$	$5.24\cdot10^{-4} \pm 6.05\cdot10^{-6}$	$4.76\cdot10^{-5} \pm 3.72\cdot10^{-6}$
82.9	$2.90\cdot10^{-4} \pm 1.13\cdot10^{-6}$	$6.27\cdot10^{-5} \pm 0.13\cdot10^{-6}$	$2.72\cdot10^{-4} \pm 0.36\cdot10^{-5}$	$2.73\cdot10^{-5} \pm 1.32\cdot10^{-6}$	$2.72\cdot10^{-4} \pm 6.77\cdot10^{-6}$	$3.16\cdot10^{-5} \pm 0.97\cdot10^{-6}$
82.6	$1.21\cdot10^{-4} \pm 13.60\cdot10^{-6}$	$6.38\cdot10^{-5} \pm 4.66\cdot10^{-6}$	$1.36\cdot10^{-4} \pm 1.39\cdot10^{-5}$	$2.66\cdot10^{-5} \pm 4.44\cdot10^{-7}$	$1.42\cdot10^{-4} \pm 1.49\cdot10^{-5}$	$3.54\cdot10^{-5} \pm 18.50\cdot10^{-7}$
81.6	$1.36\cdot10^{-4} \pm 8.42\cdot10^{-6}$	$2.12\cdot10^{-5} \pm 0.75\cdot10^{-6}$	$1.32\cdot10^{-4} \pm 0.98\cdot10^{-5}$	$1.28\cdot10^{-5} \pm 7.20\cdot10^{-6}$	$1.47\cdot10^{-4} \pm 89.00\cdot10^{-5}$	$1.84\cdot10^{-5} \pm 3.92\cdot10^{-7}$
81.5	$1.41\cdot10^{-4} \pm 7.44\cdot10^{-6}$	$2.74\cdot10^{-5} \pm 1.62\cdot10^{-6}$	$1.46\cdot10^{-4} \pm 2.02\cdot10^{-5}$	$8.73\cdot10^{-6} \pm 5.02\cdot10^{-7}$	$1.68\cdot10^{-4} \pm 2.52\cdot10^{-5}$	$1.73\cdot10^{-5} \pm 5.23\cdot10^{-7}$
80.6	$1.52\cdot10^{-4} \pm 3.61\cdot10^{-6}$	$1.14\cdot10^{-5} \pm 1.76\cdot10^{-7}$	$1.45\cdot10^{-4} \pm 2.40\cdot10^{-6}$	$5.12\cdot10^{-6} \pm 7.42\cdot10^{-8}$	$1.61\cdot10^{-4} \pm 8.90\cdot10^{-6}$	$8.53\cdot10^{-6} \pm 3.46\cdot10^{-7}$
80.6	$1.47\cdot10^{-4} \pm 4.29\cdot10^{-6}$	$1.17\cdot10^{-5} \pm 2.07\cdot10^{-7}$	$1.34\cdot10^{-4} \pm 0.15\cdot10^{-6}$	$4.82\cdot10^{-6} \pm 2.60\cdot10^{-7}$	$1.52\cdot10^{-4} \pm 3.55\cdot10^{-6}$	$7.85\cdot10^{-6} \pm 3.15\cdot10^{-7}$
80.7	$1.36\cdot10^{-4} \pm 0.60\cdot10^{-6}$	$1.08\cdot10^{-5} \pm 2.83\cdot10^{-7}$	$1.28\cdot10^{-4} \pm 4.60\cdot10^{-6}$	$4.18\cdot10^{-6} \pm 1.92\cdot10^{-7}$	$1.36\cdot10^{-4} \pm 0.67\cdot10^{-6}$	$6.93\cdot10^{-6} \pm 0.28\cdot10^{-7}$
79.7	$1.38\cdot10^{-4} \pm 5.66\cdot10^{-6}$	$8.94\cdot10^{-6} \pm 26.70\cdot10^{-8}$	$1.21\cdot10^{-4} \pm 5.49\cdot10^{-6}$	$4.85\cdot10^{-6} \pm 3.06\cdot10^{-7}$	$1.27\cdot10^{-4} \pm 5.24\cdot10^{-6}$	$6.21\cdot10^{-6} \pm 3.08\cdot10^{-7}$
79.6	$1.52\cdot10^{-4} \pm 3.08\cdot10^{-6}$	$8.17\cdot10^{-6} \pm 3.74\cdot10^{-8}$	$1.32\cdot10^{-4} \pm 4.84\cdot10^{-6}$	$4.68\cdot10^{-6} \pm 3.44\cdot10^{-7}$	$1.44\cdot10^{-4} \pm 0.18\cdot10^{-6}$	$6.88\cdot10^{-6} \pm 2.49\cdot10^{-7}$
79.6	$1.34\cdot10^{-4} \pm 4.30\cdot10^{-6}$	$7.52\cdot10^{-6} \pm 9.80\cdot10^{-8}$	$1.17\cdot10^{-4} \pm 3.16\cdot10^{-6}$	$3.95\cdot10^{-6} \pm 2.61\cdot10^{-7}$	$1.23\cdot10^{-4} \pm 3.78\cdot10^{-6}$	$5.82\cdot10^{-6} \pm 1.44\cdot10^{-7}$
78.2	$1.17\cdot10^{-4} \pm 1.35\cdot10^{-5}$		$1.06\cdot10^{-4} \pm 6.29\cdot10^{-7}$		$1.16\cdot10^{-4} \pm 0.47\cdot10^{-5}$	
78.2	$1.28\cdot10^{-4} \pm 0.65\cdot10^{-5}$		$1.13\cdot10^{-4} \pm 134.00\cdot10^{-7}$		$1.37\cdot10^{-4} \pm 1.29\cdot10^{-5}$	
78.3	$1.30\cdot10^{-4} \pm 1.35\cdot10^{-5}$		$1.15\cdot10^{-4} \pm 3.86\cdot10^{-7}$		$1.41\cdot10^{-4} \pm 1.14\cdot10^{-5}$	

Table 4. Experimental Molar Fractions of Ethanol, Water, Terpene Hydrocarbons, and Oxygenated Compounds in the Liquid (x) and Vapor (y) Phases at Equilibrium and Experimental Temperatures of the System, over Three Runs

