STUDIA UBB CHEMIA, LVII, 2, 2012 (p. 29 - 45)

VAPOR - LIQUID EQUILIBRIA IN THE BINARY SYSTEM (3*R*)-(-)-LINALOOL + (3*S*)-(-)-BETA-CITRONELLOL

IOAN BATIU[a,*], GEORGES RADOIAS[b] AND ALIN BOSILCOV[b]

ABSTRACT. Vapor-liquid equilibrium data (VLE) have been measured for the binary system (3*R*)-(-)-linalool + (3*S*)-(-)-beta-citronellol. The vapor-liquid equilibrium data were correlated by means of the Wilson, NRTL and UNIQUAC equations. The binary parameters of the corresponding models were calculated. The vapor-liquid equilibrium data were used to discuss the thermodynamic properties of the mixture taking into account the intermolecular forces, proximity effect and the effect of the steric hindrance. The Modified UNIFAC (Dortmund) group contribution model was used to check their predictive capability in mixtures containing (3*R*)-(-)-linalool and (3*S*)-(-)-beta-citronellol.

Keywords: *Vapor - liquid equilibria, Terpenoids, excess Gibbs energy, Mod. UNIFAC (Dortmund), Wilson, NRTL, UNIQUAC.*

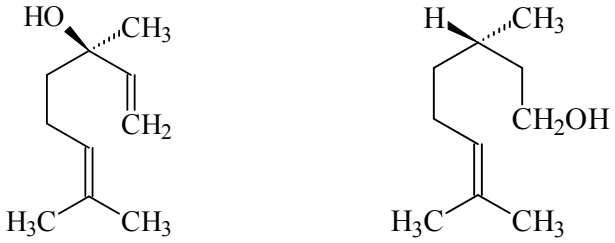
INTRODUCTION

Following up our program on measuring the vapor-liquid equilibrium data in mixtures containing terpenoids, the present work was focused on: 1. the measurement of vapor-liquid equilibria (VLE) for the binary mixtures of (3*R*)-(-)-linalool + (3*S*)-(-)-beta-citronellol; and 2. thermodynamic modeling of the experimental vapor-liquid equilibrium data of the mixtures (3*R*)-(-)-linalool + (3*S*)-(-)-beta-citronellol.

(3*R*)-(-)-Linalool [(-)-3,7-Dimethylocta-1,6-dien-3-ol] and (3*S*)-(-)-beta-citronellol [3,7-Dimethyloct-6-en-1-ol] and geraniol [3,7-Dimethylocta-2,6-dien-1-ol] are among the main components of the essential oil of geranium (*Pelargonium graveolens L, fam. Geraniaceae*), an important perfumery material. The raw essential oil is also used to isolate (3*S*)-(-)- beta-citronellol and geraniol of high purity.[1].

The chemical structures of the main components of the essential oils of geranium are presented in Figure 1. The names of the components referred to in this paper are: (-)-linalool, (-)-beta-citronellol and geraniol.

[a] "Babeş-Bolyai" University of Cluj-Napoca, Faculty of Chemistry and Chemical Engineering, Arany Janos Street 11, 400028 Cluj-Napoca, Romania, * batiu@chem.ubbcluj.ro
[b] Brüder Unterweger Essential Oils, Quality Assurance Dept., A-9911 Thal-Assling, Austria



(3*R*)-(-)-Linalool (3*S*)-(-)-beta-Citronellol

Figure 1. Chemical structure of (3*R*)-(-)-linalool, (3*S*)-(-)-beta-citronellol

Generally, essential oil components belong to the terpenoid class. Terpenoids are natural products comprising a large number of compounds with complicate chemical structures. Many essential oil components are monoterpenoids (C_{10}) and sesquiterpenoids (C_{15}), acyclic, monocyclic or bicyclic, saturated or unsaturated.

The main components of the essential oils - high value added chemicals - separate from raw essential oils by batch distillation function of their boiling points. Accurate isobaric vapor-liquid equilibrium data are necessary for the design and optimized the batch distillation column. The literature [2, 3] is very poor in the experimental vapor-liquid equilibrium data in the field of terpenoids.

No experimental VLE data are available for the binary system (-)-linalool + (-)-beta-citronellol [2, 3].

RESULTS AND DISCUSSION

Terpenoids frequently contain oxygenated functional groups, some of them being subjected to the electronic effects. Intermolecular interactions as well as steric hindrance effects or proximity effects may occur between the various functional groups.

(-)-Linalool is a acyclic terpenoid tertiary alcohol, while (-)-beta-citronellol is a acyclic terpenoid primary alcohol (Fig. 1).

The boiling points of the components

The direct experimental boiling temperature *T* of the pure terpenoids (-)-linalool and (-)-beta-citronellol were measured and presented in Table 1. The *T-P* measurements were correlated with the following Antoine equations (eqs. 1, 3).

Table 1. The experimental boiling temperatures *T*/(K) of the pure terpenoids (-)-linalool and (-)-beta-citronellol.

(-)-Linalool		(-)-beta-Citronellol	
P (Pa)	$T_{exp.}$ (K)	*P* (Pa)	$T_{exp.}$ (K)
666	343.45	666	368.55
1,333	355.55	1,333	380.80
2,000	363.10	2,000	388.25
4,000	377.25	4,000	402.70
6,666	388.45	6,666	414.15
10,000	398.45	10,000	423.25
13,332	405.65	13,332	430.85
19,998	416.55	19,998	442.20
26,664	424.85	26,664	450.25
39,996	437.45	39,996	462.85
53,328	446.65	53,328	472.25
101,325	470.15	101,325	496.40

(-)-Linalool, 12 points in the pressure range from 666 Pa to 101,325 Pa.

$$\ln(P/Pa) = 21.02499 - \frac{3{,}472.56}{(T/K) - 104.400} \quad (1)$$

In the range between 15,230 Pa and 88,730 Pa our (-)-linalool data agree well with literature data [4]. Absolute mean deviation in temperature, *AMD*(*T*) (K) was 0.50 while maximum deviation was 0.92.

