

Development of Thermodynamic Models and Parameters Determination of Solid Liquid Equilibrium for Binary and Ternary Fatty Acids and Esters

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The prediction of solid-liquid equilibrium is important to describe the phase's formation and the compositions of many chemical processes. The separation processes, which need the solid-liquid phase data, have been explored for many years, but now, with the high and new technological developments, the theoretical and practical interest in this area was increased. This work has a theoretical and computational character, whose objective is the study and application of an optimization technique for the solid-liquid equilibrium calculation. Interested of binary and ternary fatty mixtures with natural origin, this work can be applied for different profiles' mixtures of fatty acids, triglycerides and ethyl esters using the minimization of Gibbs energy free of the systems. So, it is necessary the improvement of the thermodynamic models capable to precisely represent the equilibrium, which was represented by a non-linear program, and convexity analysis ensure of optimal solution found is the global optimum. The software GAMS and Microsoft Excel were used for the equilibrium problem implementation, where the description of phases was done based in known thermodynamics models. The solid phase was characterized using a modified Slaughter and Doherty model and liquid phase with Margules 2 – suffixes. In this work the on liquid phase, the Margules model assume two forms: Margules Asymmetric (MA), where the Margules parameters are different; and Margules Symmetric (MS), with equal Margules parameters, after was used Wilson Model (W) too. In this work specifically, it was calculated the equilibrium points for mixtures contain: ethyl and methyl laurate and miristate, ethyl estearate, palmitic acid and tristearin. Experimental data was used in comparative mode of binary mixtures, with good agreement between experimental and calculated points; new equilibrium dates was predicted and obtained of ternary mixtures, and the parameters model also was discovery. The results are described in form of phase diagrams for binary mixtures and surfaces of equilibrium for ternary mixtures, where the equilibrium data and the parameters model was calculated based in the square errors, that are nearly of the experimental data.

1. Introduction

Focusing on fatty mixtures, the solid-liquid equilibrium is essential in biofuel separation process. So, it is necessary the improvement of the thermodynamic models capable to precisely represent the equilibrium (Rangaiah, 2001) that the majority of them couldn't describe specific points like eutectic and peritectic, neither the behavior between them. The separation processes, which need the solid-liquid phase data, have been explored for many years, but now, with the high and new technological developments, the theoretical and practical interest in this area was increased according different necessity related a specific compound points of mixtures and them behavior. The prediction of solid-liquid equilibrium is important to describe the phase's formation and the compositions of many chemical processes. (Rocha and Guirardello, 2009).

The correct determination of phase formation is indispensable for discovery the solid-liquid equilibrium, specifically because important points, like eutectic and peritectic points, which thermodynamic models needs to be capable to represent, more than this, needs to identify when this behavior is present (Inoue et al, 2004 a). The solid-liquid equilibrium can be calculated in many ways. In the present work, the minimization of the Gibbs free energy was chosen as a starting point to calculate the equilibrium. This technique is considered sufficient to guarantee finding the equilibrium point, if the global minimum is found (Smith et al, 2004).

The general approach in this work applies the same assumptions used by Slaughter and Doherty (Slaughter and Doherty, 1995), but the approach used here leads to an easier way to calculate the temperature profiles. The thermodynamic representation of the solid and liquid phases was done using specific models for each phase. The solid phase was modeled using a modification of the activity model described by Slaughter and Doherty (Slaughter and Doherty, 1995), using a mathematical limit. The liquid phase was modeled using Margules 2-suffix equation, in the symmetric and asymmetric form, and Wilson, but the approach is easily generalized to other models for the liquid phase. The equations obtained resulted in an expression for the Gibbs free energy. Then, the phase diagrams had been obtained by the application of Kuhn-Tucker condition and convexity analyses (Rocha and Guirardello, 2009). This method was used by Rocha et al (2014) for a set of mixtures. This work applies the same method, but for a different combination of fatty acids, triglycerides and ethyl ester.

