Physical Behavior of the Phases from the Liquid–Liquid Equilibrium of Citrus Essential Oils Systems at 298.2 K

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Supporting Information

Equations for the implementation of the UNIFAC-VISCO thermodynamic model.

The UNIFAC-VISCO model is based on the Eyring model[1] for kinematic viscosity, as eq S1.

$$\ln(vM) = \sum^{i} x_i \ln(v_i M_i) + \frac{\Delta^* G^E}{RT} \quad \text{(S1)}$$

Where $\Delta^* G^E$ is the excess molar free energy of the mixture, v and M are the kinematic viscosity and molar mass of the mixture, respectively. v_i, M_i, and x_i are the kinematic viscosity, molar mass, and the molar fraction of the pure component i present in the mixture, R is the universal gas constant, and T is the mixture temperature.

In this model, $\Delta^* G^E$ is assumed as the sum of two contributions: (i) combinatorial, $\Delta^* G^{EC}$ (eq S2), which refers to the difference among the molecules sizes, and (ii) residual, $\Delta^* G^{ER}$ (eq S3), that considers the interaction energy among the different groups present in the mixture.

$$\Delta^* G^E = \Delta^* G^{EC} + \Delta^* G^{ER} \quad \text{(S2)}$$

$$\Delta^* G^E = RT \sum^{i} x_i \ln \gamma_i^* \quad \text{(S3)}$$

Where γ_i^* is a function of the combinatorial γ_i^{*C} and the residual γ_i^{*R}. The combinatorial term ($\Delta^* G^{EC}$) is presented in eq S4.

$$\frac{\Delta^* G^{EC}}{RT} = \sum^{i} x_i \ln \frac{\Phi_i}{x_i} + \frac{z}{2} \sum^{i} q_i \, x_i \ln \frac{\theta_i}{\Phi_i} \quad \text{(S4)}$$

Where z is the coordinate number (z = 10). Φ_i and θ_i are the volume and the superficial area fractions, respectively, which can be calculated by eqs S5 and S6.

$$\theta_i = \frac{q_i x_i}{\sum^j q_j x_j} \quad \text{(S5)}$$

$$\Phi_i = \frac{r_i x_i}{\sum^j r_j x_j} \quad \text{(S6)}$$

Where q_i and r_i are the volume and superficial area parameters of the component i, respectively, which are calculated by eqs S7 and S8.

$$q_i = \sum^{k} n_k^{(i)} Q_k \tag{S7}$$

$$r_i = \sum^{k} n_k^{(i)} R_k \tag{S8}$$

Where $n_k^{(i)}$ is the number of *k* groups existing in the component *i*. R_k and Q_k are the volume and superficial area parameters of the group *k*, respectively, which were obtained from Fredenslund et al.[2] Table S1 shows the $n_k^{(i)}$ of each component *i* studied.

Table S1 – Number of *k* groups existing in each component *i* ($n_k^{(i)}$).

Component (*i*)	Group *k*					
	CH_3	CH_2	OH	CH	H_2O	C
Limonene	2	4	0	2	0	2
β-Pinene	2	4	0	2	0	0
γ-Terpinene	3	2	0	3	0	0
Linalool	3	3	1	2	0	2
Citral	3	2	0	2	1	0
Ethanol	1	1	1	0	0	0
Water	0	0	0	0	1	0

The residual term ($\Delta^* G^{ER}$) is calculated by eqs S9 and S10.

$$\frac{\Delta^* G^{ER}}{RT} = -\sum^{i} x_i \ln \gamma_i^{*R} \tag{S9}$$

$$\gamma_i^{*R} = \sum^{k} n_k^{(i)} \left(\ln \gamma_k^{*} - \ln \gamma_k^{*(i)} \right) \tag{S10}$$

Where $\ln \gamma_k^*$ is the individual contribution of each *k* group of the component *i* present in the mixture and $\ln \gamma_k^{*(i)}$ is the individual contribution of the group *k* in a reference solution composed of only the component *i* (pure solution). The term $\ln \gamma_k^*$ is calculated by eqs S11 to S14.

$$\ln \gamma_k^* = Q_k \left[1 - \ln \left(\sum^m \theta_m \varphi_{mk}^* \right) - \sum^m \frac{\theta_m \varphi_{km}^*}{\sum^n \theta_n \varphi_{nm}^*} \right] \quad \text{(S11)}$$

$$\theta_m = \frac{Q_m X_m}{\sum^n Q_n X_n} \quad \text{(S12)}$$

$$X_m = \frac{\sum^j n_m^{(j)} x_j}{\sum^j \sum^n n_n^{(j)} x_j} \quad \text{(S13)}$$

$$\varphi_{nm}^* = exp\left(-\frac{\alpha_{nm}}{T} \right) \quad \text{(S14)}$$

Where α_{nm} is the interaction parameter between the groups *n* and *m*, being $\alpha_{nm} \neq \alpha_{mn}$. The interaction parameters among the groups present in the mixtures studied were previously adjusted by Florido et al.[3] for the following systems: bergamot essential oil (limonene + linalyl acetate + linalool + ethanol + water), lemon/lime essential oil (limonene + γ-terpinene + β-pinene + citral + ethanol + water), and mint essential oil (limonene + carvone + ethanol + water), at T = (298.2 ± 0.1) K. The α_{nm} used for the prediction procedure is exposed in Table S2. Eq S11 can be also used to calculate the term $\gamma_k^{*(i)}$.

Table S2 – Interaction parameters between the *k* groups present in the components of the systems (α_{nm}).

Group *n*	Group *m*					
	CH_3	CH_2	OH	CH	H_2O	C
CH_3	-	-1015.8	1143.3	331.6	-1537.1	1570.4
CH_2	1850.0	-	-1041.5	1343.9	1130.3	399.5
OH	-445.0	-1032.0	-	-138.8	629.8	337.5
CH	-1301.1	-692.1	1905.1	-	-857.7	-79.1
H_2O	-1416.5	562.4	212.2	1267.5	-	-1254.0
C	1024.0	959.4	2006.0	-33.2	1130.3	-

References

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