Absolute mean deviation, *AMD*(*k*) was calculated using eq. (2)

$$AMD(k) = \sum_{i=1}^{N} \left| k_{\exp,i} - k_{calc,i} \right| / N \quad (2)$$

where: *k* stands for *T*, *P* or *y* representing respectively, the temperature and the pressure and the mole fraction composition of the vapor phase, while *N* is the number of experimental points.

(-)-beta-Citronellol, 12 points in the pressure range from 666 Pa to 101,325 Pa.

$$\ln(P/Pa) = 20.79777 - \frac{3{,}356.04}{(T/K) - 134.000} \quad (3)$$

The data reported in [5] for (-)-beta-citronellol, in the range between 2,000 Pa and 101,325 Pa, are 0.3 K to 2.70 K higher while in the range between 666 Pa and 2,000 Pa, are 0.57 K to 1.90 K lower than our measurements. Absolute mean deviation, *AMD*(*T*) (K) was 1.68 while maximum deviation was 2.70.

Vapor – liquid equilibrium data

A series of isobaric *T-x-y* measurements was performed at (3,333±30) Pa. The isobaric *T-x-y* measurements together with the activity coefficients, γ_i and the molar excess Gibbs energies, G^E are reported in Tab. 2 and Figs. 2 and 3.

Table 2. Experimental vapor - liquid equilibrium data of the binary system (-)-linalool (1) + (-)-beta-citronellol (2) at P = (3,333±30) Pa

T (K)	x_1	y_1	γ_1	γ_2	G^E (Jmol^{-1})
399.60	0.0000	0.0000	1.4414	1.0000	0.00
396.55	0.0350	0.1210	1.2468	1.0023	33.00
393.30	0.1030	0.3050	1.2190	1.0000	67.00
391.00	0.1590	0.4200	1.1965	1.0000	90.00
387.70	0.2450	0.5580	1.1866	1.0043	145.00
384.45	0.3460	0.6770	1.1740	1.0054	188.00
382.00	0.4250	0.7450	1.1726	1.0302	269.00
381.45	0.4460	0.7600	1.1684	1.0370	284.00
379.95	0.5100	0.8020	1.1539	1.0505	307.00
377.55	0.6250	0.8620	1.1298	1.0940	345.30
377.20	0.6470	0.8710	1.1208	1.1081	345.00
375.25	0.7840	0.9250	1.0761	1.1769	289.00
374.40	0.8840	0.9550	1.0257	1.3811	186.00
373.25	1.0000	1.0000	1.0000	1.5800	0.0000

Boiling temperature T, liquid phase, x_i and vapor phase, y_i compositions (mole fractions), activity coefficients γ_i and molar excess Gibbs energy G^E

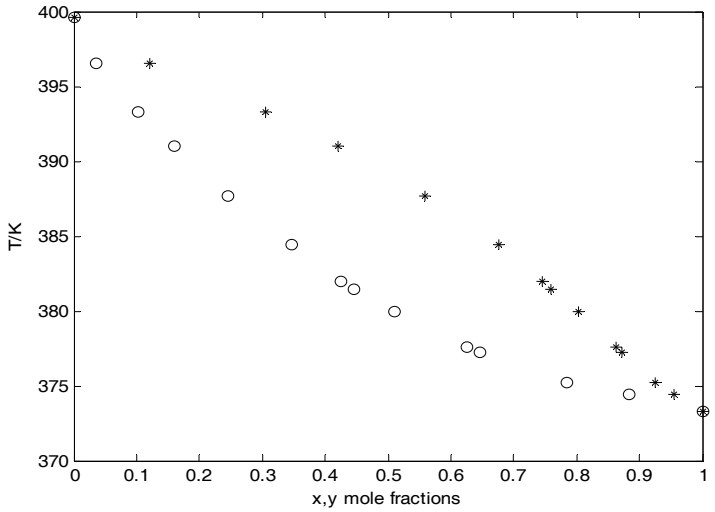


Figure 2. Experimental vapor - liquid equilibrium diagram for the binary system (-)-linalool (1) + (-)-beta-citronellol (2) at constant pressure P=3,333 Pa, temperature T/(K) as a function of the liquid phase x_i (o), or vapor phase y_i (*), mole fraction composition of component 1.

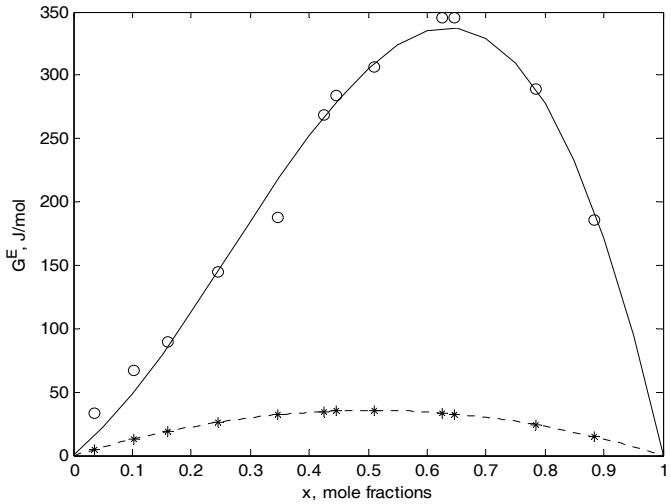


Figure 3. Variation of the molar excess Gibbs energy, G^E with mole fraction x_i, for the binary system (-)-linalool (1) + (-)-beta-citronellol (2) at a constant pressure P=3333 Pa (o) -experimental, (*) – predicted by Mod. UNIFAC (Do) model

The experimental activity coefficients γ_i were calculated by [6] (eq. 4):

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \left[\frac{\left(B_{ii} - V_i\right)\left(P - P_i^0\right) + P\delta_{ij} y_j^2}{RT} \right] \quad i,j=1,2 \qquad (4)$$

where: $\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj}$ $\quad i,j=1,2$

The standard state for the calculation of activity coefficients is the pure component at the pressure and temperature of the solution.