2. Phase Diagrams for solid-liquid equilibrium

By applying the condition of minimum G in the number of moles, at constant T and P , the phases diagrams were obtained for three different models for binary mixtures and two models for ternary mixtures, based on the division of the phases diagram in three regions, as described in Rocha et al (2014), where for a given molar fraction the equilibrium temperature is given by:

$$T = \max \{T_I, T_{II}, T_{III}\} \quad (1)$$

2.1 Margules Asymmetric (MA) – Binary mixtures

From the Margules Model, Eq(2), and its coefficients, Eq(3) and Eq(4), the solid-liquid equilibrium could be represented by regions I, Eq(5), region II, Eq(6) and region III, Eq(7).

$$G_{\text{ex}}^l = R \cdot T \cdot \sum_{i=1}^{NC} x_i^l \cdot \ln \gamma_i^l = x_1^l \cdot x_2^l \cdot (A_{21} \cdot x_1^l + A_{12} \cdot x_2^l) \quad (2)$$

$$R \cdot T \cdot \ln \gamma_1 = [A_{12} + 2 \cdot (A_{21} - A_{12}) \cdot x_1] \cdot x_2^2 \quad (3)$$

$$R \cdot T \cdot \ln \gamma_2 = [A_{21} + 2 \cdot (A_{12} - A_{21}) \cdot x_2] \cdot x_1^2 \quad (4)$$

$$T_I = \frac{\Delta h_{f2} + [A_{21} + 2 \cdot (A_{12} - A_{21}) \cdot (1 - x_1)] \cdot x_1^2}{\frac{\Delta h_{f2}}{T_{f2}} - R \cdot \ln(1 - x_1)} \quad (5)$$

$$T_{II} = \frac{\Delta h_{f1} + [A_{12} + 2 \cdot (A_{21} - A_{12}) \cdot x_1] \cdot (1 - x_1)^2}{\frac{\Delta h_{f1}}{T_{f1}} - R \cdot \ln x_1} \quad (6)$$

$$T_{III} = \frac{v_1 \cdot \Delta h_{f1} + v_2 \cdot \Delta h_{f2} + v_1 \cdot [A_{12} + 2 \cdot (A_{21} - A_{12}) \cdot x_1] \cdot (1 - x_1)^2 + v_2 \cdot [A_{21} + 2 \cdot (A_{12} - A_{21}) \cdot (1 - x_1)] \cdot x_1^2 + \Delta G_R}{v_1 \cdot \frac{\Delta h_{f1}}{T_{f1}} + v_2 \cdot \frac{\Delta h_{f2}}{T_{f2}} - v_1 \cdot R \cdot \ln x_1 - v_2 \cdot R \cdot \ln(1 - x_1)} \quad (7)$$

subject to restriction (8):

$$\frac{\Delta h_{f2} + [A_{21} + 2 \cdot (A_{12} - A_{21}) \cdot (1 - x_{1C})] \cdot x_{1C}^2}{\frac{\Delta h_{f2}}{T_{f2}} - R \cdot \ln(1 - x_{1C})} \leq \frac{\Delta h_{f1} + [A_{12} + 2 \cdot (A_{21} - A_{12}) \cdot x_{1C}] \cdot (1 - x_{1C})^2 + \frac{1}{v_1} \cdot \Delta G_R}{\frac{\Delta h_{f1}}{T_{f1}} - R \cdot \ln x_{1C}} \quad (8)$$

2.2 Margules Symmetric (MS) – Binary mixtures

Using Margules Model in the form described in Eq (9), the binaries interaction parameters, considering constant temperature, could be described in Eq (10).

$$G_{\text{ex}}^I = R \cdot T \cdot \sum_{i=1}^{NC} x_i^I \cdot \ln \gamma_i^I = \frac{1}{2} \cdot \sum_{i=1}^{NC} \sum_{j=1}^{NC} A_{ij} \cdot x_i^I \cdot x_j^I \quad (9)$$

$$A_{ji} = A_{ij} = a_{ij} \quad (10)$$

The definition of regions I, II and III are, respectively showed in Eq(11), (12) and (13):

$$T_I = \frac{\Delta h_{f2} + a_{12} \cdot x_1^2}{\frac{\Delta h_{f2}}{T_{f2}} - R \cdot \ln(1 - x_1)} \quad (11)$$

$$T_{II} = \frac{\Delta h_{f1} + a_{12} \cdot (1 - x_1)^2}{\frac{\Delta h_{f1}}{T_{f1}} - R \cdot \ln x_1} \quad (12)$$

