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ANALYSIS IN TERMS OF THE MODIFIED UNIFAC (DORTMUND) GROUP CONTRIBUTION MODEL OF THE EXPERIMENTAL VAPOR - LIQUID EQUILIBRIUM DATA IN BINARY AND TERNARY SYSTEMS CONTAINING (1*R*,4*S*)-(+)-FENCHONE, METHYL CHAVICOL AND *trans*-ANETHOLE

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ABSTRACT. The experimental vapor-liquid equilibrium data (VLE) in binary and ternary systems which contain (1*R*,4*S*)-(+)-fenchone, methyl chavicol and *trans*-anethole, reported in previous papers, were used to check the predictive capability of the Modified UNIFAC (Dortmund) group contribution model in mixtures containing terpenoids. A comparison with the experimental VLE data was done. The Mod. UNIFAC (Do) group contribution model predicts satisfactory VLE data in all the binary and ternary systems but inadequately the values of the excess Gibbs energy. The Modified UNIFAC (Dortmund) group contribution model is the most useful model to predicts vapor-liquid equilibrium data.

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

INTRODUCTION

Reliable phase equilibrium information of the system to be separated is most important for the development, design and optimization of separation processes. Since experimental data are often missing or of poor quality, group contribution methods became increasingly valuable.

The most common group contribution methods for the prediction of phase equilibria are: ASOG [1, 2, 3], original UNIFAC [4, 5, 6], Modified UNIFAC (Dortmund) [7, 8, 9], Modified UNIFAC [10] (Lyngby) and DISQUAC [11, 12].

While ASOG and the original UNIFAC method were developed mainly for the prediction of vapor-liquid equilibria (VLE) and azeotropic data, the modified versions of UNIFAC also reliable predict excess enthalpies*,* (h^E)*,* solid-liquid equiilibria (SLE) of eutectic systems, activity coefficients at infinite dilution (γ^∞) and liquid-liquid equilibria (LLE).

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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 Mod. UNIFAC (Do) model to calculate activity coefficients, γ_i, vapor-liquid equilibria (VLE) or excess Gibbs energy, G^E, are the same as in original UNIFAC [4, 5].

The activity coefficient is the sum of a combinatorial part, essentially due to differences in size and shape of the molecules in the mixture, and a residual part, essentially due to energy interactions:

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \tag{1}$$

The combinatorial part was changed in an empirical way to made it possible to deal with compounds very different in size:

$$\ln\gamma_i^C = 1 - V_i' + \ln V_i' - 5q_i\left(1 - \frac{V_i}{F_i} + \ln\left(\frac{V_i}{F_i}\right)\right) \tag{2}$$

The parameter V_i' can be calculated by using the relative van der Waals volume, R_k of the different groups:

$$V_i' = \frac{r_i^{3/4}}{\sum_j x_j r_j^{3/4}}; r_i = \sum \nu_k^{(i)} R_k \tag{3}$$

All others parameters, V_i, F_i, r_i, q_i are calculated in the same way as for the original UNIFAC model, i.e.

$$V_i = \frac{r_i}{\sum_j x_j r_j}; r_i = \sum \nu_k^{(i)} R_k \tag{4}$$

$$F_i = \frac{q_i}{\sum_j x_j q_j}; q_i = \sum \nu_k^{(i)} Q_k \tag{5}$$

where: r_i, is van der Waals volume of the molecule *i*, q_i, is van der Waals surface area of the molecule *i*. x_i, mol. fr. of the molecule *i* in mixture, $\nu_k^{(i)}$ is the number of groups of type *k* in molecule *i*.

In comparison to the original UNIFAC model, only the van der Waals properties, R_k, Q_k were changed slightly.