The second virial coefficients B_{ii} and B_{ij} were calculated by the method of Pitzer and Curl [7]. The Rackett equation (eq. 5) was used to calculate the liquid molar volumes V_i.

$$V = \frac{RT_c}{P_c}\left(0.29056 - 0.08775\omega\right)^a ; a = 1 + (1 - T_r)^{\frac{2}{7}} \qquad (5)$$

where: T_c, P_c, T_r are critical temperature, critical pressure and reduce temperature, respectively; ω is acentric factor.

The critical properties for (-)-linalool and (-)-beta citronellol were estimated by the method proposed by Bae et al. [8] and by Joback's group contribution method [9].

The molar excess Gibbs energies, G^E (J mol^{-1}) were calculated from (eq. 6):

$$G^E = RT\sum x_i \ln \gamma_i \quad (6)$$

In the binary system (-)-linalool + (-)-beta-citronellol the values of the experimental activity coefficients, γ_i range from ca. 1.00 to ca. 1.58. The experimental fugacity coefficients, φ_i are very closed to unity. This means a quasi-ideal behavior of the liquid phase and ideal behavior of the vapor phase. The binary system (-)-linalool + (-)-beta-citronellol shows positive deviations from ideality (Fig. 3). The molar excess Gibbs energies, G^E calculated from the isobaric *T-x-y* measurements range from 0 ($Jmol^{-1}$) to ca. + 345 ($Jmol^{-1}$)

Another series of *T-P* measurements was performed at four constant liquid phase compositions, x_i (mol.fr.). For the mixtures of (-)-linalool (1) + (-)-beta-citronellol (2): x_1=0.1590±0.001; x_1=0.4250±0.001; x_1=0.5100±0.001; x_1=0.7840±0.001. The *T-P-x* measurements are reported in Tab. 3.

Table 3. Experimental vapor - liquid equilibrium data of the binary system (-)-linalool (1) + (-)-beta-citronellol (2).

T (K)	x_1	*P* (Pa)
362.35	0.1590	666
374.35	0.1590	1,333
381.55	0.1590	2,000
387.15	0.1590	2,666
391.75	0.1590	3,333
354.15	0.4250	666
365.75	0.4250	1,333
372.95	0.4250	2,000
378.15	0.4250	2,666
383.15	0.4250	3,333
349.65	0.5100	666
361.75	0.5100	1,333
370.05	0.5100	2,000
375.25	0.5100	2,666
379.75	0.5100	3,333
344.55	0.7840	666
357.05	0.7840	1,333
364.55	0.7840	2,666
376.45	0.7840	3,333

Boiling temperature *T*, liquid phase compositions, x_i (mol.fr.) and pressure *P*.

Check the thermodynamically consistency

The isobaric *T-x-y* measurements of the mixtures (-)-linalool + (-)-beta-citronellol were found to be thermodynamically consistent as tested by using the maximum likelihood multimodel fitting method described by Panaitescu [10]. The objective function (S) is defined as follows (eq. 7):

$$S = \sum_{i=1}^{N} \left[\left(P_{ie} - P_{ic}\right)^2 / \sigma_P^2 + \left(T_{ie} - T_{ic}\right)^2 / \sigma_T^2 + \left(x_{ie} - x_{ic}\right)^2 / \sigma_x^2 + \left(y_{ie} - y_{ic}\right)^2 / \sigma_y^2 \right] \quad (7)$$

where: N is the number of experimental points; P_{ie}, T_{ie}, x_{ie} and y_{ie} are the experimental data and P_{ic}, T_{ic}, x_{ic} and y_{ic} are the corresponding calculated values for pressure, temperature, and the liquid and the vapor phase compositions, respectively; σ_P, σ_T, σ_x and σ_y are the standard deviations for pressure, temperature and liquid and vapor phase compositions. In this paper, the standard deviations were set to: σ_P = 60 Pa, σ_T = 0.05 K, σ_x = 0.001 mol. fr. and σ_y = 0.001 mol. fr., respectively. According to this test the isobaric *T-x-y* measurements are considered consistent if the values of the statistic criterion of selection of the each experimental point (*Ro*) and of the all experimental points (*global Ro*) are less than 2.45. At *P* = (3,333±30) Pa the values of the (*global Ro*) criterions were: 0.487 (Wilson), 0.622 (NRTL) and 1.154 (UNIQUAC), while the all values of the (*Ro*) criterions are less than 2.45.

The thermodynamic consistency of the isobaric *T-x-y* measurements was also checked against the point-to-point test of Van Ness, modified by Fredenslund [11] using a fourth order Legendre polynomial. According to this test, the data are considered consistent if the absolute mean deviation in *y*, *AMD(y)* (mol.fr.) is less than 0.01. At *P*=(3,333±30) Pa we found *AMD(*y) (mol.fr.) = 0.00387.

Reduction of the experimental VLE data by non-electrolyte solutions models

The experimental VLE data of the binary system (-)-linalool + (-)-beta-citronellol have been correlated by means of the Wilson [12], NRTL [13, 14] and UNIQUAC [15] equations. The equations used are the same as in others applications, see for example [16] and need not to be repeated here.

