Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

ELECTRONIC SUPPLEMENTARY INFORMATION

Deduction of the SLE equations considering polymorphism phenomena

The isofugacity criteria establish that, in case of solid-liquid equilibrium (SLE), the fugacity of the compound f_i in both solid (*S*) and liquid (*L*) phases are equal.

$$f_i^S = f_i^L \qquad \text{S1}$$

Equation S1 can be written in terms of the standard fugacity of the compounds f_i^0 in each phase as follows:

$$x_i \gamma_i^L f_i^{L^0} = z_i \gamma_i^S f_i^{S^0} \longrightarrow \frac{x_i \gamma_i^L}{z_i \gamma_i^S} = \frac{f_i^{S^0}}{f_i^{L^0}} \qquad \text{S2}$$

where x_i and z_i are mole fractions of the compound *i* in both liquid and solid phases, respectively, and γ_i^L and γ_i^S are the activity coefficients of both liquid and solid phases, respectively. It means that the temperature *T* of the system must be the same in both solid and liquid phases. This is attended considering a subcooled liquid state. The $x_i \gamma_i^L / z_i \gamma_i^S$ ratio can be calculated by the variation of the Gibbs energy ΔG as follows,

$$\Delta G = \mathrm{R}T \ \ln \frac{f_i^{S^0}}{f_i^{L^0}} \qquad \text{S3}$$

of the following process: heating the system from *T* to the melting temperature T_{fus}, followed by the complete melting and then cooling to the temperature *T*. The ΔG of such a process is calculated by Equation S4, knowing the variation of the enthalpy ΔH (Equation S5) and entropy ΔS (Equation S6) of the process, and considering the *n* solid-solid transitions.

$$\Delta G = \Delta H + T\Delta S \qquad \text{S4}$$

$$\Delta H = \sum_{\mathrm{tr}=1}^{\mathrm{n}}\left(\int_{T}^{T_{\mathrm{tr}}} Cp_{\mathrm{i}}^{\mathrm{S}}\mathrm{d}T + \Delta_{\mathrm{tr}}H\right) + \int_{T}^{T_{\mathrm{fus}}} Cp_{\mathrm{i}}^{\mathrm{S}}\mathrm{d}T + \Delta_{\mathrm{fus}}H + \int_{T_{\mathrm{fus}}}^{T} Cp_{\mathrm{i}}^{\mathrm{L}}\mathrm{d}T + \sum_{\mathrm{tr}=1}^{\mathrm{n}}\left(\int_{T_{\mathrm{tr}}}^{T} Cp_{\mathrm{i}}^{\mathrm{L}}\mathrm{d}T\right) \qquad \text{S5}$$

$$\Delta S = \sum_{\mathrm{tr}=1}^{\mathrm{n}}\left(\int_{T}^{T_{\mathrm{tr}}} \frac{Cp_{\mathrm{i}}^{\mathrm{S}}}{T}\mathrm{d}T + \frac{\Delta_{\mathrm{tr}}H}{T_{\mathrm{tr}}}\right) + \int_{T}^{T_{\mathrm{fus}}} \frac{Cp_{\mathrm{i}}^{\mathrm{S}}}{\mathrm{T}}\mathrm{d}T + \frac{\Delta_{\mathrm{fus}}H}{T_{\mathrm{fus}}} + \int_{T_{\mathrm{fus}}}^{T} \frac{Cp_{\mathrm{i}}^{\mathrm{L}}}{T}\mathrm{d}T + \sum_{\mathrm{tr}=1}^{\mathrm{n}}\left(\int_{T_{\mathrm{tr}}}^{T} \frac{Cp_{\mathrm{i}}^{\mathrm{L}}}{T}\mathrm{d}T\right) \qquad \text{S6}$$