The residual part can be obtained by using the equations (eqs. 6, 7):

$$\ln\gamma_i^R = \sum_k \nu_k^{(i)}\left(\ln\Gamma_k - \ln\Gamma_k^{(i)}\right) \tag{6}$$

$$\ln\Gamma_k = Q_k\left[1-\ln\left(\sum_m \theta_m\psi_{mk}\right)-\sum_m\frac{\theta_m\psi_{km}}{\sum_n\theta_n\psi_{nm}}\right] \tag{7}$$

where: Γk 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*, ψ_{nm} is the interaction parameters between main groups *n* and *m*. In equation (6) the term $\Gamma_k^{(i)}$ is necessary to obtain the normalization that activity coefficient γ_i becomes unity as $x_i \to 1$.The group area fraction, θ_m and group mole fraction, X_m are given by the following equations:

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n};\quad X_m = \frac{\sum_j \nu_m^{(j)} x_j}{\sum_j\sum_n \nu_n^{(j)} x_j} \tag{8}$$

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} to permit a better description of the real phase behavior (activity coefficients) as a function of temperature:

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

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

The Mod. UNIFAC (Do) is revised and extended periodicaly [13-19] to improve the capability of prediction.

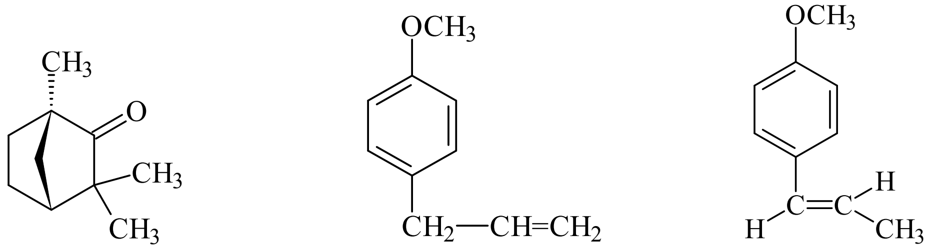
(1*R*,4*S*)-(+)-Fenchone [(1*R*,4*S*)-(+)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-one], methyl chavicol [4-allyl-1-methoxybenzene] and *trans*-anethole [*trans*-1-methoxy-4(prop-1-en-1-yl) benzene] are the main components of the essential oil from the fruits of bitter fennel (*Foeniculum vulgare Mill, fam. Umbelliferae*). Both the raw essential oils and its isolated pure components are used in perfumery, cosmetics, pharmacy, aromatherapy and food industry [20].

Generally, essential oil components belong to the terpenoid class. Terpenoids are natural products comprising a large number of compounds with complicate chemical structures. Due to their chemical structure the compounds present complex intermolecular interactions.

In previous paper [21] has been examinated intermolecular interactions in binary systems containing: (S)-(+)-carvone + (+)-limonene; (-)-beta-pinene + eucalyptol; (R)-(-)-carvone + eucalyptol; *n*-octane + (+)-limonene; (R)-(-)-carvone + *n*-decane; *n*-decane + (-)-menthone, *n*-decane + (+)-fenchone and (-)-beta-pinene + (+)-fenchone and has been analyzed the applicability of the group contribution models, DISQUAC and Mod. UNIFAC (Do) to predict VLE data and excess Gibbs energy in the same mixtures.

In [22], the thermodynamic properties of the mixtures containing (1R,4S)-(+)-fenchone, methyl chavicol and *trans*-anethole have been examined in terms of intermolecular forces.

The chemical structures of the compounds are presented in Figure 1.



(1*R*,4*S*)-(+)-Fenchone Methyl chavicol t*rans*-Anethole

Figure 1. Chemical structure of (1*R*,4*S*)-(+)-fenchone, methyl chavicol and *trans*-anethole

The names of the components referred to in this paper are: (+)-fenchone, methyl chavicol and *trans*-anethole.

The literature [23, 24] is very poor in vapor-liquid equilibrium data in the field of terpenoids. Since VLE data are often missing we check the capability of the Mod. UNIFAC (Do) model to predict VLE data in systems containing terpenoids.

Terpenoids and nonterpenoid compounds, main components of the essential oils, frequently contain oxygenated functional groups, some of them being in mesomeric relationship or being subjected to other electronic effects, steric hindrance effects or proximity effects.

One of the main objectives of the planned research work referred to the Mod. UNIFAC (Do) model is the consideration of the proximity and isomeric effects.

RESULTS AND DISCUSSION

(+)-Fenchone is a bi-cyclic terpenoid ketone while methyl chavicol and *trans*-anethole are two *semi*-aromatic ethers which do not belong to the terpenoid class.

Assessment of geometrical parameters

The molecules of (+)-fenchone, methyl chavicol and *trans*-anethole have been decomposed in structural groups according to the Mod. UNIFAC (Do) model. Table 1 lists the van der Waals values of R_k and Q_k for the all groups referred to in this paper.