T/K	ethanol		water		α-pinene		D-limonene		linalool		citral (Z and E)		linalool oxide (Z and E)	
	x	y	x	y	x	y	x	y	x	y	x	y	x	y
369.95	0.0120	0.0891	0.9880	0.9103					$1.66 \cdot 10^{-6}$	$1.85 \cdot 10^{-4}$	$2.83 \cdot 10^{-6}$	$1.81 \cdot 10^{-4}$	$6.83 \cdot 10^{-6}$	$2.08 \cdot 10^{-4}$
369.95	0.0110	0.0888	0.9890	0.9107					$1.85 \cdot 10^{-6}$	$1.66 \cdot 10^{-4}$	$2.92 \cdot 10^{-6}$	$1.54 \cdot 10^{-4}$	$7.81 \cdot 10^{-6}$	$1.63 \cdot 10^{-4}$
370.15	0.0101	0.0858	0.9899	0.9137					$1.54 \cdot 10^{-6}$	$1.73 \cdot 10^{-4}$	$2.90 \cdot 10^{-6}$	$1.75 \cdot 10^{-4}$	$6.73 \cdot 10^{-6}$	$1.92 \cdot 10^{-4}$
362.25	0.0560	0.3466	0.9439	0.6528		$7.61 \cdot 10^{-7}$		$2.54 \cdot 10^{-6}$	$2.45 \cdot 10^{-5}$	$2.93 \cdot 10^{-4}$	$2.57 \cdot 10^{-5}$	$1.90 \cdot 10^{-4}$	$3.11 \cdot 10^{-5}$	$12.30 \cdot 10^{-5}$
362.35	0.0562	0.3315	0.9437	0.6681		$16.50 \cdot 10^{-7}$		$4.48 \cdot 10^{-6}$	$2.06 \cdot 10^{-5}$	$2.26 \cdot 10^{-4}$	$2.06 \cdot 10^{-5}$	$1.26 \cdot 10^{-4}$	$2.33 \cdot 10^{-5}$	$8.32 \cdot 10^{-5}$
362.15	0.0618	0.3678	0.9382	0.6317		$7.34 \cdot 10^{-7}$		$3.72 \cdot 10^{-6}$	$1.62 \cdot 10^{-5}$	$2.40 \cdot 10^{-4}$	$1.48 \cdot 10^{-5}$	$1.19 \cdot 10^{-4}$	$1.69 \cdot 10^{-5}$	$7.44 \cdot 10^{-5}$
359.25	0.0979	0.4729	0.9020	0.5228		$4.17 \cdot 10^{-6}$		$1.37 \cdot 10^{-5}$	$1.16 \cdot 10^{-5}$	$8.43 \cdot 10^{-5}$	$1.38 \cdot 10^{-5}$	$3.79 \cdot 10^{-5}$	$1.60 \cdot 10^{-5}$	$2.72 \cdot 10^{-5}$
359.15	0.1007	0.4762	0.8992	0.5237		$5.52 \cdot 10^{-6}$		$1.49 \cdot 10^{-5}$	$1.32 \cdot 10^{-5}$	$8.71 \cdot 10^{-5}$	$1.41 \cdot 10^{-5}$	$3.86 \cdot 10^{-5}$	$1.47 \cdot 10^{-5}$	$2.81 \cdot 10^{-5}$
359.15	0.1035	0.5832	0.8965	0.4165		$5.56 \cdot 10^{-6}$		$2.00 \cdot 10^{-5}$	$1.46 \cdot 10^{-5}$	$9.53 \cdot 10^{-5}$	$1.46 \cdot 10^{-5}$	$4.54 \cdot 10^{-5}$	$1.59 \cdot 10^{-5}$	$3.25 \cdot 10^{-5}$
357.75	0.1350	0.4854	0.8649	0.5120		$2.39 \cdot 10^{-6}$		$2.57 \cdot 10^{-5}$	$2.21 \cdot 10^{-5}$	$7.12 \cdot 10^{-5}$	$2.15 \cdot 10^{-5}$	$3.48 \cdot 10^{-5}$	$2.01 \cdot 10^{-5}$	$2.55 \cdot 10^{-5}$
357.65	0.1365	0.4813	0.8634	0.5186		$2.10 \cdot 10^{-6}$		$2.51 \cdot 10^{-5}$	$1.80 \cdot 10^{-5}$	$4.98 \cdot 10^{-5}$	$2.11 \cdot 10^{-5}$	$2.43 \cdot 10^{-5}$	$2.15 \cdot 10^{-5}$	$2.15 \cdot 10^{-5}$
357.55	0.0957	0.4915	0.9043	0.5084	$0.57 \cdot 10^{-6}$	$6.73 \cdot 10^{-6}$	$1.42 \cdot 10^{-6}$	$1.58 \cdot 10^{-5}$	$1.71 \cdot 10^{-5}$	$4 \cdot 10^{-5}$	$1.62 \cdot 10^{-5}$	$1.89 \cdot 10^{-5}$	$1.84 \cdot 10^{-5}$	$1.60 \cdot 10^{-5}$
356.25	0.1992	0.5324	0.8007	0.4191	$2.44 \cdot 10^{-6}$	$4.85 \cdot 10^{-5}$	$4.13 \cdot 10^{-6}$	$5.91 \cdot 10^{-5}$	$1.94 \cdot 10^{-5}$	$2.59 \cdot 10^{-5}$	$2.00 \cdot 10^{-5}$	$10.20 \cdot 10^{-6}$	$1.92 \cdot 10^{-5}$	$13.60 \cdot 10^{-6}$
356.05	0.2066	0.5529	0.7931	0.4469	$1.44 \cdot 10^{-6}$	$9.13 \cdot 10^{-5}$	$4.49 \cdot 10^{-6}$	$9.27 \cdot 10^{-5}$	$6.80 \cdot 10^{-5}$	$1.59 \cdot 10^{-5}$	$6.73 \cdot 10^{-5}$	$6.74 \cdot 10^{-6}$	$7.33 \cdot 10^{-5}$	$9.38 \cdot 10^{-6}$
356.05	0.2083	0.5546	0.7916	0.4453	$1.62 \cdot 10^{-6}$	$4.72 \cdot 10^{-5}$	$1.77 \cdot 10^{-6}$	$5.55 \cdot 10^{-5}$	$4.49 \cdot 10^{-5}$	$0.14 \cdot 10^{-5}$	$4.26 \cdot 10^{-5}$	$6.02 \cdot 10^{-6}$	$3.81 \cdot 10^{-5}$	$6.24 \cdot 10^{-6}$
355.75	0.2936	0.5350	0.7064	0.4379	$1.97 \cdot 10^{-6}$	$2.71 \cdot 10^{-5}$	$3.82 \cdot 10^{-6}$	$2.64 \cdot 10^{-5}$	$2.07 \cdot 10^{-5}$	$13.50 \cdot 10^{-6}$	$2.34 \cdot 10^{-5}$	$5.68 \cdot 10^{-6}$	$2.18 \cdot 10^{-5}$	$6.77 \cdot 10^{-6}$
354.75	0.2665	0.5953	0.6412	0.4046	$3.01 \cdot 10^{-6}$	$6.72 \cdot 10^{-5}$	$5.19 \cdot 10^{-6}$	$5.61 \cdot 10^{-5}$	$2.11 \cdot 10^{-5}$	$4.77 \cdot 10^{-6}$	$2.07 \cdot 10^{-5}$	$2.92 \cdot 10^{-6}$	$2.06 \cdot 10^{-5}$	$3.76 \cdot 10^{-6}$
354.65	0.3049	0.5981	0.6950	0.4018	$6.79 \cdot 10^{-6}$	$7.61 \cdot 10^{-5}$	$7.95 \cdot 10^{-6}$	$6.39 \cdot 10^{-5}$	$2.43 \cdot 10^{-5}$	$6.19 \cdot 10^{-6}$	$2.55 \cdot 10^{-5}$	$2.00 \cdot 10^{-6}$	$2.63 \cdot 10^{-5}$	$3.55 \cdot 10^{-6}$
353.75	0.3940	0.5875	0.6059	0.3427	$7.54 \cdot 10^{-6}$	$6.97 \cdot 10^{-5}$	$7.92 \cdot 10^{-6}$	$3.83 \cdot 10^{-5}$	$2.86 \cdot 10^{-5}$	$2.47 \cdot 10^{-6}$	$2.77 \cdot 10^{-5}$	$1.12 \cdot 10^{-6}$	$2.75 \cdot 10^{-5}$	$1.67 \cdot 10^{-6}$
353.75	0.4217	0.6574	0.5782	0.3425	$6.36 \cdot 10^{-6}$	$7.23 \cdot 10^{-5}$	$7.54 \cdot 10^{-6}$	$4.16 \cdot 10^{-5}$	$2.85 \cdot 10^{-5}$	$2.78 \cdot 10^{-6}$	$2.62 \cdot 10^{-5}$	$1.15 \cdot 10^{-6}$	$2.66 \cdot 10^{-5}$	$1.68 \cdot 10^{-6}$
353.85	0.3861	0.6704	0.6138	0.3295	$8.60 \cdot 10^{-6}$	$6.34 \cdot 10^{-5}$	$9.42 \cdot 10^{-6}$	$3.90 \cdot 10^{-5}$	$2.54 \cdot 10^{-5}$	$2.59 \cdot 10^{-6}$	$2.43 \cdot 10^{-5}$	$1.01 \cdot 10^{-6}$	$2.30 \cdot 10^{-5}$	$1.50 \cdot 10^{-6}$
352.85	0.5365	0.6568	0.4634	0.3032	$6.08 \cdot 10^{-6}$	$4.00 \cdot 10^{-5}$	$7.76 \cdot 10^{-6}$	$2.13 \cdot 10^{-5}$	$2.96 \cdot 10^{-5}$	$2.07 \cdot 10^{-6}$	$2.62 \cdot 10^{-5}$	$1.14 \cdot 10^{-6}$	$2.47 \cdot 10^{-5}$	$1.30 \cdot 10^{-6}$
352.75	0.5444	0.7038	0.4555	0.2962	$9.23 \cdot 10^{-6}$	$3.48 \cdot 10^{-5}$	$9.33 \cdot 10^{-6}$	$2.13 \cdot 10^{-5}$	$3.28 \cdot 10^{-5}$	$2.00 \cdot 10^{-6}$	$2.89 \cdot 10^{-5}$	$1.16 \cdot 10^{-6}$	$2.82 \cdot 10^{-5}$	$1.53 \cdot 10^{-6}$
352.75	0.5516	0.6548	0.4483	0.3451	$2.18 \cdot 10^{-5}$	$5.17 \cdot 10^{-5}$	$1.87 \cdot 10^{-5}$	$2.25 \cdot 10^{-5}$	$2.90 \cdot 10^{-5}$	$1.77 \cdot 10^{-6}$	$2.58 \cdot 10^{-5}$	$0.94 \cdot 10^{-6}$	$2.43 \cdot 10^{-5}$	$1.24 \cdot 10^{-6}$
351.35	0.9068	0.8407	0.0931	0.1338	$1.96 \cdot 10^{-5}$	$2.55 \cdot 10^{-5}$	$1.74 \cdot 10^{-5}$	$0.97 \cdot 10^{-5}$	$3.31 \cdot 10^{-5}$		$3.03 \cdot 10^{-5}$		$2.97 \cdot 10^{-5}$	
351.35	0.8937	0.9166	0.1062	0.0834	$1.99 \cdot 10^{-5}$	$2.60 \cdot 10^{-5}$	$1.79 \cdot 10^{-5}$	$1.09 \cdot 10^{-5}$	$3.59 \cdot 10^{-5}$		$3.19 \cdot 10^{-5}$		$3.47 \cdot 10^{-5}$	
351.45	0.8815	0.8896	0.1183	0.1104		$2.82 \cdot 10^{-5}$		$1.12 \cdot 10^{-5}$	$3.61 \cdot 10^{-5}$		$3.23 \cdot 10^{-5}$		$3.53 \cdot 10^{-5}$	