$$T_{III} = \frac{v_1 \cdot \Delta h_{f1} + v_2 \cdot \Delta h_{f2} + v_1 \cdot a_{12} \cdot (1 - x_1)^2 + v_2 \cdot a_{12} \cdot x_1^2 + \Delta G_R^\circ}{v_1 \cdot \frac{\Delta h_{f1}}{T_{f1}} + v_2 \cdot \frac{\Delta h_{f2}}{T_{f2}} - v_1 \cdot R \cdot \ln x_1 - v_2 \cdot R \cdot \ln(1 - x_1)} \quad (13)$$

subject to restriction given by (14):

$$\frac{\Delta h_{f2} + a_{12} \cdot x_{1C}^2}{\frac{\Delta h_{f2}}{T_{f2}} - R \cdot \ln(1 - x_{1C})} \leq \frac{\Delta h_{f1} + a_{12} \cdot (1 - x_{1C})^2 + \frac{1}{v_1} \cdot \Delta G_R^\circ}{\frac{\Delta h_{f1}}{T_{f1}} - R \cdot \ln x_{1C}} \quad (14)$$

2.3 Wilson (W) – Binary mixtures

The Wilson model have their activity coefficients showed in Eqs (15) and (16):

$$\ln \gamma_1 = -\ln(x_1 + x_2 \Lambda_{12}) + x_2 \left(\frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1 \Lambda_{21}} \right) \quad (15)$$

$$\ln \gamma_2 = -\ln(x_2 + x_1 \Lambda_{21}) + x_1 \left(\frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1 \Lambda_{21}} \right) \quad (16)$$

The region's equations that describe the equilibrium curves are Eqs (17), (18) and (19):

$$T_I = \frac{\Delta h_{f2}}{\frac{\Delta h_{f2}}{T_{f2}} - R \cdot \left(\ln(1 - x_1) - \ln((1 - x_1) + x_1 \Lambda_{21}) + x_1 \left(\frac{\Lambda_{12}}{x_1 + (1 - x_1) \Lambda_{12}} - \frac{\Lambda_{21}}{(1 - x_1) + x_1 \Lambda_{21}} \right) \right)} \quad (17)$$

$$T_{II} = \frac{\Delta h_{f1}}{\frac{\Delta h_{f1}}{T_{f1}} - R \cdot \left(\ln x_1 - \ln(x_1 + (1 - x_1) \Lambda_{12}) + (1 - x_1) \cdot \left(\frac{\Lambda_{12}}{x_1 + (1 - x_1) \Lambda_{12}} - \frac{\Lambda_{21}}{(1 - x_1) + x_1 \Lambda_{21}} \right) \right)} \quad (18)$$

$$T_{III} = \frac{v_1 \cdot \Delta h_{f1} + v_2 \cdot \Delta h_{f2} + \Delta G_R^\circ}{v_1 \cdot \frac{\Delta h_{f1}}{T_{f1}} - v_1 \cdot R \cdot \left(\ln x_1 - \ln(x_1 + (1 - x_1) \Lambda_{12}) + (1 - x_1) \cdot \left(\frac{\Lambda_{12}}{x_1 + (1 - x_1) \Lambda_{12}} - \frac{\Lambda_{21}}{(1 - x_1) + x_1 \Lambda_{21}} \right) \right)} \quad (19)$$

$$+ \frac{v_1 \cdot \Delta h_{f1} + v_2 \cdot \Delta h_{f2} + \Delta G_R^\circ}{v_2 \cdot \frac{\Delta h_{f2}}{T_{f2}} - v_2 \cdot R \cdot \left(\ln(1 - x_1) - \ln((1 - x_1) + x_1 \Lambda_{21}) + x_1 \left(\frac{\Lambda_{12}}{x_1 + (1 - x_1) \Lambda_{12}} - \frac{\Lambda_{21}}{(1 - x_1) + x_1 \Lambda_{21}} \right) \right)}$$

subject to restriction by (20):