Table 1. R_k and Q_k parameters and group assignment for the Modified UNIFAC (Dortmund) Method [8]

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=CH	6	1.2832	1.2489
	CH=C	7	1.2832	0.8962
3 ‘ACH”	ACH	9	0.3763	0.4321
	AC	10	0.3763	0.2113
9 “CH_2CO”	CH_3CO	18	1.7048	1.6700
	CH_2CO	19	1.7048	1.5542
	CCO		1.7048	1.5542
13. “CH_2O”	CH_3O	24	1.1434	1.6022
42 “c-CH_2”	c-CH_2	78	0.7136	0.8635
	c-CH	79	0.3479	0.1071
	c-C	80	0.3470	0.0000

The Mod. UNIFAC (Do) model [8] does not define a CCO subgroup for (+)-fenchone. For this subgroup we have considered the existing van der Waals properties, R_k and Q_k defined for the CH_2CO (19) subgroup. The CCO subgroup is sterically hindered by three adjacent methyl groups.

Table 2. Modified UNIFAC (Dortmund) group interaction parameters [8] and revised Modified UNIFAC (Dortmund) group interaction parameters [9] for the main group 42 (c-CH_2) with the main groups 1, 2, 3, 9 and 13.

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	3	114.2	0.0933	0.000E+00	16.07	-0.2998	0.000E+00
1	5	2777	-4.674	1.551E-03	1606	-4.7460	9.181E-04
**1	9	433.6	0.1473	0.000E+00	199	-0.8709	0.000E+00
1	13	233.1	-0.3155	0.000E+00	-9.654	-0.0324	0.000E+00
*1	42	-117.10	0.5481	-0.00098	170.90	-0.8062	0.00129
2	3	174.1	-0.5886	0.000E+00	-157.2	0.6166	0.000E+00
2	5	2649	-6.5080	4.822E-03	1566	-5.809	5.197E-03
**2	9	179.8	0.6991	0.000E+00	91.811	-0.7171	0.000E+00
**2	13	733.3	-2.509	0.000E+00	-844.3	2.945	0.000E+00
*2	42	2.4060	-0.1882	0.00	60.20	0.1565	0.00
**3	9	146.2	-1.237	4.237E-03	-57.53	1.212	-3.715E-03
3	13	-87.08	-0.1859	0.000E+00	179	0.0562	0.000E+00
*3	42	134.60	-1.2310	0.00149	-2.6190	1.0940	-0.00156
**9	13	3645	-26.91	4.757E-02	695.8	-0.9619	-2.462E-03
*9	42	168.20	-0.8197	0.00	464.50	0.1542	0.00
*13	42	397.00	-1.3790	0.00	-214.10	1.1340	0.00

* Revised Mod. UNIFAC (Do) group interaction parameters
** unpublished revised Mod. UNIFAC (Do) group interaction parameters

Assessment of interaction parameters

We used the group interaction parameters published in [8]. For the main group (42) we used the revised group interactions parameters published in [9]. Table 2 lists the Modified UNIFAC (Do) Group Interaction Parameters [8] and revised Modified UNIFAC (Do) Group Interaction Parameters [9] of the main group 42, ("c-CH_2"), with the main groups 1 ("CH_3"), 2 ("C=C"), 3 ("ACH"), 9 ("CH_2CO") and 13 ("CH_2O"), respectively. It should be pointed out that some revised interactions parameters (between 1-9, 2-9, 2-13, 3-9 and 9-13 groups) are not published, being used only inside the UNIFAC Consortium. It was not possible to use these revised interactions parameters to predict VLE data in the systems referred to in this paper.

Comparison with experiment

A comparison between experimental VLE data (*T*-*P*-*x*-*y*) and predicted VLE data is presented in Table 3. The excess Gibbs energy, G^E provides a more accurate comparison (Figs. 2 – 5). More discussions are necessary for each binary mixture.

Table 3. Comparison between experimental isobaric VLE data *T-x-y* and predicted isobaric VLE data *T-x-y* using Mod. UNIFAC (Do) model in binary and ternary systems containing (+)-fenchone, methyl chavicol and *trans*-anethole at *P*=4000 Pa and *P*=4270 Pa*, respectively.

