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ANALYSIS IN TERMS OF INTERMOLECULAR FORCES OF THE THERMODYNAMIC PROPERTIES OF THE MIXTURES CONTAINING (1R,4S)-(+)-FENCHONE, METHYL CHAVICOL AND *TRANS*-ANETHOLE

IOAN BÂTIU[*]

ABSTRACT. The experimental vapor-liquid equilibrium data (VLE) in binary and ternary systems containing (1R,4S)-(+)-fenchone, methyl chavicol and trans-anethole, reported in previous papers, were used to discuss the thermodynamic properties of the mixtures, taking into account the intermolecular forces, intramolecular electronic effects and the effect of the steric hindrance.

Keywords: *Terpenoids, Intermolecular forces, Vapor - liquid equilibria,*

INTRODUCTION

(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 [1].

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

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 or proximity effects.

The chemical structures of the main components of the essential oils of fennel are presented in Figure 1. The names of the components referred to in this paper are: (+)-fenchone, methyl chavicol and *trans*-anethole.

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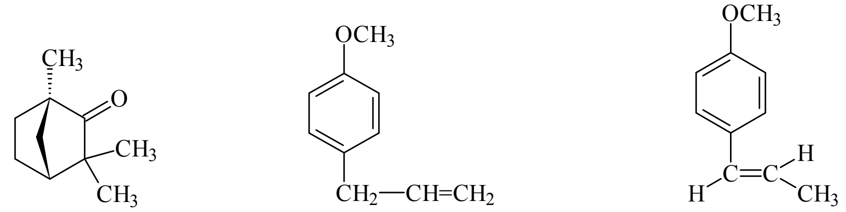
[*] Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering, Arany Janos Str. No. 11, RO-400028, Cluj Napoca, Romania, *batiu@chem.ubbcluj.ro*



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

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

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

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 [2]. A brief discussion of the intermolecular forces in molecular thermodynamics of fluid-phase equilibria [2] and in supramolecular chemistry [3] was done.

In previous papers [4] we have discussed intermolecular interactions in similar binary systems containing terpenoids: (S)-(+)-carvone+(+)-limonene; (-)-beta-pinene+eucalyptol; (R)-(-)-carvone+eucalyptol; *n*-octane+(+)-limonene; (R)-(-)-carvone+*n*-decane; *n*-decane+(-)-menthone and *n*-decane+(+)-fenchone, respectively.

In the present paper we selected and discussed other terpenoids and nonterpenoids, main components of the essential oil of bitter fennel: (+)-fenchone, methyl chavicol and *trans*-anethole. Due to their chemical structure, the compounds present complex intermolecular interactions.

Literature describes different types of intermolecular forces [2], but for our purpose here, only *electrostatic forces* (between permanent dipoles), *induction forces* (between a permanent dipole and 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 association and solvation, i.e., to the formation of loose chemical bonds; hydrogen bonds and charge-transfer complexes are perhaps the best example. Also we take into consideration the van der Waals forces [3] and the steric hindrance effect and the mesomeric effect.

RESULTS AND DISCUSSION

In the binary systems containing (+)-fenchone, methyl chavicol and *trans*-anethole the values of the experimental activity coefficients, γ_i range from ca. 0.75 to ca. 1.08. The experimental fugacity coefficients, φ_i are very close to unity. This means a quasi-ideal behaviour of the liquid phase and ideal behaviour of the vapor phase.

The binary system methyl chavicol + (+)-fenchone shows positive and negative deviations from ideality (Fig. 2, 3).

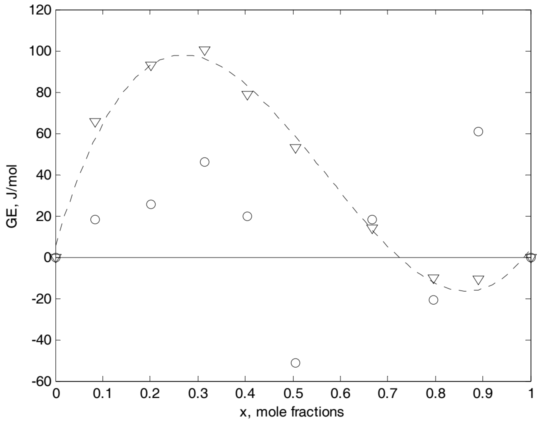


Figure 2. Variation of the molar excess Gibbs energy, G^E with mole fraction x_i, for the binary system (+)-fenchone (1) + methyl chavicol (2) at a constant pressure P=4000 Pa: (o), - experimental; (▽), – calculated using binary parameters of the NRTL model (the object function - the boiling points condition).