Table 5. Constants Used in eq 4 for Computing the Pure Compound Vapor Pressures in P^{sat}/Pa at a Given Temperature T/K

compound	A_i	B_i	C_i	D_i	E_i	ref
ethanol	74.475	−7164.3	−7.327	3.134×10^{-6}	2	41
water	73.649	−7258.2	−7.304	4.165×10^{-6}	2	41
α-pinene	97.752	−8491.6	−11.124	5.330×10^{-6}	2	41
D-limonene	75.574	−8079.7	−7.560	8.387×10^{-18}	6	41
linalool	125.570	−12 294.0	−15.084	0	1	42
citral (Z and E)	24.418	−6320.0	0	0	0	43
linalool oxide (Z and E)	739.370	−34 104.0	−115.795	0.120	1	44

$$f_i^{L}(T, \overline{x}) = \gamma_i(T, \overline{x}) x_i P_i^{sat}(T) \tag{2}$$

Vapor fugacity of the compound i depends on y_i, the vapor molar fraction of the compound i, and the pressure of the system P/Pa. Due to nonideality, liquid fugacity of the compound i depends not only on temperature T/K and liquid molar fraction of the compound i, x_i, but also on the composition, $\overline{x}$, and more particularly on the liquid molar fractions of the ethanol and water because the aroma compounds are at infinite dilution. We thus deduce the following equation (3).

$$y_i P = \gamma_i(T, \overline{x}) x_i P_i^{sat}(T) \tag{3}$$

The activity coefficient $\gamma_i(T,\overline{x})$ is a multiplying factor of the liquid fugacity of compound i in an ideal mixture. It represents the behavior departure from the ideal solution due to molecular interactions. For each pure compound i, the saturated vapor pressure P_i^{sat} depends on the temperature T/K and is determined with the Riedel equation (eq 4).[40]

$$P_i^{sat} = \exp\!\left(A_i + \frac{B_i}{T} + C_i \ln T + D_i T^{E_i}\right) \tag{4}$$

Coefficients A_i to E_i are specific for each compound i (Table 5).
α-Pinene, D-limonene, water, and ethanol are present in the ProSim database[41] with their coefficients of P^{sat}. For linalool and citral, the coefficients were found in works by Díaz et al.[42] and Clara et al.,[43] respectively. For the linalool oxide, the coefficients were produced by ProPred software by CAPEC.[44]

The absolute volatility of each compound i in the solution is expressed by the vapor–liquid partition coefficient or equilibrium constant, K_i of the compound i (eq 5).[45]

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i(T, \overline{x}) P_i^{sat}(T)}{P} \tag{5}$$

The relative volatility $\alpha_{i/j}$ is expressed by the ratio between the absolute volatilities of the compounds i and j (eq 6).

$$\alpha_{i/j} = \frac{K_i}{K_j} \tag{6}$$

When $\alpha_{i/j} > 1$, compound i is more volatile than compound j, and when $\alpha_{i/j} = 1$ the compounds have the same volatility.