$$\frac{\Delta h_{f2}}{\frac{\Delta h_{f2}}{T_{f2}} - R \cdot \left(\ln(1 - x_{1C}) - \ln((1 - x_{1C}) + x_{1C} \Lambda_{21}) + x_{1C} \left(\frac{\Lambda_{12}}{x_{1C} + (1 - x_{1C}) \Lambda_{12}} - \frac{\Lambda_{21}}{(1 - x_{1C}) + x_{1C} \Lambda_{21}} \right) \right)} \leq \frac{\Delta h_{f1} + \frac{1}{v_1} \cdot \Delta G_R^\circ}{\frac{\Delta h_{f1}}{T_{f1}} - R \cdot \left(\ln x_{1C} - \ln(x_{1C} + (1 - x_{1C}) \Lambda_{12}) + (1 - x_{1C}) \cdot \left(\frac{\Lambda_{12}}{x_{1C} + (1 - x_{1C}) \Lambda_{12}} - \frac{\Lambda_{21}}{(1 - x_{1C}) + x_{1C} \Lambda_{21}} \right) \right)} \quad (20)$$

2.4 Margules Asymmetric (MA) – ternary mixtures

This development model was based on solidification temperature in solid-liquid equilibrium for ternary mixtures. Considering three compounds (A_1, A_2, A_3) and the intermediate solid compound (peritectic point) formed only by two of them, which the solidification temperature was chosen at maximum temperature of each composition. The Margules Asymmetric model leads to Eq(21) and Eq(22) for the peritectic point.

$$T_i = \frac{\Delta h_i^f + c_i}{\frac{\Delta h_i^f}{T_i^f} - R \cdot \ln x_i} \quad i = 1,2,3 \quad (21)$$

$$T_p = \frac{v_1 \cdot \Delta h_{f1} + v_2 \cdot \Delta h_{f2} + v_1 \cdot c_1 + v_2 \cdot c_2 + \Delta G_R^\circ}{v_1 \cdot \frac{\Delta h_{f1}}{T_{f1}} + v_2 \cdot \frac{\Delta h_{f2}}{T_{f2}} - v_1 \cdot R \cdot \ln x_1 - v_2 \cdot R \cdot \ln x_2} \quad (22)$$

where

$$\begin{aligned} c_1 &= A_{12} \cdot x_2^2 \cdot (1 - 2 \cdot x_1) + 2 \cdot A_{21} \cdot x_1 \cdot x_2 \cdot (1 - x_1) + A_{13} \cdot x_3^2 \cdot (1 - 2 \cdot x_1) + 2 \cdot A_{31} \cdot x_1 \cdot x_3 \cdot (1 - x_1) \\ &\quad - 2 \cdot A_{23} \cdot x_2 \cdot x_3^2 - 2 \cdot A_{32} \cdot x_2^2 \cdot x_3 + \left[\frac{1}{2} \cdot (A_{12} + A_{21} + A_{13} + A_{31} + A_{23} + A_{32}) - Q \right] \cdot (x_2 \cdot x_3 - 2 \cdot x_1 \cdot x_2 \cdot x_3) \\ c_2 &= A_{21} \cdot x_1^2 \cdot (1 - 2 \cdot x_2) + 2 \cdot A_{12} \cdot x_1 \cdot x_2 \cdot (1 - x_2) + A_{23} \cdot x_3^2 \cdot (1 - 2 \cdot x_2) + 2 \cdot A_{32} \cdot x_2 \cdot x_3 \cdot (1 - x_2) \\ &\quad - 2 \cdot A_{13} \cdot x_1 \cdot x_3^2 - 2 \cdot A_{31} \cdot x_1^2 \cdot x_3 + \left[\frac{1}{2} \cdot (A_{12} + A_{21} + A_{13} + A_{31} + A_{23} + A_{32}) - Q \right] \cdot (x_1 \cdot x_3 - 2 \cdot x_1 \cdot x_2 \cdot x_3) \\ c_3 &= A_{31} \cdot x_1^2 \cdot (1 - 2 \cdot x_3) + 2 \cdot A_{13} \cdot x_1 \cdot x_3 \cdot (1 - x_3) + A_{32} \cdot x_2^2 \cdot (1 - 2 \cdot x_3) + 2 \cdot A_{23} \cdot x_2 \cdot x_3 \cdot (1 - x_3) \\ &\quad - 2 \cdot A_{12} \cdot x_1 \cdot x_2^2 - 2 \cdot A_{21} \cdot x_1^2 \cdot x_2 + \left[\frac{1}{2} \cdot (A_{12} + A_{21} + A_{13} + A_{31} + A_{23} + A_{32}) - Q \right] \cdot (x_1 \cdot x_2 - 2 \cdot x_1 \cdot x_2 \cdot x_3) \end{aligned}$$

with $Q = 0$

2.5 Wilson (W) – ternary mixtures

In the same way of Margules, the Wilson model was developed using the Eq(23) and (24).