The binary parameters of the models were obtained from the isobaric *T-x-y* measurements and from the *T-P-x* measurements. They were calculated by minimizing the following objective functions (***S***): the maximum likelihood multimodel fitting method [10] (eq. 7) (B_{12}, B_{21}) and the boiling points condition, (eq. 8) (A_{12}, A_{21}):

$$S = \sum_{i=1}^{N} [1 - (P_1^0 / P) x_1 \gamma_1(A_{12}, A_{21}) - (P_2^0 / P) x_2 \gamma_2(A_{12}, A_{21})]_i = \min. \quad (8)$$

where: N is the number of experimental points, P is the total pressure, P_1^0 and P_2^0 are the vapor pressures of the pure components 1 and 2, A_{12} and A_{21} are, respectively, the binary parameters of the Wilson, NRTL and UNIQUAC models, γ_1 and γ_2 are the activity coefficients, x_1 and x_2 are the mole fractions of the pure components 1 and 2 in the liquid phase.

The purport of the calculated binary parameters (B_{12}, B_{21}) (eq. 7) is: $[(\lambda_{12}-\lambda_{11}),(\lambda_{21}-\lambda_{22})]$ (Wilson); $[(g_{12}-g_{22}),(g_{21}-g_{11})]$ (NRTL) and $[(u_{12}-u_{22})/R$, $(u_{21}-u_{11})/R]$ (UNIQUAC). The purport of the calculated binary parameters (A_{12}, A_{21}) (eq.8) is: $[\Lambda_{12},\Lambda_{21}]$ (Wilson); $[\tau_{12},\tau_{21}]$ (NRTL) and $[(u_{12}-u_{22}),(u_{21}-u_{11})]$ (UNIQUAC).

The values of the binary parameters of each model (B_{12}, B_{21}), respectively (A_{12}, A_{21}), the statistic criterions of the all experimental points (*global Ro*), the absolute mean deviations in the vapor phase compositions, *AMD(y)* (mol. fr.) and in pressure, *AMD(P)* (Pa) are reported in Tables 4 and 5.

Table 4. Binary parameters (B_{12}, B_{21}) of the Wilson and NRTL (α = 0.3) and UNIQUAC models for the binary system (-)-linalool (1) + (-)-beta-citronellol (2) obtained from isobaric *T-x-y* measurements at constant pressure *P*=3,333 Pa (the object function - the maximum likelihood multimodel fitting method). ($^*A_{12}$, $^*A_{21}$) are the corresponding binary parameters calculated from (B_{12}, B_{21}).

Models	T-P-x-y		*global Ro*
	B_{12}/($^*A_{12}$)	B_{21}/($^*A_{21}$)	
Wilson	-1757.99/ *1.75904	4981.51/ *0.21474	0.487
NRTL (α=0.3)	5565.46/ *1.73669	-2796.93/ *-0.87278	0.622
UNIQUAC	220.81/ *1835.81	-159.41/ *-1325.33	1.154

(B_{12}, B_{21}): Wilson $[(\lambda_{12}-\lambda_{11}),\ (\lambda_{21}-\lambda_{22})]$ and NRTL $[(g_{12}-g_{22}),\ (g_{21}-g_{11})]$ parameters unit (Jmol^{-1}); UNIQUAC $[(u_{12}-u_{22})/R,(u_{21}-u_{11})/R]$ parameter unit (K); ($^*A_{12}$, $^*A_{21}$) Wilson and NRTL dimensionless parameters; UNIQUAC parameter unit (Jmol^{-1}). The statistic criterion of the all experimental points (*global Ro*).

It should be noted that the values of the binary parameters of the Wilson, NRTL and UNIQUAC models, for the same isobaric *T-x-y* measurements, are not identical when the two objective functions are used. Using the same objective function - the boiling points condition – the calculated binary parameters from the isobaric *T-x-y* measurements and from *T-P-x* measurements are different. This fact do not affect the vapor-liquid prediction if the binary parameters are used only to calculate vapor-liquid equilibrium data at the same pressure or at others pressures. Consequently, the vapor phase compositions, y_i (mol. fr.) at the pressure of *P*=3,333 Pa, calculated using the Wilson, NRTL and UNIQUAC binary parameters, obtained from our *P-T-*x_i measurements, are in good agreement with our *P-T-*x_i*-*y_i experimental data. The absolute mean deviations in the vapor phase composition, *AMD(y)* (mol.fr.) are: 0.01 (Wilson); 0.01 (NRTL) and 0.007 (UNIQUAC), respectively. The absolute mean deviations in pressure, *AMD(P)* (Pa) are: 130 (Wilson); 124 (NRTL) and 35 (UNIQUAC), respectively.

Table 5. Binary parameters (A_{12}, A_{21}) of the Wilson and NRTL (α = 0.3) and UNIQUAC models for the binary system (-)-linalool (1) + (-)-beta-citronellol (2) obtained from isobaric *T-x-y* measurements at constant pressure *P*=3,333 Pa, respectively from *T-P-x* measurements (the object function - the boiling points condition).