3.2.2. Ethanol Data. First of all, experimental data were compared to calculated VLE data of the hydro-alcoholic binary solutions (without aroma compounds) at 101.3 kPa (Figure.1). Such calculated data was generated using Simulis Thermodynamics from ProSim[41] and the NRTL model, with its binary interaction parameters stored in the ProSim database. These parameters are given in the first line of Table 6.

Experimental data of ethanol have good overall correlation with the binary ethanol–water curves confirming that, at infinite dilution, the influence of aroma compounds on the phase equilibrium of the hydro-alcoholic binary systems can be negligible.

3.2.3. Aroma Compounds Data. Absolute volatilities of the monoterpene hydrocarbons (Figure 2) and oxygenated compounds (Figure 3) were calculated and represented in logarithm scale as a function of the liquid ethanol molar fraction x_{Ethanol}.

Liquid molar fractions of monoterpene hydrocarbons from (370 to 358) K were not detected, and therefore, the K_i could not be calculated.

The absolute volatilities of α-pinene and D-limonene are greater than 1 on almost all the x_{Ethanol} range. The compounds are thus very volatile as they are more concentrated in the vapor phase. Beyond 0.9 x_{Ethanol}, their absolute volatilities become less than 1.

For the lowest equilibrium temperature, around 351 K, oxygenated compounds were not detected in the vapor phases. The K_i therefore could not be calculated.

The absolute volatilities of linalool, linalool oxide and citral are less than 1 from 0.15 to 1 x_{Ethanol}. These compounds are a little volatile as they are more concentrated in the liquid phase. Beyond 0.15 x_{Ethanol}, their absolute volatilities are less than 1.

Experimental data of linalool were compared to those measured by Athès et al.[24] (Figure 4).

The experimental data are coherent as a set. This observation makes it possible to confirm that the experimental data are correct.

We observe that the increase in the ethanol concentration decreases dramatically the absolute volatility K_i of all aroma compounds. It is due to the fact that these aroma compounds are hydrophobic regarding their log K_{ow}, and therefore their solubility increases with the ethanol concentration, leading to a lower absolute volatility.

Relative volatility coefficients α (compared with ethanol, $\alpha_{i/\text{Ethanol}} = K_i/K_{\text{Ethanol}}$) of aroma compounds were calculated. These values make it possible to understand the behavior of aroma compounds according to the ethanol concentration. α-pinene is more volatile than ethanol between 0 and 0.9 of x_{Ethanol} and D-limonene between 0 and 0.7 of x_{Ethanol}. In the case of the 3 oxygenated compounds, they are more volatile than ethanol between 0 and 0.06–0.08 of x_{Ethanol}.

3.3. Modeling. The experimental data were compared to those calculated from the NRTL and Henry's law type models. To select a representative model, we used parity plots to compare the relative volatility coefficients against ethanol for the experimental (α^{exp}) and calculated data (α^{calc}). The model gives a good representation, when α values correspond to each other (on the bisector).

3.3.1. Comparison between Experimental Data and Values Calculated by the NRTL Model. In the NRTL model, the activity coefficient is given by eq 7.

$$\ln \gamma_i = \frac{\sum_{j=1}^{n} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{n} G_{ki} x_k} + \sum_{j=1}^{n} \frac{G_{ij} x_j}{\sum_{k=1}^{n} G_{kj} x_k}$$
$$\times \left(\tau_{ij} - \frac{\sum_{k=1}^{n} G_{kj} \tau_{kj} x_k}{\sum_{k=1}^{n} G_{kj} x_k} \right) \tag{7}$$
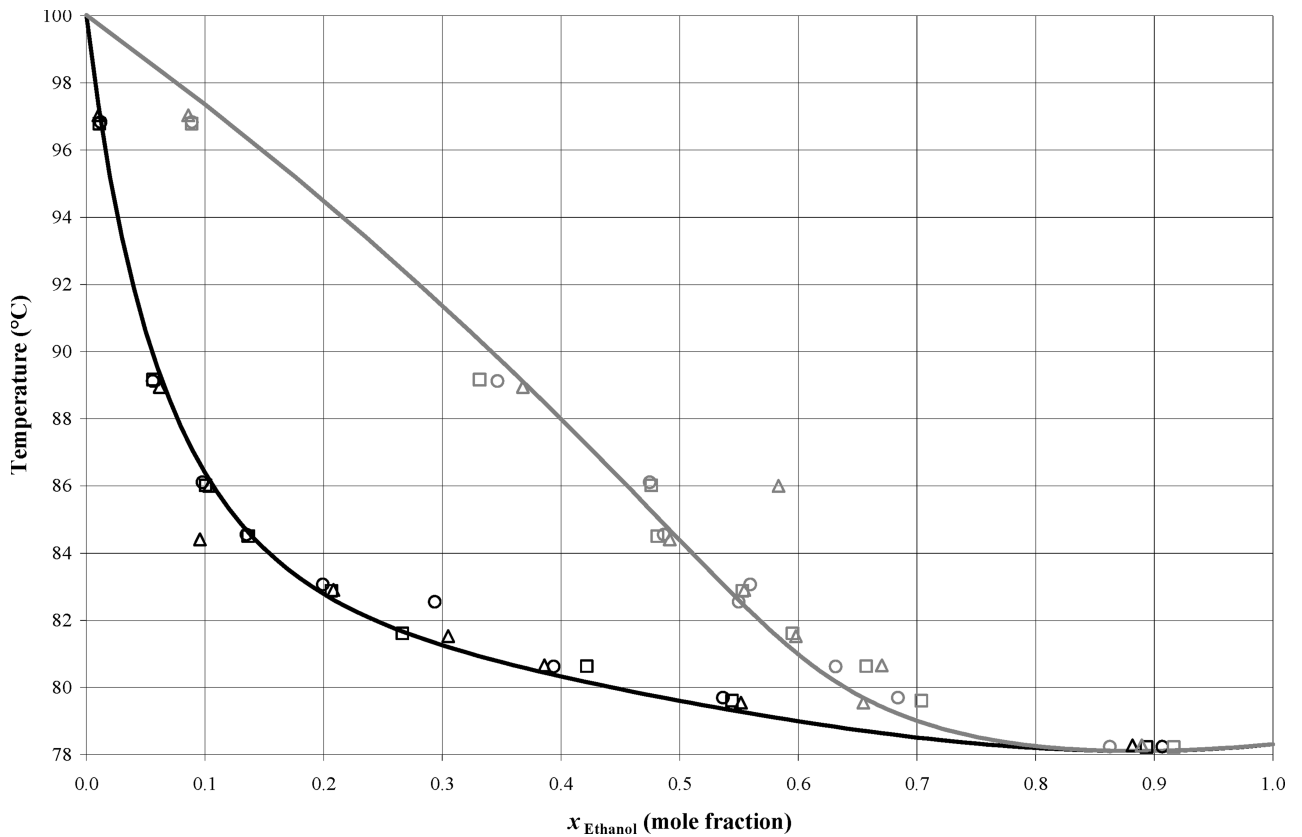
Figure 1. Comparisons of the experimental molar fractions of ethanol during (○) the 1st run, (□) the 2nd run, and (△) the 3rd run with calculated data of the binary ethanol—water generated with the NRTL model at 101.3 kPa.