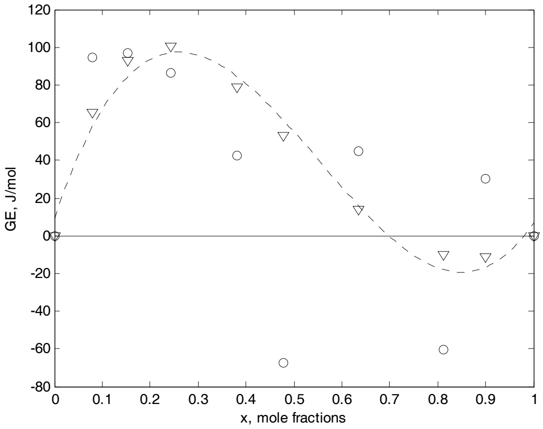


Figure 3. Variation of the molar excess Gibbs energy, G^E with mole fraction x_i, for the binary system (+)-fenchone (1) + methyl chavicol (2) at a constant pressure P=4270 Pa: (o), - experimental: (▽), - calculated using binary parameters of the NRTL model (the object function - the boiling points condition).

The binary system *trans*-anethole + (+)-fenchone shows only negative deviations (Fig. 4).

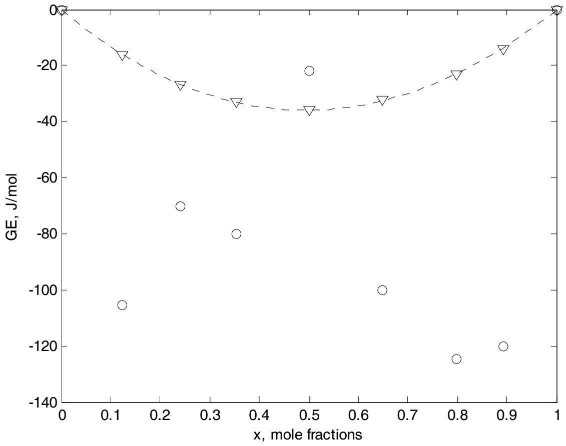


Figure 4. Variation of the molar excess Gibbs energy, G^E with mole fraction x_i, for the binary system (+)-fenchone (1) + *trans*-anethole (2) at a constant pressure *P*=4000 Pa: (o), - experimental; (▽), – calculated using binary parameters of the NRTL model (the object function - the boiling points condition).

The binary system methyl chavicol + *trans*-anethole shows only positive deviations from ideality (Fig. 5).

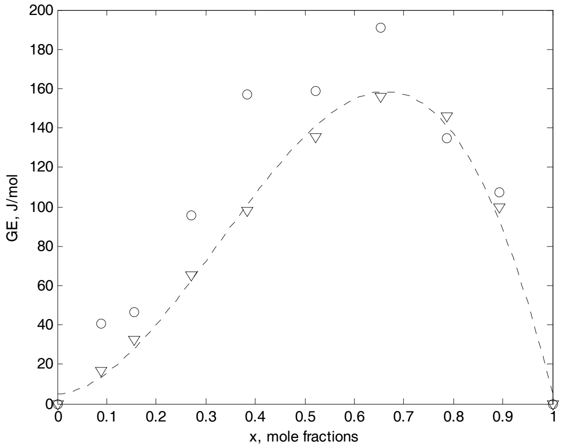
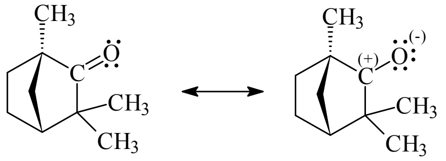


Figure 5. Variation of the molar excess Gibbs energy, G^E with mole fraction x_i, for the binary system {methyl chavicol (1) + *trans*-anethole (2)} at a constant pressure *P*=4000 Pa: (o), - experimental; (▽), - calculated using binary parameters of the NRTL model (the object function - the boiling points condition).

The dispersion of the experimental values of G^E (Figs. 2, 3, 4) is owing to the small values of G^E 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 [5].

The calculated dipole moment of the (+)-fenchone, methyl chavicol and *trans*-anethole are: 2.73 D, 1.17 D and 1.41 D, respectively. The values of the calculated dipole moment 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).

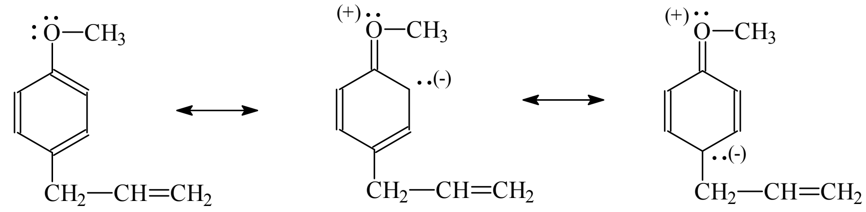
(+)-Fenchone could be assimilated with a simple cyclic ketone, having only an active functional group, >C=O. The ketone group, >CO is sterically hindered by three adiacent methyls, -CH_3 (Scheme 1).