Models	**T-P-x-y**		*AMD(y)* (mol. fr.)	*AMD(P)* (Pa)	**T-P-x**		*AMD(P)* (Pa)
	A_{12}	A_{21}			A_{12}	A_{21}	
Wilson	1.98464	0.13072	0.0035	13	2.65891	0.01148	57
NRTL (α=0.3)	16.8535	18.8344	0.0143	84	2.97777	-1.33218	57
UNIQUAC	607.230	405.87	0.0048	21	725.885	-465.710	60

Absolute mean deviations in the vapor phase composition, *AMD(y)* and in pressure, *AMD(P)*; Wilson and NRTL dimensionless parameters; UNIQUAC parameter unit ($Jmol^{-1}$)

Table 7. Modified UNIFAC (Dortmund) group interaction parameters [24]

n	m	a_{nm} (K)	b_{nm}	c_{nm} (K^{-1})	a_{mn} (K)	b_{mn}	c_{mn} (K^{-1})
1	2	189.66	-0.2723	0.000E+00	-95.418	0.0617	0.000E+00
1	5	2777	-4.674	1.551E-03	1606	-4.7460	9.181E-04
2	5	2649	-6.5080	4.822E-03	1566	-5.809	5.197E-03

Boiling points correlation

The boiling points of the binary systems (-)-linalool + (-)-beta-citronellol were correlated by the equation proposed by Wisniak and Tamir [17] (eq. 9).

$$T/K = \sum_{i=1}^{n} x_i T_i^0 / K + \sum_{i,j=1}^{n} \{x_i x_j \sum_{k=0}^{m} C_k (x_i - x_j)^k\} + \\ + x_1 x_2 x_3 \{A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3)\} \quad (9)$$

where: n is the number of components (n = 2 or 3), T_i^0 is the boiling point of the pure components i and m is the number of terms in the series expansion of $(x_i - x_j)$, C_k are the binary constants while A, B, C, D are ternary constants.

Root mean square deviation (RMSD) is defined by eq. (10)

$$RMSD(T) = \left[\sum_{i=1}^{i=N} (T_{i,\exp} - T_{i,calc.})^2 / (N-1) \right]^{1/2} \quad (10)$$

For the binary system (-)-linalool + (-)-beta-citronellol, with 4 coefficients *C(i)* (eq. 9): C(1) =-23.01009; C(2) = 1.22011; C(3) =-0.29773; C(4)=9.98300, the absolute mean deviation *AMD*(*T*) (K) (eq. 2) and the root mean square deviation *RMSD*(*T*) (K) (eq. 10) are 0.057 and respectively 0.021.

Check the predictive capability of the Modified UNIFAC (Dortmund) group contribution model

The most common group contribution methods for the prediction of phase equilibria are: ASOG [18, 19, 20], original UNIFAC [11, 21, 22], Modified UNIFAC (Dortmund) [23, 24, 25], Modified UNIFAC [26] (Lyngby) and DISQUAC [27, 28].

The Modified UNIFAC (Dortmund) group contribution model is the most useful model to predicts vapor-liquid equilibrium data.

According to the Mod. UNIFAC (Do) model the molecules are decomposed in structural groups. Each structural group is characterized by van der Waals volume, R_k and van der Waals surface area, Q_k.

The equations used in Modified UNIFAC (Dortmund) model [24] to calculate activity coefficients, γ_i, VLE data or G^E are the same as in the original UNIFAC [11, 21].

The Mod. UNIFAC (Do) is revised and extended periodicaly [29-35] to improve the capability of prediction.

One of the main differences between original UNIFAC (eq. 9) and Modified UNIFAC (Do) (eq. 10) is the introduction of temperature dependent of the interaction parameters, ψ_{nm}, between main structural groups n and m,

to permit a better description of the real phase behavior as a function of temperature:

$$\text{Original UNIFAC: } \psi_{nm} = \exp\left[-\frac{a_{nm}}{T}\right] \tag{9}$$

$$\text{Mod. UNIFAC (Do): } \psi_{nm} = \exp\left[-\frac{a_{nm} + b_{nm}T + c_{nm}T^2}{T}\right] \tag{10}$$

Assessment of geometrical parameters

The molecules of (-)-linalool and (-)-beta-citronellol have been decomposed in structural groups according to the Mod. UNIFAC (Do) model. Table 6 lists the van der Waals values of R_k and Q_k for the all structural groups referred to in this paper.

Table 6. R_k and Q_k parameters and group assignment for the Modified UNIFAC (Dortmund) Method [24]

Main group	Subgroup	No	R_k	Q_k
1 "CH_3"	CH_3	1	0.6325	1.0608
	CH_2	2	0.6325	0.7081
	CH	3	0.6325	0.3554
	C	4	0.6325	0.0000
2 "C=C"	CH_2=CH	5	1.2832	1.6016
	CH=C	7	1.2832	0.8962
5. "OH"	OH(p)	14	1.2302	0.8927
	OH(t)	82	0.6895	0.8345

Assessment of interaction parameters

We used the group interaction parameters published in [24].Table 7 lists the Modified UNIFAC (Do) Group Interaction Parameters.

Comparison with experiment

A comparison between experimental VLE data (*T-P-x-y*) and predicted VLE data (the vapor phase compositions y_i and the temperatures T_i) is done. More discussions are necessary for the binary mixture (-)-linalool + (-)-beta-citronellol.

The Mod. UNIFAC (Do) model predicts satisfactory the composition of the vapor phase, y_i. The absolute mean deviation in the vapor phase composition, *AMD(y)* (mol.fr.) is 0.009. The absolute mean deviation in temperature, *AMD(T)* (K) is 1.52. We appreciate that the temperature prediction is rather poor.

The excess Gibbs energy, G^E, provides a more accurate comparison. The experimental excess Gibbs energy, G^E_{exp} presents positive deviations from ideality (Figure 3). At ca. *T*=377.55 K, G^E_{exp} (*x* = 0.6250) is ca. 345 (Jmol^{-1}).

The Mod. UNIFAC (Do) model predicts small deviations from ideality. The excess Gibbs energy predictions, G^E_{UNI} are positive on the all range of the compositions of the liquid phase, x_i. At ca. *T*=377.55 K, the equimolecular G^E_{UNI} is ca. 35 (Jmol^{-1}) (Fig. 3) The conclusion is that the excess Gibbs energy predictions are unsatisfactorily.