System/Mod. UNIFAC (Do)	*AMD(y) (*mol. fr.)	*AMD(T)* (K)
Binary systems:		
(+)-fenchone + methyl chavicol	0.01	0.44
*(+)-fenchone + methyl chavicol	0.01	0.81
(+)-fenchone + *trans*-anethole	0.007	0.22
methyl chavicol + *trans*-anethole	0.002	1.00
Ternary system		
(+)-fenchone + methyl chavicol + *trans*-anethole	0.01	1.13

AMD(y) - Absolute mean deviation in the vapor phase compositions*;*
AMD(T) - Absolute mean deviation in temperature.

Binary system (+)-fenchone + methyl chavicol

The Mod. UNIFAC (Do) model, using the existing geometrical parameters van der Waals, R_k and Q_k defined for the "CH_2CO" (19) subgroup, is appropriate to predict the VLE data in the binary system (+)-fenchone + methyl chavicol (Table 3). The absolute mean deviation in the vapor phase composition, *AMD(y)* (mol.fr.) is 0.01 and the absolute mean deviations in temperature, *AMD(T)* (K) is smaller than 0.81.

The experimental excess Gibbs energy, $G^E_{\exp}$ presents positive and negative deviations from ideality (Figs. 2, 3). At T = 375.35 K, the equimolecular $G^E_{\exp}$ is ca. -50 (Jmol^{-1}) (P=4000 Pa) while at T = 377.75 K, the equimolecular $G^E_{\exp}$ is ca. -65 (Jmol^{-1}) (P=4270 Pa), negative deviations at both pressures.

The Mod. UNIFAC (Do) model predicts small deviations from ideality. At T=375.35 K the equimolecular G^E prediction is ca. 15 (Jmol^{-1}) (P=4000 Pa), respectively at T = 377.75 K, the equimolecular G^E prediction is ca. 5 (Jmol^{-1}) (P=4270 Pa), positive deviations at both pressures.

It should be noted the continue variation of the G^E prediction, presenting negative deviations from ideality until the equimolecular composition of the liquid phase, x_i and positive deviations after the equimolecular composition. At small compositions of (+)-fenchone in mixture, the unlike dipole/dipole interactions, >CO/-O-, as well as the dipole/induced dipole interactions, >CO/π, from -C_6H_4- and -$CH=CH_2$ does not compensate the like weak dipole/dipole, -O-/-O- interactions, the dipole/induced dipole interactions, –O-/π, from -C_6H_4- (phenylene) and -$CH=CH_2$ (double bonds) and the induced dipole/induced dipole interactions, π/π, from -C_6H_4-/-C_6H_4-, -C_6H_4-/-$CH=CH_2$

and -CH=CH$_2$/-CH=CH$_2$ in methyl chavicol [22]. Hence, the G^E predictions could not be negative until the equimolecular composition of the liquid phase. The conclusion is that the G^E predictions are unsatisfactorily.

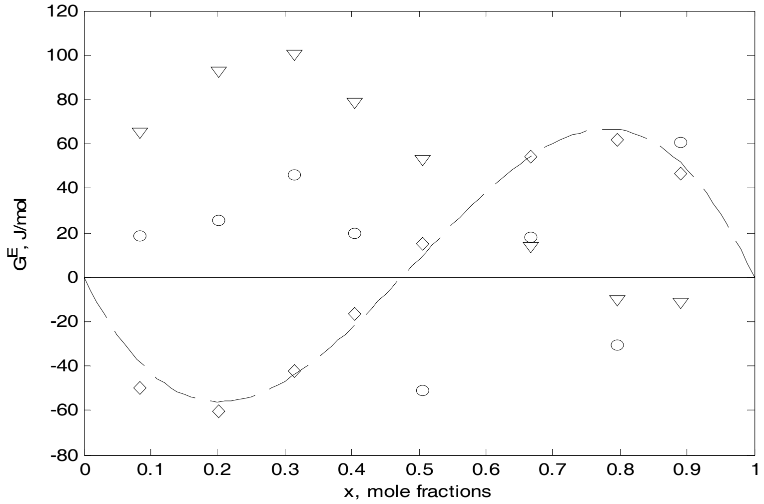


Figure 2. Variation of the molar excess Gibbs energy, G^E with mole fraction x_i, for the binary system (+)-fenchone (1) + methyl chavicol (2) at the constant pressure *P*=4000 Pa. (o) - experimental, (◊) - Mod. UNIFAC (Do) model, (∇) - calculated using binary parameters of the NRTL model.