where $\Delta_{\mathrm{fus}}H$ and T_{fus} are the melting enthalpy and temperature of the compound *i*, and $\Delta_{\mathrm{tr}}H$ and T_{tr} are the solid-solid transitions enthalpy and temperature of the compound *i*. Knowing that the behavior of the heat capacity of the compound *i* in both liquid $Cp_{\mathrm{i}}^{\mathrm{L}}$ and solid $Cp_{\mathrm{i}}^{\mathrm{S}}$ phases as a function of the temperature is small[1-3] (in the range evaluated), $Cp_{\mathrm{i}}^{\mathrm{L}}$ and $Cp_{\mathrm{i}}^{\mathrm{S}}$ can be considered as constants as well as the variation of the heat capacity $\Delta_{\mathrm{fus}}Cp = Cp^{\mathrm{L}} - Cp^{\mathrm{S}}$. Thus, the SLE can be determined by Equation S7 from $T_{\mathrm{tr}} < T < T_{\mathrm{fus}}$, by Equation S8 for $T < T_{\mathrm{tr}}$, and analogously, in case of more than one solid-solid transition.

$$\ln\frac{x_{\mathrm{i}}\,\gamma_{\mathrm{i}}^{\mathrm{L}}}{z_{\mathrm{i}}\,\gamma_{\mathrm{i}}^{S}} = \frac{\Delta_{\mathrm{fus}}H}{R}\left(\frac{1}{T_{\mathrm{fus}}} - \frac{1}{T}\right) + \frac{\Delta_{\mathrm{fus}}C_p}{R}\left(\frac{T_{\mathrm{fus}}}{T} - \ln\frac{T_{\mathrm{fus}}}{T} - 1\right) \qquad \text{S7}$$

$$\ln\frac{x_{\mathrm{i}}\,\gamma_{\mathrm{i}}^{\mathrm{L}}}{z_{\mathrm{i}}\,\gamma_{\mathrm{i}}^{S}} = \frac{\Delta_{\mathrm{fus}}H}{R}\left(\frac{1}{T_{\mathrm{fus}}} - \frac{1}{T}\right) + \frac{\Delta_{\mathrm{tr}}H}{R}\left(\frac{1}{T_{\mathrm{tr}}} - \frac{1}{T}\right) + \frac{\Delta_{\mathrm{fus}}C_p}{R}\left(\frac{T_{\mathrm{fus}}}{T} - \ln\frac{T_{\mathrm{fus}}}{T} - 1\right) \qquad \text{S8}$$

Table S1. Melting temperatures (T_{fus} / K) and enthalpies ($\Delta_{\mathrm{fus}}H$ / kJ·mol^{-1}) and solid-solid temperatures (T_{tr} / K) and enthalpies ($\Delta_{\mathrm{tr}}H$ / kJ·mol^{-1}) of the pure compounds used in the modeling procedure and obtained in this work or from literature.

Compound	T_{fus}	ref.	$\Delta_{\mathrm{fus}}H$	ref.	T_{tr1}	ref.	$\Delta_{\mathrm{tr1}}H$	lit.	T_{tr2}	ref.	$\Delta_{\mathrm{tr2}}H$	ref.
Trilaurin	319.39		116.45		308.25	4	86.00	4	288.75	4	69.80	4
Trimyristin	330.90		141.97	this work	319.05	4	106.00	4	305.75	4	81.90	4
Tripalmitin	338.98	this work	165.88		328.85	4	126.50	4	317.85	4	95.80	4
1-hexadecanol	322.61		33.60	5	321.89	this work	23.70	5	-		-	
1-octadecanol	331.42		40.10	6	330.55		26.50	6	-		-	