Analysis in terms of intermolecular forces of the thermodynamic properties of the mixtures containing (-)-linalool + (-)-beta-citronellol

Thermodynamic properties of any pure substance are determined by intermolecular forces that operate between the molecules of that substance. Thermodynamic properties of the mixtures depend on intermolecular forces that operate between the molecules belonging to the same component, but also to interaction between dissimilar molecules of the mixture. Frequently, the theory of intermolecular forces gives us no more than a qualitative, or perhaps semiquantitative basis for understanding phase behaviour, but even such a limited basis can be useful for understanding and correlating experimental results. A brief discussion of the intermolecular forces in molecular thermodynamics of fluid-phase equilibria [36] and in supramolecular chemistry [37] was done.

Literature describes different types of intermolecular forces [36], but for our purpose here, only *induction forces* (between an induced dipole – e.g. a dipole induced in a molecule with polarizable electrons), *dispersion forces* (forces of attraction between nonpolar molecules based on *hydrophobic interactions*) and, respectively *specific (chemical) forces* leading to hydrogen bonds were considerated. Also we take into consideration the van der Waals forces [37] and the steric hindrance effect.

The calculated dipole moment of the (-)-linalool is 1.42 D, while the calculated dipole moment of the (-)-beta-citronellol is 2.50 D, indicating possible strong electrostatic forces of associations between these two compounds. The values of the calculated dipole moments were obtained using, for geometry optimization - hamiltonian: B3LYP (density functional theory); basis set: 6-31G(d) (Gaussian98) and for dipole moment - hamiltonian: B3LYP; basis set: 6-31G(d) (Gaussian98).

(-)-Linalool and (-)-beta-citronellol contain two active functional groups, hydroxyl, –OH and double bonds, -CH=CH$_2$ and/or –CH=C<. In (-)-linalool hydroxyl group, –OH is sterically hindered by methyl group, -CH$_3$. Between hydroxyl group, –OH and double bond, -CH=CH$_2$ there is a proximity effect.

The major contribution to the non-ideality of the mixture comes from the hydrogen bonds between hydroxyl groups, and from the like weak dipole/ dipole, -O-/-O- interactions, due to non bonding electrons from the hydroxyl group.

When a strongly hydrogen-bonded substance is dissolved in a nonpolar solvent (such as hexane o cyclohexane), hydrogen bonds are broken until all the molecules exist as monomers rather then dimers, trimers, or higher aggregates. The solvation of the alcohol broke the hydrogen bond and, such braking requires energy, much heat is absorbed (positive deviations from ideality) [36].

Linear primary alcohols exhibit large deviations from ideality, e.g. binary system (1-butanol + hexane) has a G^E (x_1=0.50) of the order of 1186 (J mol^{-1}) at 333 K, respectively, binary system (1-butanol + cyclohexane) has G^E (x_1==0.50) of the order of 1100 (J mol^{-1}) at 318 K [38]. *Tertiary alcohols*, due to the steric hindrance, exhibit smaller deviations than primary linear alcohols, e.g. binary system {2-methyl-2-propanol (*tert*-butanol) + cyclohexane} has G^E (x_1=0.50) of the order of 935 (J mol^{-1}) at 318 K [38].

In a mixture of two alcohols, the hydrogen bonds compensate and this results in small deviation from ideality. Binary system (ethanol + 2-propanol) has G^E (x_1==0.50) of the order of 35 (J mol^{-1}) at 313.15 K [38].

In (-)-linalool due to additional alkyl groups and to the two double bonds, to the like weak dipole/dipole, -O-/-O- interactions, the dipole/induced dipole interactions, –O-/π, from H_2C=CH- and >C=CH- (double bonds) and the induced dipole/induced dipole interactions, π/π, from H_2C=CH-/H_2C=CH-, H_2C=CH-/>C=CH- and respectively >C=CH-/>C=CH- are added. In mixture with primary linear alcohols, e.g. in the binary system (linalool + 1-butanol), the (-)-linalool's interactions are added and this results in a relatively higher deviation from ideality. At 357 K, G^E (x_1=0.69) is ca. 213 (J mol^{-1}) [4].

In (-)-beta-citronellol, due to additional alkyl groups and to the one double bond, to the like weak dipole/dipole, -O-/-O- interactions, the dipole/ induced dipole interactions, –O-/π, from >C=CH- (double bond) and the induced dipole/induced dipole interactions, π/π, from >C=CH-/>C=CH- are added. In the binary system (-)-linalool + (-)-beta-citronellol}, the (-)-beta-citronellol's interactions are added and this results in a relatively higher deviation from ideality. At ca 377 K, G^E (x_1=0.625) is ca. 345 (J mol^{-1}) (Fig.3) (this paper).

Due to the important hydrocarbon part of the involved molecules, *hydrophobic interactions* could not be negligible [36, 37]. The hydrophobic effect arises mainly from the attractive forces between hydrophobic parts of the molecules. Hydrophobic effects generally relate to the exclusion from polar solvent of large particles or those are weekly solvated (e.g. hydrogen bonds or dipolar interactions). This can produce effects resembling attraction between one organic molecule and another, although there are in addition van der Waals and π/π attractions between organic molecules themselves. The hydrophobic

effect creates a higher degree of local order, producing a decrease in entropy that leads to an unfavorable Gibbs energy. The entropic contribution, TS^E to the excess Gibbs energy, G^E is even larger than the enthalpic contribution, H^E [36].

CONCLUSIONS

This paper has reported original vapor - liquid equlibrium data in binary system (-)-linalool + (-)-beta-citronellol.