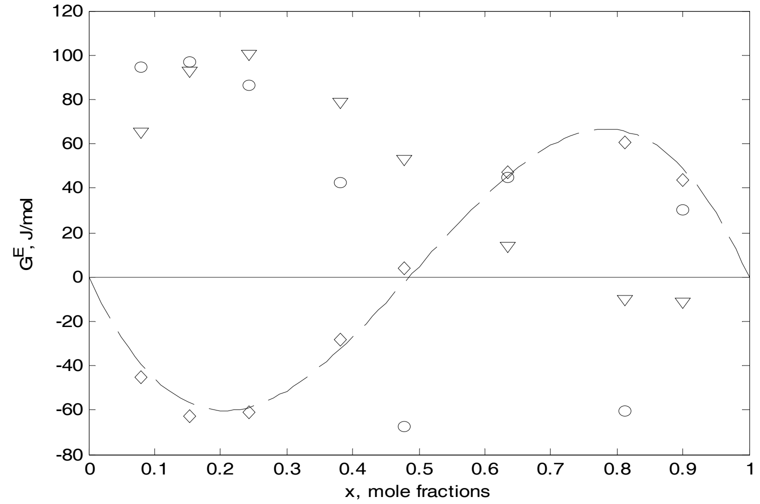


Figure 3. Variation of the molar excess Gibbs energy, G^E with mole fraction x_i, for the binary system (+)-fenchone (1) + methyl chavicol (2) at a constant pressure *P*=4270 Pa. (o) - experimental, (◊) - Mod. UNIFAC (Do) model, (∇) - calculated using binary parameters of the NRTL model.

The mesomeric effect in methyl chavicol, extended on the ether group, -O- and phenylene, $-C_6H_4-$, decrease the values of the excess Gibbs energy, G^E_{exp}. Between phenylene, $–C_6H_4-$ and double bond, $-CH=CH_2$ there is a proximity effect.

Binary system (+)-fenchone + trans-anethole

A very good prediction of the VLE data, using Mod. UNIFAC (Do) model, was found for the mixture (+)-fenchone + *trans*-anetole (Table 3). The absolute mean deviations in the vapor phase composition, *AMD(y)* (mol. fr.) is 0.007 and absolute mean deviations in temperature, *AMD(T)* (K) is 0.22.

The experimental excess Gibbs energy, G^E_{exp} presents negative deviations from ideality (Figure 4). At T=378.45 K, the equimolecular G^E_{exp} is ca. -20 ($Jmol^{-1}$).

The Mod. UNIFAC (Do) model predicts small deviations from ideality. At T=378.45 K, the predicted equimolecular G^E is ca. 4 ($Jmol^{-1}$).

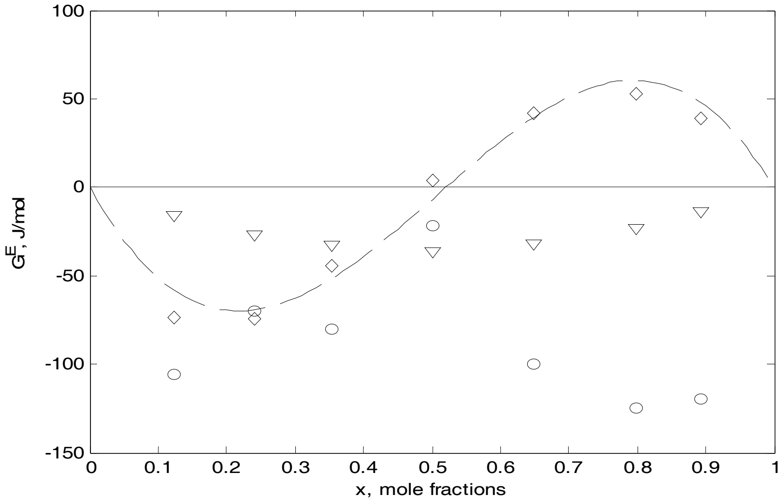


Figure 4. Variation of the molar excess Gibbs energy, G^E with mole fraction x_i, for the binary system (+)-fenchone (1) + *trans*-anethole (2) at a constant pressure P=4000 Pa. (o) -experimental, (◊) - Mod. UNIFAC (Do) model, (∇) – calculated using binary parameters of the NRTL model.