Table S2. Experimental solid-liquid equilibrium data for the triacylglycerols + fatty alcohols systems for mole fraction x and temperature T for *solidus* and *liquidus* line.†

trilaurin (1) + 1-hexadecanol (2)			trilaurin (1) + 1-octadecanol (2)			trimyristin (1) + 1-hexadecanol (2)		
x_1	*Solidus* / *K*	*Liquidus* / *K*	x_1	*Solidus* / *K*	*Liquidus* / *K*	x_1	*Solidus* / *K*	*Liquidus* / *K*
0.000		322.61	0.000		331.42	0.000		322.61
0.097	315.39	321.13	0.101	317.31	330.00	0.042	320.35	321.68
0.197	315.44	319.48	0.197	317.42	328.56	0.100		319.98
0.295	315.55	318.38	0.294	317.50	327.25	0.137		320.82
0.402	315.96	317.30	0.395	317.67	325.84	0.192	320.11	322.05
0.503		315.86	0.501	317.56	323.71	0.246	319.89	322.98
0.592	315.85	316.28	0.597	318.01	321.73	0.394	319.11	324.71
0.703	315.18	316.79	0.701	317.76	319.85	0.498	319.30	326.30
0.781	315.06	317.15	0.790	317.76	318.67	0.594	318.99	326.78
0.863	315.00	318.58	0.884	317.70	318.77	0.694	318.80	327.59
1.000		319.39	1.000		319.39	0.778	319.10	328.24
						0.894	323.55 ‡	329.24
						1.000		330.90

trimyristin (1) + 1-octadecanol (2)			tripalmitin (1) + 1-hexadecanol (2)			tripalmitin (1) + 1-octadecanol (2)		
x_1	*Solidus* / *K*	*Liquidus* / *K*	x_1	*Solidus* / *K*	*Liquidus* / *K*	x_1	*Solidus* / *K*	*Liquidus* / *K*
0.000		331.42	0.000		322.61	0.000		331.42
0.100	325.99	329.88	0.050		322.60	0.058	329.20	330.27
0.199	326.26	328.60	0.101	322.90	328.69	0.099	328.90	329.80
0.300	326.01	327.28	0.201	321.90	331.98	0.151		329.56
0.393		325.90	0.299	321.93	333.62	0.200	328.95	331.40
0.493		325.88	0.408	321.68	334.75	0.300	328.80	333.40
0.592	325.77	326.73	0.501	321.90	335.93	0.401	329.50	334.79
0.691	325.65	327.67	0.597	322.00	336.61	0.502	328.80	335.63
0.793	325.48	328.90	0.701	321.82	337.35	0.595	329.00	336.63
0.878	325.61	329.52	0.800	330.45 ‡	338.32	0.697	329.20	337.35
1.000		330.90	0.894	336.05 ‡	338.85	0.797	332.05 ‡	338.16
			1.000		338.98	0.906	335.85 ‡	338.82
						1.000		338.98

† Uncertainties for molar fraction and *liquidus* line temperature are ± 0.001 and 0.38 K. Uncertainty for *solidus* line temperature measured by DSC and by microscopy ‡ is ± 0.58 K.