Table 6. Binary Parameters in the NRTL Model[a]

system	C_{12}^0	C_{21}^0	α_{12}^0	C_{12}^T	C_{21}^T	α_{12}^T
ethanol (1) + water (2)	−635.56	1616.81	0.1448	0.9907	2.0177	0
α-pinene (1) + water (2)	3226.16	4833.31	0.3	−35.76	8.69	0
D-limonene (1) + water (2)	3247.38	4261.50	0.3	−18.23	10.74	0
linalool (1) + water (2)	645.89	3407.97	0.3	−35.98	133.33	0
citral (Z and E) (1) + water (2)	1685.31	4226.78	0.3	−45.31	117.15	0
linalool oxide (Z and E) (1) + water (2)	279.57	2727.44	0.3	−33.03	138.24	0
α-pinene (1) + ethanol (2)	1875.14	477.02	0.3	−43.28	56.68	0
D-limonene (1) + ethanol (2)	1599.74	562.46	0.3	−37.85	48.64	0
linalool (1) + ethanol (2)	−367.43	882.43	0.3	−26.21	93.48	0
citral (Z and E) (1) + ethanol (2)	−392.15	949.32	0.3	−27.27	92.02	0
linalool oxide (Z and E) (1) + ethanol (2)	−360.33	1156.91	0.3	−26.85	106.51	0

[a]The parameters α_{12} are adimensional, the parameters C_{ij}^0 are given in cal·mol^{-1}, and the parameters C_{ij}^T in cal·mol^{-1}·°C^{-1}.

with

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} \text{ and } G_{ij} = \exp(-\alpha_{ji}\tau_{ji})$$

where R/cal·mol^{-1}·K^{-1} is the perfect gas constant and its value is 1.987; τ, α, and G are adimensional binary parameters and g/cal·mol^{-1} is a binary parameter representing the free enthalpy of the NRTL model. The evolution of these parameters with the temperature is given by

$$\tau_{ii} = \tau_{jj} = 0$$

$$\alpha_{ii} = \alpha_{jj} = 0$$

$$g_{ij} - g_{jj} = C_{ij}^0 + C_{ij}^T(T - 273.15)$$

$$\alpha_{ij} = \alpha_{ij}^0 + \alpha_{ij}^T(T - 273.15)$$

$$G_{ii} = G_{jj} = 1$$

Hence, the NRTL model has, for each binary, six adjustable parameters estimated from experimental data: C_{ij}^0 and C_{ji}^0/cal·mol^{-1}, C_{ij}^T and C_{ji}^T /cal·mol^{-1}·°C^{-1}, and $\alpha_{ij}^0 = \alpha_{ji}^0$ and $\alpha_{ij}^T = \alpha_{ji}^T$/°C. As the aroma compounds are in infinite dilution, the interactions between them are negligible. Then, in this work, only the parameters for the binaries aroma compound i + ethanol and aroma compound i + water were estimated.
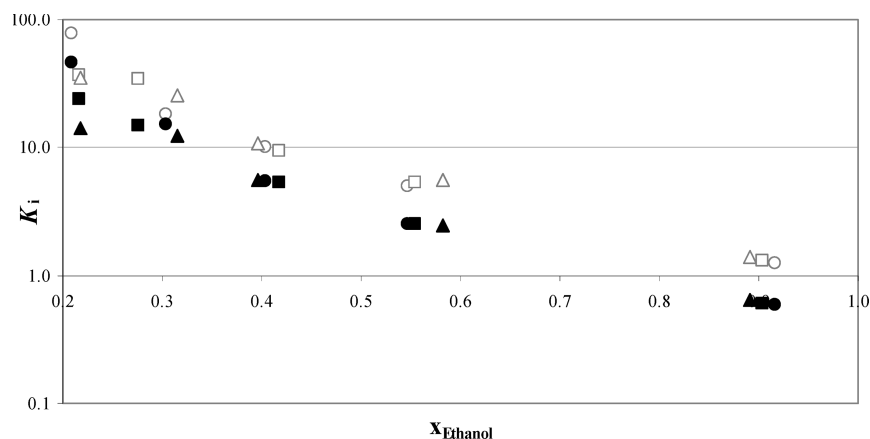
Figure 2. Evolution of K of α-pinene (open symbols) and D-limonene (plain symbols), during ($\bigcirc$) the 1st run, ($\square$) the 2nd run, and ($\triangle$) the 3rd run, according to x_{Ethanol} at 101.3 kPa.
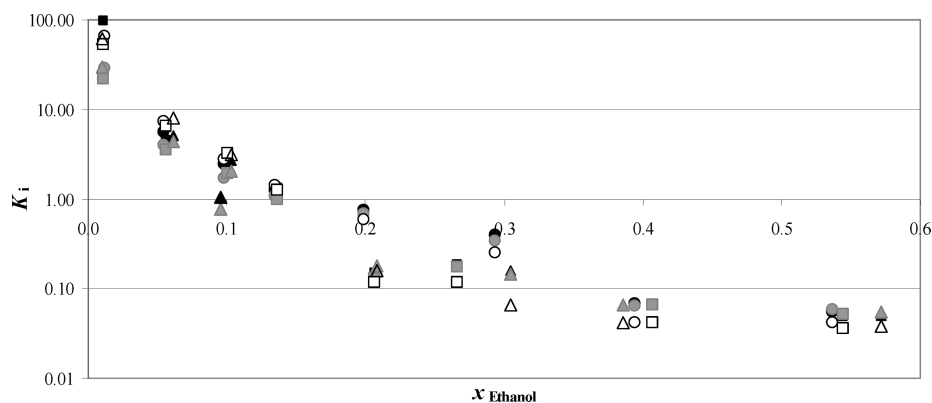
Figure 3. Evolution of K of linalool (plain black symbols), citral (black symbols), and linalool oxide (plain gray symbols), during ($\bigcirc$) the 1st run, ($\square$) the 2nd run, and ($\triangle$) the 3rd run, according to x_{Ethanol} at 101.3 kPa.
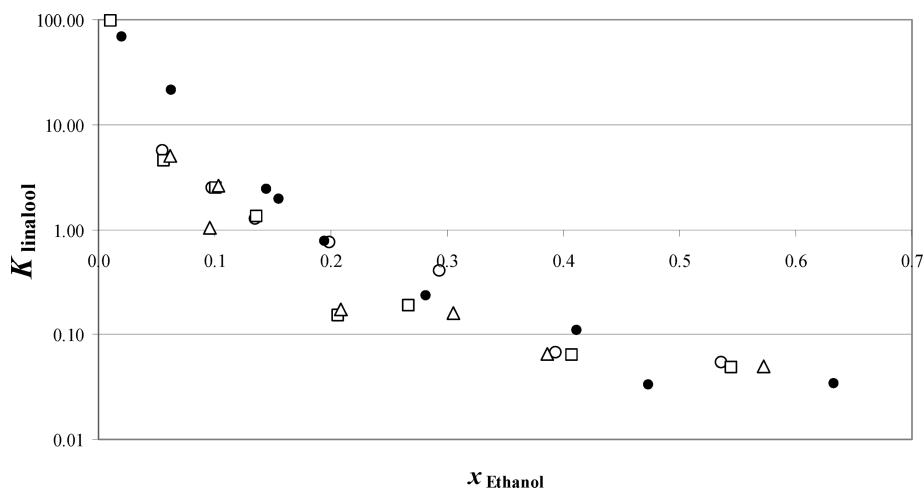
Figure 4. Comparison of the experimental K_{Linalool} values during ($\bigcirc$) the 1st run, ($\square$) the 2nd run, and ($\triangle$) the 3rd run with those produced by Athès et al.[25] ($\bullet$) according to x_{Ethanol} at 101.3 kPa.