It should be noted the continue variation of the G^E predictions, presenting negative deviations from ideality until the equimolecular composition of the liquid phase, x_i and positive deviations after the equimolecular composition. At small compositions of (+)-fenchone in mixture, the unlike dipole/dipole interactions, >CO/-O-, as well as the dipole/induced dipole interactions, >CO/π, from -C_6H_4- and -CH=CH_2 does not compensate the like weak dipole/dipole, -O-/-O- interactions, the dipole/induced dipole interactions, –O-/π, from -C_6H_4- (phenylene) and –CH=CH- (double bonds) and the induced dipole/induced dipole interactions, π/π, from -C_6H_4-/-C_6H_4-, -C_6H_4-/-CH=CH- and -CH=CH-/-CH=CH- in *trans*-anetole [22]. Hence, the G^E predictions could not be negative until the equimolecular composition of the liquid phase. The conclusion is that the G^E predictions are unsatisfactorily.

The mesomeric effect in *trans*-anethole, extended on the ether group, -O- and phenylene -C_6H_4- as well as on the double bond, -CH=CH-, decrease the values of the experimental excess Gibbs energy $G^E_{\exp}$.

Because the –O-C_6H_4-CH=CH- dipole in *trans*-anethole is stronger than the –O-C_6H_4- dipole in methyl chavicol, the binary system (+)-fenchone + *trans*-anethole show negative deviation from ideality on the whole range of compositions of the liquid phase (Fig. 4).

Binary system methyl chavicol + trans-anethole

In binary system methyl chavicol + *trans*-anethole the Mod. UNIFAC (Do) model predicts very accurate the composition of the vapor phase, y_i. The absolute mean deviation, *AMD(y)* (mol. fr.) is 0.002. The absolute mean deviation in temperature, *AMD(T)* (K) is 1.00. (Table 3).

The big difference between the boiling temperatures of the two isomeric compounds, methyl chavicol (216 °C/760 mmHg) and of it more stable isomer, *trans*-anethole (236 °C/760 mmHg), due to the more extended mesomeric effect in *trans*-anethole, explain the poor accuracy of the temperature prediction using the Mod. UNIFAC (Do) model.

The experimental excess Gibbs energy, $G^E_{\exp}$ presents positive deviations from ideality (Figure 5). At T=394.95 K, the equimolecular $G^E_{\exp}$ is ca. 160 ($Jmol^{-1}$).

The Mod. UNIFAC predictions, G^E are negative on the whole range of the liquid phase compositions. The G^E values are very close to zero. At T=394.95 K, the equimolecular G^E predictions is ca. -2 ($Jmol^{-1}$). The conclusion is that the G^E predictions are unsatisfactorily.

The Mod. UNIFAC (Do) model predicts satisfactory the composition of the vapor phase, y_i. (Table 3). The absolute mean deviation in the vapor phase composition, *AMD(y)* (mol.fr.) is 0.01. The absolute mean deviation in temperature, *AMD(T)* (K) is 1.13. The mesomeric effect in methyl chavicol and *trans*-anethole, explain the poor accuracy of the temperature prediction using the Mod. UNIFAC (Do) model.