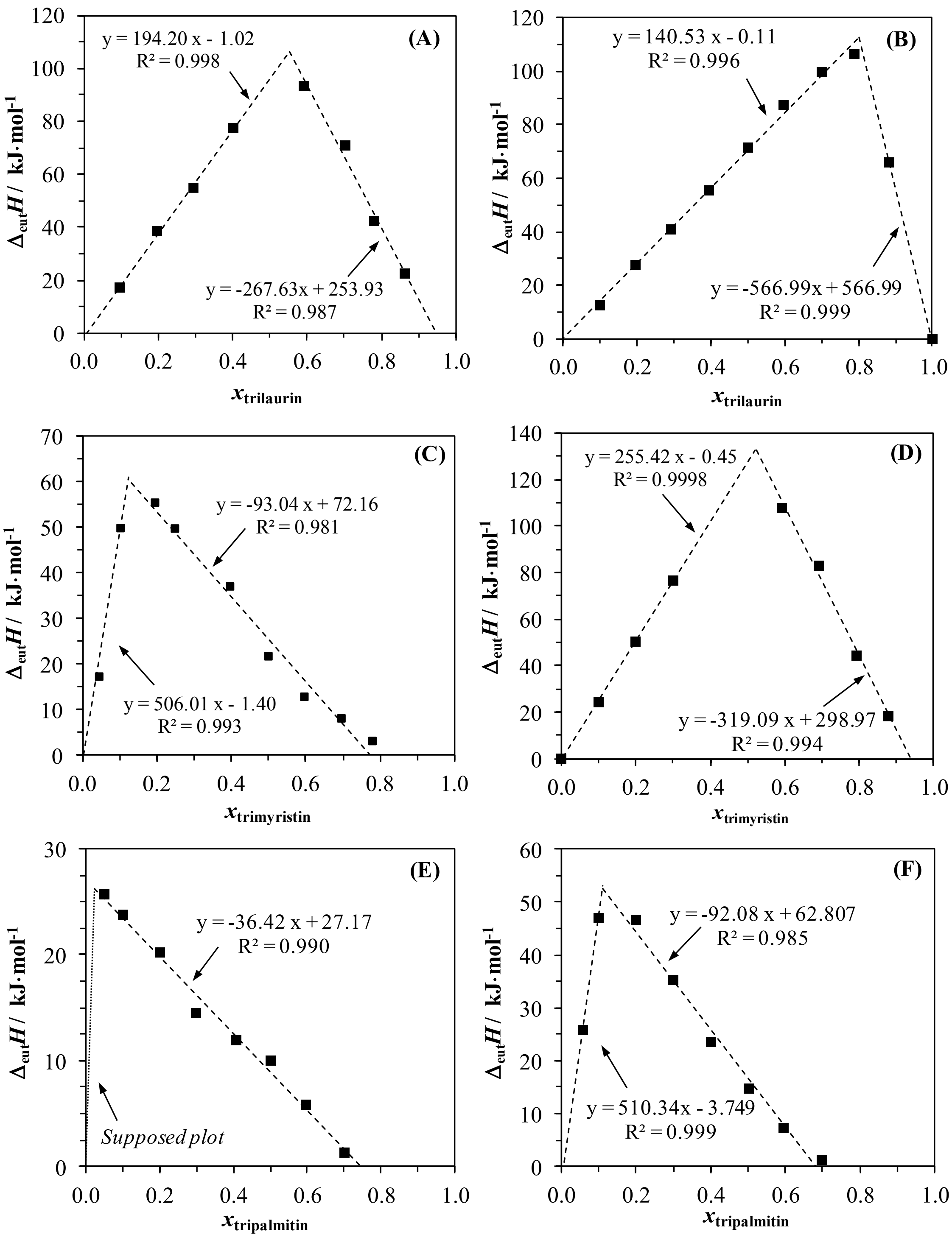

Figure S1. Tammann plots of the experimental eutectic transition enthalpy $\Delta_{eut}H$ (■) and linear regression (dashed lines) for the systems A) trilaurin (1) + 1-hexadecanol (2), B) trilaurin (1) + 1-octadecanol (2), C) trimyristin (1) + 1-hexadecanol (2), D) trimyristin (1) + 1-octadecanol (2), E) tripalmitin (1) + 1-hexadecanol (2), F) tripalmitin (1) + 1-octadecanol (2).

REFERENCES

1. G. Charbonnet and W. S. Singleton, *J. Am. Oil Chem. Soc.*, 1947, **24**, 140.

2. R. Ceriani, R. Gani and A. J. A. Meirelles, *Fluid Phase Equilibr.*, 2009, **283**, 49.

3. J. Xing, Z. C. Tan, Q. Shi, B. Tong, S. X. Wang and Y. S. Li, *J. Therm. Anal. Calorim.*, 2008, **92**, 375.

4. L. H. Wesdorp, Liquid-multiple solid phase equilibria in fats, theory and experiments, Doctoral Thesis, Delft University of Technology, Delft, 1990.

5. C. Mosselman, J. Mourik and H. Dekker, *J. Chem. Thermodyn.*, 1974, **6**, 477.

6. L. Ventolà, M. Ramírez, T. Calvet, X. Solans, M. A. Cuevas-Diarte, P. Negrier, D. Mondieig, J. C. van Miltenburg and H. A. J. Oonk, *Chem. Mater.*, 2002, **14**, 508.