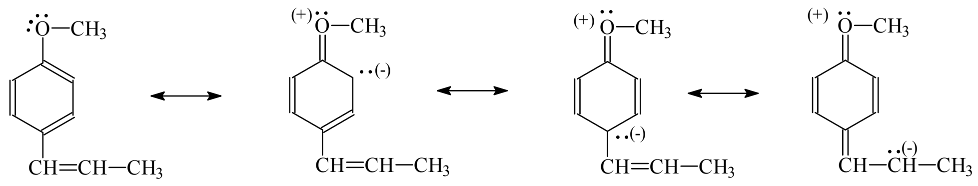
Scheme 1

In mixtures containing ketones the like strong dipole/dipole, >CO/>CO interactions occur due to the high value of the dipole moment.

Methyl chavicole and *trans*-anethole contain three active functional groups, oxygen, –O-; phenylene, –C_6H_4- and double bond, -CH=CH_2, in methyl chavicol or –CH=CH-, in *trans*-anethole (Scheme 2, 3).



Scheme 2



Scheme 3

It is possible that double bonds, -CH=CH_2, from allyl position, to be disturbed, therefore to behave like a simple alkene, but the oxygen from methoxy is very different from a dialkylic ether. Between phenylene, –C_6H_4- and double bond, -CH=CH_2 there is a proximity effect.

In methyl chavicol and *trans*-anethole complex intermolecular interactions and mesomeric effect occur. To the like weak dipole/dipole, -O-/-O- interactions the dipole/induced dipole interactions, –O-/π, from -C_6H_4- (phenylene) and -CH=CH_2 or –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_2 or -C_6H_4-/-CH=CH- and -CH=CH_2/-CH=CH_2 or -CH=CH-/-CH=CH- are added. In methyl chavicol the mesomeric effect is extended only on the ether group, -O- and phenylene, -C_6H_4- due to the allyl position of the double bond, -CH=CH_2 in the molecule (Scheme 2) while in *trans*-anethole the mesomeric effect is extended on the ether group, -O- and phenylene, -C_6H_4- as well as on the double bond, –CH=CH- (Scheme 3). The more extended mesomeric effect in *trans*-anethole explains the big difference between the boiling temperatures of the two isomeric compounds, methyl chavicol (216 ^{o}C/760 mmHg) and of its more stable isomer, *trans*-anethole (236 ^{o}C/760 mmHg).

In order to understand the thermodynamic properties of the mixtures containing (+)-fenchone, methyl chavicol and *trans*-anethole have to discuss the intermolecular interactions in more simple binary systems containing the same functional groups.

Linear ketones exhibit fairly large deviations from ideality, e.g. the binary system (nonan-5-one + hexane) has a G^E of the order of 300 J mol^{-1}, at 340 K [6]. *Cyclic ketones*, e. g., cyclohexanone, have larger deviations than linear ketones. G^E (x_1=0.5) at 298 K of the binary system (cyclohexanone + heptane) is ca. 830 J/mol [7]. Due to additional alkyl groups and to the steric hindrance by three adjacent methyls groups, the binary system (+)-fenchone + n-decane has smaller G^E. At ca 370 K, G^E (x_1=0.5) is ca. 450 Jmol^{-1} [4].

Dialkylic ethers exhibit fairly large deviations from ideality, e.g. the binary system (methyl, 1,1-dimethyl ethyl ether + hexane) has a G^E (x_1=0.547) of the order 172 J mol^{-1} at 329 K [8]. *Semi-aromatic ethers*, e.g., methyl phenyl ether (anisole) have larger deviations than *dialkylic ethers*. G^E (x_1=0.5) at 353 K of the binary system (methyl phenyl ether + hexane) is ca. 720 J mol^{-1} [9]. In methyl phenyl ether (anisole) to the like weak dipole/dipole, -O-/-O- interactions the dipole/induced dipole interactions, –O-/π, from -C_6H_4- (phenylene) are added. A mixture of *semi-aromatic ether* with *unsaturated terpenoid hydrocarbon* e.g. the binary system (methyl phenyl ether + beta-pinene) has smaller G^E. At 393 K, G^E (x_1=0.6) is ca. 533 Jmol^{-1} [10]. In beta-pinene the induced dipole/induced dipole interactions, π/π, from >C=CH_2/>C=CH_2 compensate the methyl phenyl ether's interactions.

Aromatic π/π interactions occur between aromatic rings, often in situations where one is relatively electron rich and one is electron poor. There are two general types of π/π interactions: face-to-face and edge-to-face, although a wide variety of intermediate geometries are known [3]. In *aromatic hydrocarbons* the induced dipole/induced dipole interactions, π/π, from -C_6H_4-/-C_6H_4- show fairly large deviations from ideality, e.g. the binary system (benzene + hexane) has a G^E of the order of 384 J mol^{-1} at 298 K [11].