Moreover $\alpha_{ij} = \alpha_{ji}$ were fixed to 0.3. Finally, 40 binary parameters had to be estimated on the basis of the equilibrium model given by eq 5.

These parameters were first initialized from the UNIFAC modified Dortmund model.[29,31,33] They were then estimated from the experimental absolute volatilities $K_i^{\text{exp}} = y_i^{\text{exp}}/x_i^{\text{exp}}$ by

the method of least-squares. The criterion to minimize is the sum of the absolute deviations squared (least-squares error) between experimental values K_i^{exp} and calculated values $K_i^{\text{cal}} = P_i^{\text{sat}}(T)\gamma_i^{\text{NRTL}}(T,\bar{x})/P$. Table 6 gives the NRTL parameters which were estimated from experimental data using Simulis Thermodynamics from ProSim.[41]
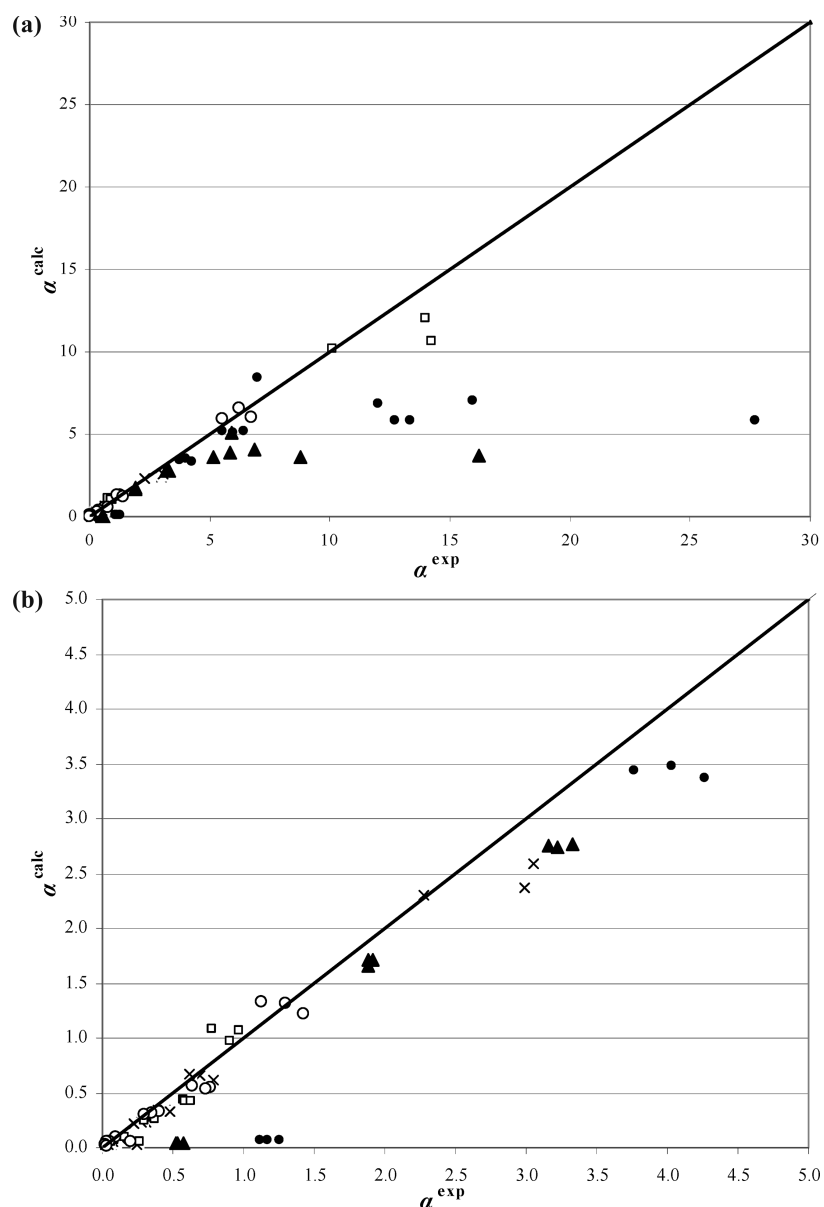
Figure 5. (a) Comparison of the α^{exp} and α^{calc} from 0 to 30 of the NRTL model for α-pinene (●), D-limonene (▲), linalool (□), citral (○), and linalool oxide (×). (b) Comparison of the α^{exp} and α^{calc} from 0 to 5 of the NRTL model for α-pinene (●), D-limonene (▲), linalool (□), citral (○), and linalool oxide (×).

Experimental and calculated data were compared. Correlations of relative volatility coefficients α^{calc} from NRTL model against α^{exp} are expressed in Figure 5a. As the experimental K_{Ethanol} values are sometimes less than 1, in the formula (eq 6) of the α^{exp}, we consider the calculated K_{Ethanol} values from the NRTL model.