Reduction of the vapor-liquid equlibrium data was carried out by means of the Wilson, NRTL and UNIQUAC equations. The binary parameters of the corresponding models were calculated from the isobaric *T-x-y* measurements and from the *T-P-x* measurements.

The Modified UNIFAC (Dortmund) group contribution model was used to check their predictive capability in mixtures containing (3*R*)-(-)-linalool and (3*S*)-(-)-beta-citronellol. The Mod. UNIFAC (Do) model predicts satisfactory the composition of the vapor phase, y_i. We appreciate that the temperature prediction is rather poor.

(-)-Linalool, (-)-beta-citronellol, main components of the essential oils of geranium are molecules containing various functional groups. It was presented an analysis in terms of intermolecular forces of the thermodynamic properties of the mixtures containing (-)-linalool, (-)-beta-citronellol taking into consideration the values of the molar excess Gibbs energy, G^E.

EXPERIMENTAL SECTION

Chemicals

(-)-Linalool [(-)-3,7-Dimethylocta-1,6-dien-3-ol], CAS RN 78-70-6, Brüder Unterweger GmbH, Austria, material of started purity >99.4 %, tested by Hewlett-Packard 6890 gas-chromatograph, was used without further purification.

(-)-beta-Citronellol [3,7-Dimethyloct-6-en-1-ol], CAS RN 106-22-9, Brüder Unterweger GmbH, Austria, material of started purity >99.4 %, tested by Hewlett-Packard 6890 gas-chromatograph, was used without further purification.

Apparatus and procedure

An all-glass 240-cm^3 recirculation still (Sieg and Röck Type, Normag Labor-und Verfahrenstechnik GmbH & Co., Hofheim am Taunus, Germany) was used. The equilibrium temperature *T* was measured by means of a termistor thermometer connected to a digital multimeter (YSI 4600, USA) calibrated against ITS-90, within $\sigma(T)$ (K)=0.05. A pressure controller (Normag) maintained the pressure *P* within 30 Pa around the desired values. *P* was measured using a mercury-filled U-tube together with a cathetometer within $\sigma(P)$ (Pa)=30. Atmospheric pressure was measured by a barometer with an accuracy of $\sigma(P)$ (Pa)=13.

Prior to an experimental run, the equilibrium still was thoroughly cleaned and evacuated. It was then charged with the appropriate amounts of components and pressure was adjusted to the required value by means of a vacuum pump. Equilibrium was attained under continuous stirring and recirculation of the two phases for 1 h. Samples of the liquid and condensed vapor were taken after pressurizing the apparatus to atmospheric pressure.

The equilibrium still (Stage Type, i-Fischer Labodest, Model 602-D, Germany) was also used. These equilibrium still does not work properly to obtain accurate vapor-liquidequilibrium data in the field of terpenoids.

Sample analysis

The equilibrium vapor and liquid compositions were determined by gas chromatography, carried out on two different instruments.

Dual channel analysis was performed on a Hewlett-Packard 5890 Series II gas-chromatograph, equipped with flame ionization detectors (GC-FID), using two fused silica capillary columns coated with stationary phases of different polarity: Supelcowax TA-10, (60m x 0.32 mm i.d., film thickness 0.5 μm) (polar) and SPP – 1, (60 m, 0.32 mm i.d., film thickness 0.25 μm) (nonpolar). Oven temperature was programmed as follows: 333 °K (held 3 min), then at a rate of 4°K/min to 483 °K and held 20 min. Injector and detector temperatures were 533 K, respectively 543 K. Hydrogen was used as carrier gas at a pressure of 1.2 bar. Injection volume was 0.5×10^{-3} mL (split mode), at a split ratio of 1:20.

A Hewlett-Packard 6890 gas-chromatograph equipped with a flame ionization detector (GC-FID) was also used. The semi-polar system consisted of a HP-5 fused silica capillary column (30m x 0.25 mm i.d., film thickness 0.25 μm). The temperature program was: 323 °K (held 2 min) at 2 °K/min to 453 °K, and then at 20 °K/min to 523 °K and held 2 min. Carrier gas was He at a flow rate of 1 mL/min. Injector and detector temperatures were 523 °K. Injection volume was 0.5×10^{-3} mL (split mode), with a split ratio of 1:20.

Calibration was performed using gravimetrically prepared solutions. The response factor of the detector was 0.973 (polar column), 1.036 (non-polar column) and 1.05 (semi-polar column). Very good separations were achieved under these conditions. The precision of the analyses was generally within $\sigma(x_i) = \sigma(y_i) = 0.001$ in mole fraction, at any concentration.

ACKNOWLEDGMENTS

The authors gratefully acknowledges to Dr. Răzvan Podea (S.C. Natex S.R.L. Cluj-Napoca, Romania) and Dr. Szücs-Balàzs Jòzsef-Zsolt (“Babeş-Bolyai” University of Cluj-Napoca, Romania) for their help in the analytical work and to M.Sc. Ing. Jesus Manuel Flores Arizaca (Universidad Nacional Amazónica Madre de Dios, Puerto Maldonado, Perú) for their help in the experimental work.