In *unsaturated hydrocarbons* the induced dipole/induced dipole interactions, π/π, from H_2C=CH-/H_2C=CH- show very small deviations from ideality, e.g. the binary system (1-hexene + hexane) has a G^E of the order of 25 J mol^{-1} at 328 K [11].

The unlike dipole/induced dipole interactions, –O-/π, from -C_6H_4- (phenylene) compensate the induced dipole/induced dipole interactions, π/π, from -C_6H_4-/-C_6H_4- e.g. the binary system (methyl butyl ether + benzene) has a G^E (x_1=0.5) of the order 40 J mol^{-1} at 343 K [11].

The unlike induced dipole/induced dipole interactions, π/π, from H_2C=CH-/-C_6H_4- compensate the induced dipole/induced dipole interactions, π/π, from -C_6H_4-/-C_6H_4- e.g. the binary system (1-hexene + benzene) has a G^E (x_1=0.5) of the order 246 J mol^{-1} at 298 K [11].

The major contribution to the non-ideality of the mixtures containing (+)-fenchone, methyl chavicol and trans-anethole comes from the like strong dipole/dipole, >CO/>CO interactions in (+)-fenchone and from the like weak dipole/dipole, -O-C_6H_4-/-O-C_6H_4- in methyl chavicole as well as the like weak dipole/dipole, -O-C_6H_4-HC=CH-/-O-C_6H_4-HC=CH- in *trans*-anethole.

In mixtures with (+)-fenchone the complex intermolecular interactions from methyl chavicol and *trans*-anethole are compensated by the like dipole/dipole interactions, >CO/-O-, as well as the dipole/induced dipole interactions, CO/π, from -C_6H_4- and -CH=CH_2 or –CH=CH- and the like dipole/dipole interactions, >CO/-O-C_6H_4-, respectively >CO/-O-C_6H_4-HC=CH-and this results in a small deviations from ideality. The binary system methyl chavicol + (+)-fenchone has a G^E ($x_1=0.4$) of the order of 40 J mol^{-1} at 380 K (Fig. 2, 3) while the binary system *trans*-anethole + (+)-fenchone has a G^E ($x_1=0.4$) of the order of -80 J mol^{-1} at 384 K (Fig.4). Due to higher dipole moment in *trans*-anethole, the like dipole/dipole interactions, >CO/-O-C_6H_4-HC=CH- are stronger than the like dipole/dipole interactions, >CO/-O-C_6H_4-, in methyl chavicol and this results in negative deviation from ideality in binary system (+)-fenchone + *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 methyl chavicol + (+)-fenchone (Figs. 2, 3) and only negative deviations from ideality in the binary system *trans*-anethole + (+)-fenchone (Fig. 4) and only positive deviations from ideality in the binary system methyl chavicol + *trans*-anethole (Fig. 5).

CONCLUSION

We have analyzed in terms of intermolecular forces the thermodynamic properties of the mixtures containing (+)-fenchone, methyl chavicol and *trans*-anethole. The chemical structures of the compounds contain the following active functional groups: carbonyl group, >C=O; ether group, -O-; phenylene, $-C_6H_4-$ and double bonds, $-CH=CH_2$ in methyl chavicol or –CH=CH- in *trans*-anethole. The oxygenated functional groups are in mesomeric relationship or are subjected to other electronic effects and steric hindrance effect. The compounds present complex intermolecular interactions. Due to the compensation of the intermolecular interactions the mixtures show quasi-ideal behaviour of the liquid phase and ideal behaviour of the vapor phase. The binary system methyl chavicol + (+)-fenchone shows positive and negative deviations from ideality and the binary system *trans*-anethole + (+)-fenchone shows only negative deviations while the binary system methyl chavicol + *trans*-anethole shows only positive deviations from ideality. The values of the molar excess Gibbs energies, G^E calculated from the isobaric *T-x-y* measurements range from ca. -135 $\mathrm{Jmol^{-1}}$ to ca. +190 $\mathrm{Jmol^{-1}}$.

EXPERIMENTAL SECTION

In previous papers [12, 13, 14] 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 [12, 13, 14]. Another series of *T-P-x* measurements were performed at three constant liquid-phase compositions [12, 13]. For the binary system (+)-fenchone (1) + methyl chavicol (2) a series of isobaric *T-x-y* measurements were performed at (4270±30) Pa [12].

VLE data in binary systems were found to be thermodynamically consistent as tested by using the maximum likelihood multimodel fitting method described by Panaitescu [15]. 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 (4000±30) Pa 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 [16] modified by Wisniak and Tamir [17]. 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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