Overall, the oxygenated compounds are better represented than monoterpene hydrocarbons with the NRTL model. Moreover beyond relative volatilities of 5, the NRTL model does not properly represent the VLE. Note that for distillation applications, the most important is to have a satisfactory representation in the low volatility domain. A zoom of the results in the interval [0–5] is presented in Figure 5b.

3.3.2. Comparison between Experimental Data and Calculated Values from the Henry's Law Type Model. The characteristic constant for a solute at infinite dilution is Henry's

constant. It provides incisive information regarding solute–solvent interactions in the absence of solute interactions.[46,47] As the aroma compounds are present in infinite dilution, the system can be described by Henry's law for dilute compounds. In this approach, the reference state for aroma compounds is the infinite dilution at T, P of the mixture. The reference state for water and ethanol, which constitute the solvent, is the pure compound at T, P of the mixture. This asymmetric convention consists in using the equilibrium relation (eq 3) only for ethanol and water. For aroma compounds, the following eq (8)[42] is used:

$$Py_i = x_i H_i^{P^{\text{sat}}_{\text{solvent}}}(T, \overline{x})$$
(8a)

with

$$H_i^{P^{\text{sat}}_{\text{solvent}}}(T, \overline{x}) = P_i^{\text{sat}}(T)\gamma_i^{\infty}(\overline{x}, T)$$
(8b)
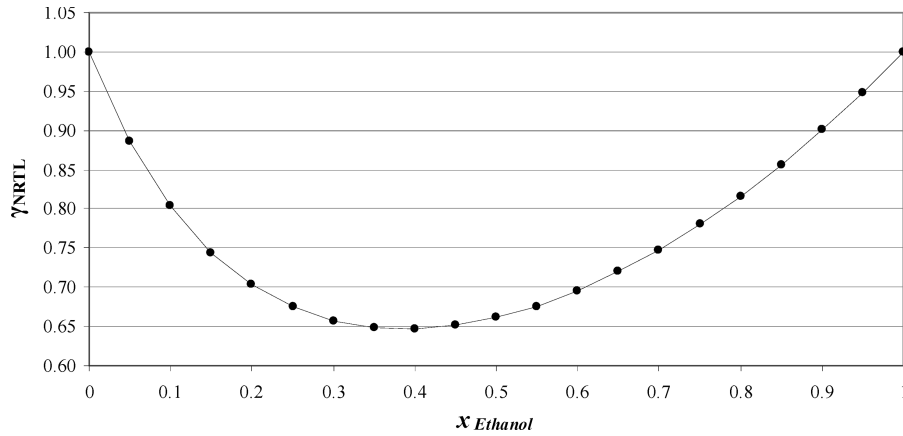
Figure 6. Characteristic curve of γ_{NRTL}^{∞} function of $x_{Ethanol}$.
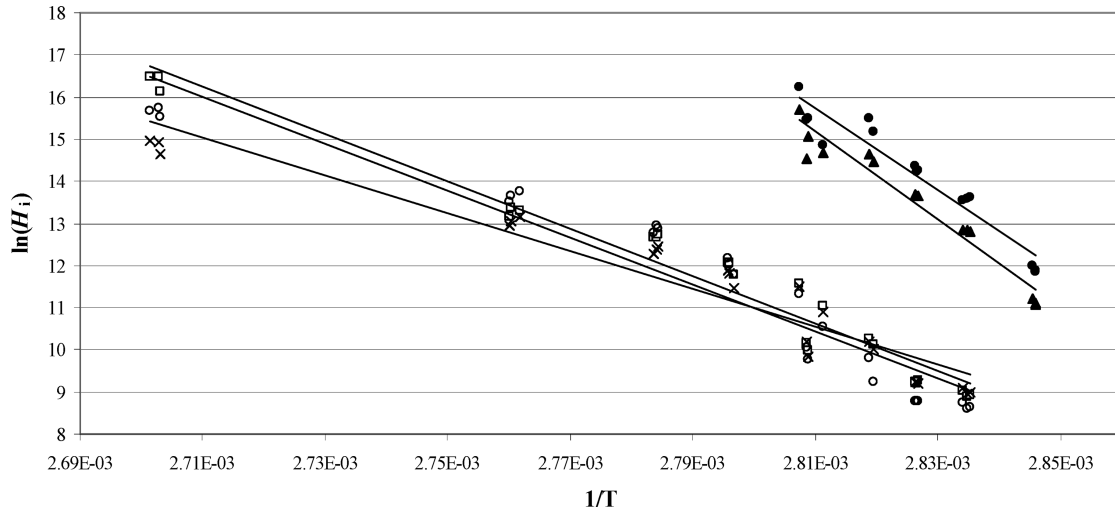
Figure 7. Representation of experimental values of ln H_i^{exp} versus $1/T$, to determine the pseudo Henry's constants of α-pinene ($\bullet$), D-limonene ($\blacktriangle$), linalool ($\square$), citral ($\bigcirc$), and linalool oxide ($\times$).

$H_i^{P_{solvent}^{sat}}$ depends not only on the temperature T/K but also on the solvent composition, which means in our case on the ethanol concentration of the solution. γ_i^{∞} is the activity coefficient of compound i at infinite dilution, a function of temperature and solvent composition. Due to the limited amount of experimental data in comparison to the number of parameters to be estimated, the Henry's constant model was simplified to

$$H_i^{P_{solvent}^{sat}}(T, \bar{x}) = H_i(T)\gamma_{NRTL}^{\infty}(\bar{x}, T) \qquad (8c)$$

where H_i is a pseudo Henry's constant of compound i only as a function of temperature

$$\ln H_i(T) = A_i' + \frac{B_i'}{T} \qquad (8d)$$

The influence of the ethanol composition on $H_i^{P_{solvent}^{sat}}$ is represented by $\gamma_{NRTL}^{\infty}(\bar{x},T)$. The activity coefficient of any solute at infinite dilution in boiling hydro-alcoholic solution was calculated by the NRTL model with only the binary interaction parameters of the solvent. Hence, from experimental data $K_i^{exp} = y_i^{exp}/x_i^{exp}$, the parameters A_i' and B_i' of the Henry's constants of aroma compounds were estimated by the method of least-squares. The criterion is to minimize the sum of the