REFERENCES

1. G. Radoias, A. Bosilcov, I. Batiu, “Odorante Naturale în Parfumeria Modernă (Natural Fragrances in Modern Parfumery)”, Editura Casa Cărţii de Ştiinţă, Cluj-Napoca, **2005**, chapter 4.
2. I. Wichterle, J. Linek, Z. Wagner and H.V. Kehiaian, “Vapor-Liquid Equilibrium Bibliographic Database”, 9th Ed. CD-ROM, ELDATA, Paris, France, **2004**.
3. I. Wichterle, J. Linek, Z. Wagner, J.-C. Fontaine, K. Sosnkowska-Kehiaian and H.V. Kehiaian, „Vapor-Liquid Equilibrium in Mixtures and Solutions”. Landolt-Boernstein Numerical Data and Functional Relationships in Science and Technology, New Series. W. Martienssen Ed., Vol. IV/13A. Springer-Verlag, Berlin-Heidelberg, Germany, **2007**.
4. D. Dongshun, L. Haoran, H. Shijun, *J. Chem. Thermodynamics,* **2002**, *34*, 1431.
5. ◊ ◊ ◊ “Perry’s Chemical Engineer’s Handbook”, Seventh Edition, McGraw-Hill, Late Editor, R.H. Perry, Editor D.W. Green, Assoc. Editor J.O. Malonay, New York, **1997**, section 2.
6. H.C. Van Ness and M.M. Abbott, “Classical Thermodynamics of Non-electrolyte Solutions”, Mc Graw-Hill Book Co. New York, **1982**.
7. K.S. Pitzer and R.F. Curl, *J. Am. Chem. Soc.*, **1957**, *79*, 2369.
8. H.K. Bae, S.Y. Lee and A.S. Teja, *Fluid Phase Equilib.*, **1991**, *66*, 225.
9. R.C. Reid, J.M. Prausnitz and B.E. Poling. “The Properties of Gases and Liquids”, 4th Ed. Mc Graw-Hill, Book Company USA, New York, **1987**.
10. G.M. Panaitescu, *Rev. Chim.,* **1982**, *33*, 1110; *Ind. Chem. Eng.,* **1985**, *25*, 68.
11. Aa. Fredenslund, J. Gmehling and P. Rasmunsen, “Vapor-Liquid Equilibria using UNIFAC, A Group Contribution Methods”, Elsevier, Amsterdam, **1977**, chapter 4.
12. G.M. Wilson, *J. Am. Chem.Soc.,* **1964**, *86*, 127.
13. H. Renon and J.M. Prausnitz, *A.I.Ch.E. J.,* **1968**, *14*, 135.
14. H. Renon and J.M. Prausnitz, *Ind. and Eng. Chem. Process. Des. Dev.,* **1969**, *8*, 413.
15. D.S. Abrams and J.M. Prausnitz, *A.I.Ch.E. J.*, **1975**, *21*, 116.
16. I. Batiu, *Studia UBB Chemia,* **2011**, *LVI*, 37.
17. J. Wisniak, A. Tamir *Chem. Eng Sci.*, **1976**, 31, 631.
18. E.L. Derr, C.H. Deal, *Inst. Chem. Eng. Symp. Ser.* (London), **1969**, *32*, 40.
19. K. Kojima, K. Tochigi, “Prediction of Vapor-Liquid Equilibria by the ASOG Method”, Kodansha-Elsevier Tokyo, **1979**.
20. K. Kojima, D. Tiegs, J. Gmehling, K. Tochigi*, J. Chem. Eng. Jpn.,* **1990**, *23*, 453.
21. Aa. Fredenslund, R. L. Jones, J. M. Prausnitz, *AIChE Journal*, **1975**, *21*, 1086.
22. H.K. Hansen, P. Rasmussen, Aa. Fredenslund, M. Schiller, J. Gmehling, *Ind. Eng. Chem. Res.,* **1991**, *30*, 2352.
23. U. Weidlich, J. Gmehling, *Ind. Eng. Chem. Res.,* **1987**, *26*, 1372.

24 J. Gmehling, J. Li, M. Schiller, *Ind. Eng. Chem. Res.,* **1993**, *32*, 178.

25. J. Gmehling, J. Lohmann, A. Jakob, J. Li, R. Joh, *Ind. Eng. Chem. Res.,* **1998**, *37*, 4876.
26. B.L. Larsen, P. Rasmussen, Aa. Fredenslund, *Ind. Eng. Chem. Res.,* **1987**, *26*, 2274.
27. H.V. Kehiaian, J-P.E. Grolier, G.C. Benson, *Journal of Chimie Physique,* **1978**, *75*, 1031.
28. H.V. Kehiaian, B. Marongiu, *Fluid Phase Equilib.*, **1988**, *40*, 23.
29. J. Lohmann, R. Joh, J. Gmehling, *Ind. Eng. Chem. Res.,* **2001**, *40*, 957.
30. R. Wittig, J. Lohmann, R. Joh, S. Horstmann, J. Gmehling, *Ind. Eng. Chem. Res.,* **2001**, *40*, 5831.
31. J. Lohmann, J. Gmehling, *J. Chem. Eng. Jpn,* **2001**, *34*, 43.
32. J. Gmehling, R. Wittig, J. Lohmann, R. Joh, *Ind. Eng. Chem. Res.,* **2002**, *41*, 1678.
33. R. Wittig, J. Lohmann, J. Gmehling, *AIChE Journal*, **2003**, *49*, 530.
34. A. Jakob, H. Grensemann, J. Lohmann, J. Gmehling, *Ind. Eng. Chem. Res.,* **2006**, *45*, 7924.
35, 36. S. Nebig, J. Gmehling, *Fluid Phase Equilib*, **2010**, *294*, 206.
36. J.M. Prausnitz, R.N. Lichtenthaler, E.G. Azevedo, "Molecular Thermodynamics of Fluid-Phase Equilibria" Printece Hall PTR Printice-Hall Inc. Upper Saddle River, New Jersey, **1999**, chapter 4.
37. J.W. Steed, J.L. Atwood "Supramolecular Chemistry", John Wiley & Sons, Ltd, Baffins Lane, Chickester, **2009**, chapter 1.
38. D.R. Lide, H.V. Kehiaian "CRC Handbook of Thermophysical and Thermochemical Data" CRC Press Inc. Boca Raton Ann Arbor London Tokyo, **1994**, section 3.