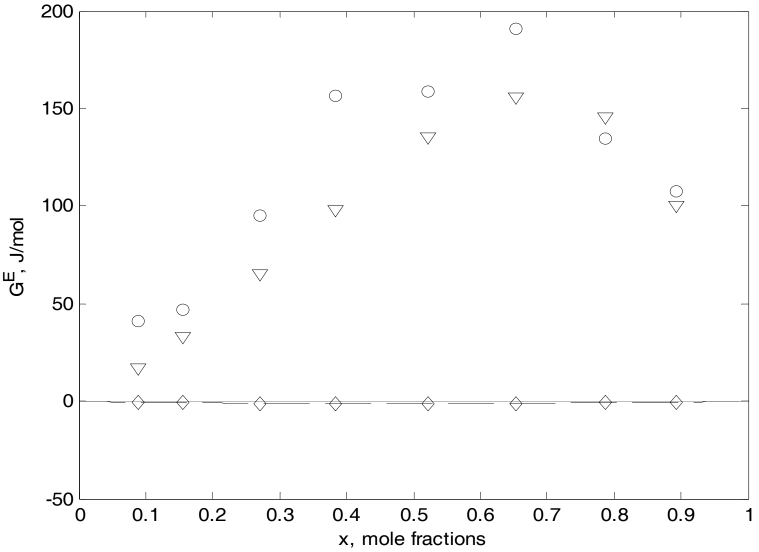


Figure 5. Variation of the molar excess Gibbs energy, G^E with mole fraction x_i, for the binary system methyl chavicol (1) + *trans*-anethole (2) at a constant pressure P=4000 Pa (o) - experimental, (◊) - Mod. UNIFAC (Do) model, (∇) - calculated using binary parameters of the NRTL model.

Ternary system {(+)-fenchone + methyl chavicol + trans-anethole}

Due to the hydrocarbon part of the involved molecules, *hydrophobic interactions* could not be negligible. The hydrophobic effect arises mainly from the attractive forces between hydrophobic parts of the molecules. It creates a higher degree of local order, producing a decrease in entropy that leads to an unfavorable Gibbs energy. The *hydrophobic interactions*, in addition with van der Waals and π/π attractions, contribute to positive and negative deviations from ideality in the binary system (+)-fenchone + methyl chavicol (Figs. 2, 3) and only negative deviations from ideality in the binary system (+)-fenchone + *trans*-anethole (Fig. 4) and only positive deviations from ideality in the binary system methyl chavicol + *trans*-anethole (Fig. 5) [22].

The dispersion of the experimental values of G^E (Figs. 2 - 5) is owing to the small values of G^E_{exp} and to the errors of the temperature measurements, (σ_T = 0.1 K) and of the vapor and liquid phase compositions measurements ($\sigma_{x,y}$ = 0.003 mol. fr.) as well as due to maintaining the pressure, P within 30 Pa around the desired values (σ_P = 60 Pa). The values of G^E were calculated using the binary parameters of the NRTL model published in [25].

CONCLUSIONS

The present investigation set out to check the capability of the Modified UNIFAC (Dortmund) group contributions model to predict the VLE data and excess Gibbs energy in binary and ternary systems containing (+)-fenchone, methyl chavicol and *trans*-anethole. Due to the various intermolecular interactions, mesomeric effects, steric hindrance effects and proximity effect the predictions are seriously affected. The Mod. UNIFAC (Do) group contribution model predicts satisfactory VLE data in all the binary and ternary systems but inadequately the values of the excess Gibbs energy. The poor predictions are due to of the complex structure of the investigated molecules.

EXPERIMENTAL SECTION

In previous papers [26, 27, 28] we reported experimental vapor-liquid equilibrium data for the following binary and ternary systems: methyl chavicol + (+)-fenchone; *trans*-anethole + (+)-fenchone; methyl chavicol + *trans*-anethole; methyl chavicol + *trans*-anethole + (+)-fenchone.

A series of isobaric *T-x-y* measurements were performed at (4000±30) Pa [26, 27, 28]. Another series of *T-P-x* measurements were performed at three constant liquid-phase compositions [26, 27]. For the binary system methyl chavicol + (+)-fenchone a series of isobaric *T-x-y* measurements were performed at (4270±30) Pa [26].

VLE data in binary systems were found to be thermodynamically consistent as tested by using the maximum likelihood multimodel fitting method described by Panaitescu [29]. The standard deviations for pressure, temperature and liquid and vapor phase compositions were set to σ_P = 60 Pa, σ_T = 0.1 K, σ_x = 0.003 mol. fr. and σ_y = 0.003 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 both pressure *P* (Pa) = (4000±30) and respectively *P (*Pa) = 4270±30), the values of the (*global Ro*) criterions and of the all values of the (*Ro*) criterions are less than 2.45. The thermodynamic consistency of the isobaric *T-x-y* measurements in the ternary system was checked using the McDermott-Ellis method [30] modified by Wisniak and Tamir [31]. According to these references two experimental points *a* and *b* are considered thermodynamically consistent if the local deviation, *D* is less than maximum deviation, D_{max}. For all the experimental points reported, *D* never exceeded 0.156 while the smallest value of D_{max} was 0.500.

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