Table 7. Henry's Constants A' and B' (from the Equation Form $A' + B'/T$) of the Aroma in Pure Water, Expressed in Pa with Respect to the Aroma Mole Fraction

compounds	A'	B'
α-pinene	288.87	−97 207
D-limonene	305.82	−103 438
linalool	168.20	−56 072
citral (Z and E)	167.14	−55 769
linalool oxide (Z and E)	137.23	−45 088

absolute deviations squared (least-squares error) between experimental values

$$\ln H_i^{exp} = \ln\left(\frac{K_i^{exp}P^{exp}}{\gamma_{NRTL}^{\infty}(\bar{x}^{exp}, T^{exp})}\right) \qquad (9a)$$

and calculated values:

$$\ln H_i^{cal} = A_i' + \frac{B_i'}{T} \qquad (9b)$$

A characteristic curve of the influence of solvent composition (ethanol molar fraction $\bar{x}_{ethanol}$) on γ_{NRTL}^{∞}, determined with the NRTL model, is represented in the Figure 6.
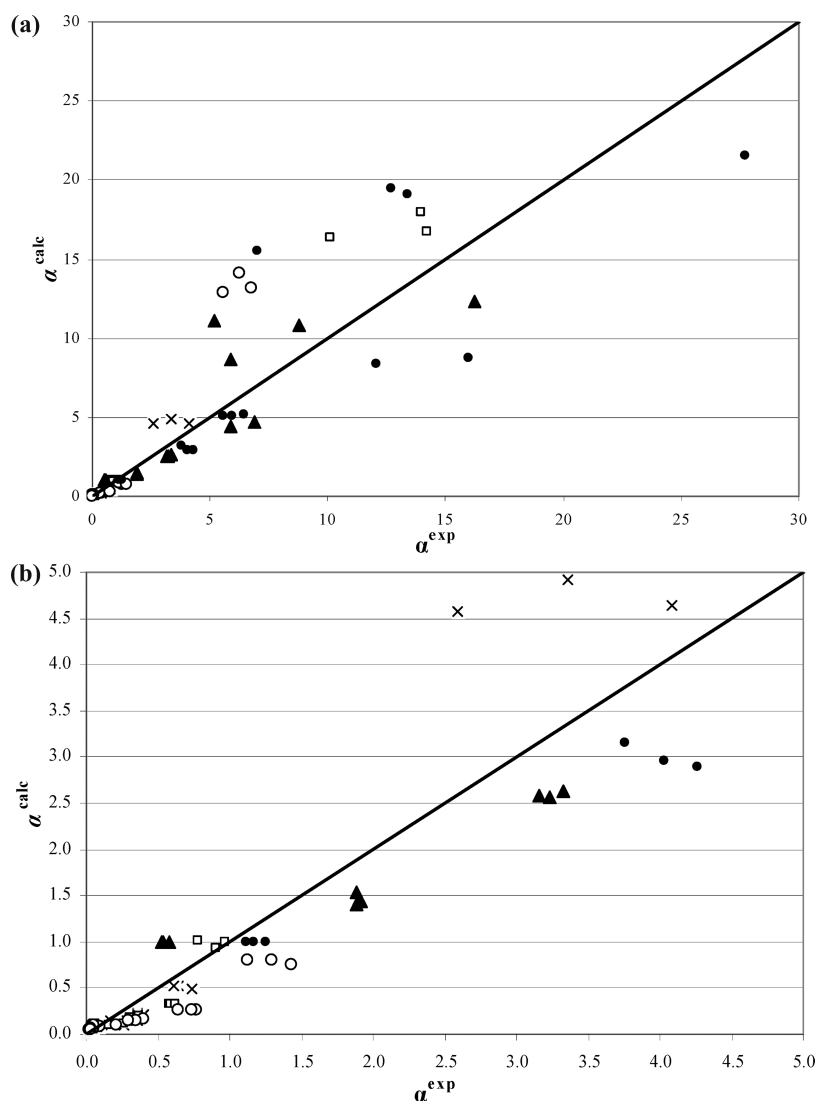
Figure 8. (a) Comparison of the α^{exp} and α^{calc} from 0 to 30 by the Henry's law type model for α-pinene (●), D-limonene (▲), linalool (□), citral (○), and linalool oxide (×). (b) Comparison of the α^{exp} and α^{calc} from 0 to 5 by the Henry's law type model for α-pinene (●), D-limonene (▲), linalool (□), citral (○), and linalool oxide (×).

A representation of experimental values of $\ln H_i^{exp}$ versus $1/T/K$ is presented in Figure 7, to determine the pseudo Henry's constants of aroma compounds.

Note that all experimental measurements of Henry's constants were obtained at boiling points. For this reason, quite good linearity is observed for all aroma compounds. The coefficients of determination R^2 were calculated: 0.96 for linalool, 0.95 for limonene, and 0.92 for linalool oxide, citral and α-pinene. We therefore validated the Henry's law type model to represent the behavior of the aroma compounds in infinite dilution and at 101.3 kPa in hydro-alcoholic solutions. The constants of the Henry's law type model are given in Table 7.

Experimental and calculated data were also compared in terms of relative volatilities. Correlations of relative volatility coefficients α^{calc} from the Henry's law type model against α^{exp} are expressed in Figure 8a. The represented α^{exp} measurements are calculated from values given in Table 4, using all data. As the experimental $K_{Ethanol}$ values are sometimes less than 1, in

the formula (eq 6) of the α^{exp}, we consider the calculated $K_{Ethanol}$ values from the NRTL model.

A zoom of the results in the interval $[0-5]$ is presented in Figure 8b.

All aroma compounds are relatively well represented by the Henry's law type model.

Mean relative errors ε between calculated values and experimental values were calculated for both models as follows (eq 10):

$$\varepsilon = \frac{1}{n} \sum \frac{|\alpha^{exp} - \alpha^{calc}|}{\alpha^{exp}} \times 100\% \tag{10}$$

where n is the number of α^{exp} measurements.

Table 8 indicates that for all of the aroma compounds, the ε values are much lower with the Henry's law type model ((2.94–22.89) %) than with the NRTL model ((12.56–56.37) %). This demonstrates that the Henry's law type model predicts the behavior of all the aroma compounds with better accuracy.

Table 8. Mean Relative Errors (ε in %) between the α^{exp} and α^{calc} for the NRTL and Henry's Law Models, According to eq 10, with n Being the Number of α Measurements

	α-pinene	D-limonene	linalool	citral (Z and E)	linalool oxide (Z and E)
n	15	15	24	24	24
ε with NRTL model	37.05	35.15	12.56	56.37	17.34
ε with Henry's law model	2.94	15.17	9.99	12.56	22.89

4. CONCLUSION

Vapor–liquid equilibria of five aroma compounds in hydro-alcoholic solutions were measured with a recirculation apparatus at a boiling point of 101.3 kPa. The presence of ethanol has a very strong effect on the partition coefficients of the aroma compounds. The NRTL and Henry's law type models were tested to correlate the experimental data. Both models well represent the behavior of the linalool and linalool oxide. However, the Henry's law type model gives better results for the representation of the monoterpene hydrocarbons and citral. The knowledge of vapor–liquid equilibria data are necessary to design and optimize distillation processes. Attention must be paid to low α values (lower than 2), because it is more difficult to separate volatile compounds from hydro-alcoholic mixtures. The Henry's law type model can thus be considered as a satisfactory model to carry out the simulation with batch distillation simulation software.

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Notes

The authors declare no competing financial interest.

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