$$T_i = \frac{\Delta h_i^f}{\frac{\Delta h_i^f}{T_i^f} - R \cdot [\ln x_i + \ln \gamma_i]} \quad i = 1,2,3 \quad (23)$$

$$T_p = \frac{v_1 \cdot \Delta h_{f1} + v_2 \cdot \Delta h_{f2} + \Delta G_R^\circ}{v_1 \cdot \frac{\Delta h_{f1}}{T_{f1}} + v_2 \cdot \frac{\Delta h_{f2}}{T_{f2}} - v_1 \cdot R \cdot [\ln x_1 + \ln \gamma_1] - v_2 \cdot R \cdot [\ln x_2 + \ln \gamma_2]} \quad (24)$$

with the activity coefficients described by Eq(25), (26) and (27).

$$\ln \gamma_1 = 1 - \ln(x_1 + x_2 \Lambda_{12} + x_3 \Lambda_{13}) - \left(\frac{x_1}{x_1 + x_2 \Lambda_{12} + x_3 \Lambda_{13}} + \frac{x_2 \Lambda_{21}}{x_1 \Lambda_{21} + x_2 + x_3 \Lambda_{23}} + \frac{x_3 \Lambda_{31}}{x_1 \Lambda_{31} + x_2 \Lambda_{32} + x_3} \right) \quad (25)$$

$$\ln \gamma_2 = 1 - \ln(x_1 \Lambda_{21} + x_2 + x_3 \Lambda_{23}) - \left(\frac{x_1 \Lambda_{12}}{x_1 + x_2 \Lambda_{12} + x_3 \Lambda_{13}} + \frac{x_2}{x_1 \Lambda_{21} + x_2 + x_3 \Lambda_{23}} + \frac{x_3 \Lambda_{32}}{x_1 \Lambda_{31} + x_2 \Lambda_{32} + x_3} \right) \quad (26)$$

$$\ln \gamma_3 = 1 - \ln(x_1 \Lambda_{31} + x_2 \Lambda_{32} + x_3) - \left(\frac{x_1 \Lambda_{13}}{x_1 + x_2 \Lambda_{12} + x_3 \Lambda_{13}} + \frac{x_2 \Lambda_{23}}{x_1 \Lambda_{21} + x_2 + x_3 \Lambda_{23}} + \frac{x_3}{x_1 \Lambda_{31} + x_2 \Lambda_{32} + x_3} \right) \quad (27)$$

where the coefficient are represented by the Wilson's parameters $\Lambda_{12}, \Lambda_{21}, \Lambda_{13}, \Lambda_{31}, \Lambda_{23}, \Lambda_{32}$.

3. Curve Fitting

The parameters in the models were fitted using the least square method, comparing the experimental and calculated values of the equilibrium temperature:

$$\min SQE = \sum_{i=1}^N (T_i^{\text{calc}} - T_i^{\text{exp}})^2 \quad (28)$$

However, two strategies were used to formulate the problem:

- as a nonlinear program model (NLP), where the experimental points were previously assigned to one of the possible regions in the equilibrium diagram. This requires knowing in advance the region where each point belongs.

- as a discontinuous nonlinear program model (DNLP), where it is not known in advance which region each points belongs. The calculated temperature for a given molar fraction is given by Equation (1), for any given thermodynamic model.

The numerical fitting was done using the software GAMS. Both strategies gave the same results, however a NLP and a DNLP require different solvers in GAMS.

4. Results of case studies

The main difference between this work and the one from Rocha et al (2014) is that this work considered a different set of mixtures, which are the case studies of this work. For binary mixtures, the case studies was: ethyl miristate (1) ethyl palmitate (2), ethyl palmitate (1) ethyl stearate (2), methyl miristate (1) methyl palmitate (2) and palmitic acid (1) tristearin (2), the results are demonstrated by phases diagrams, in Figure 1 a-d. The ternaries mixtures are methyl stearate (1) methyl palmitate (2) methyl miristate (3) and ethyl palmitate(1) ethyl stearate (2) ethyl miristate (3) the results is a equilibrium surface (Figure 2 and 3).

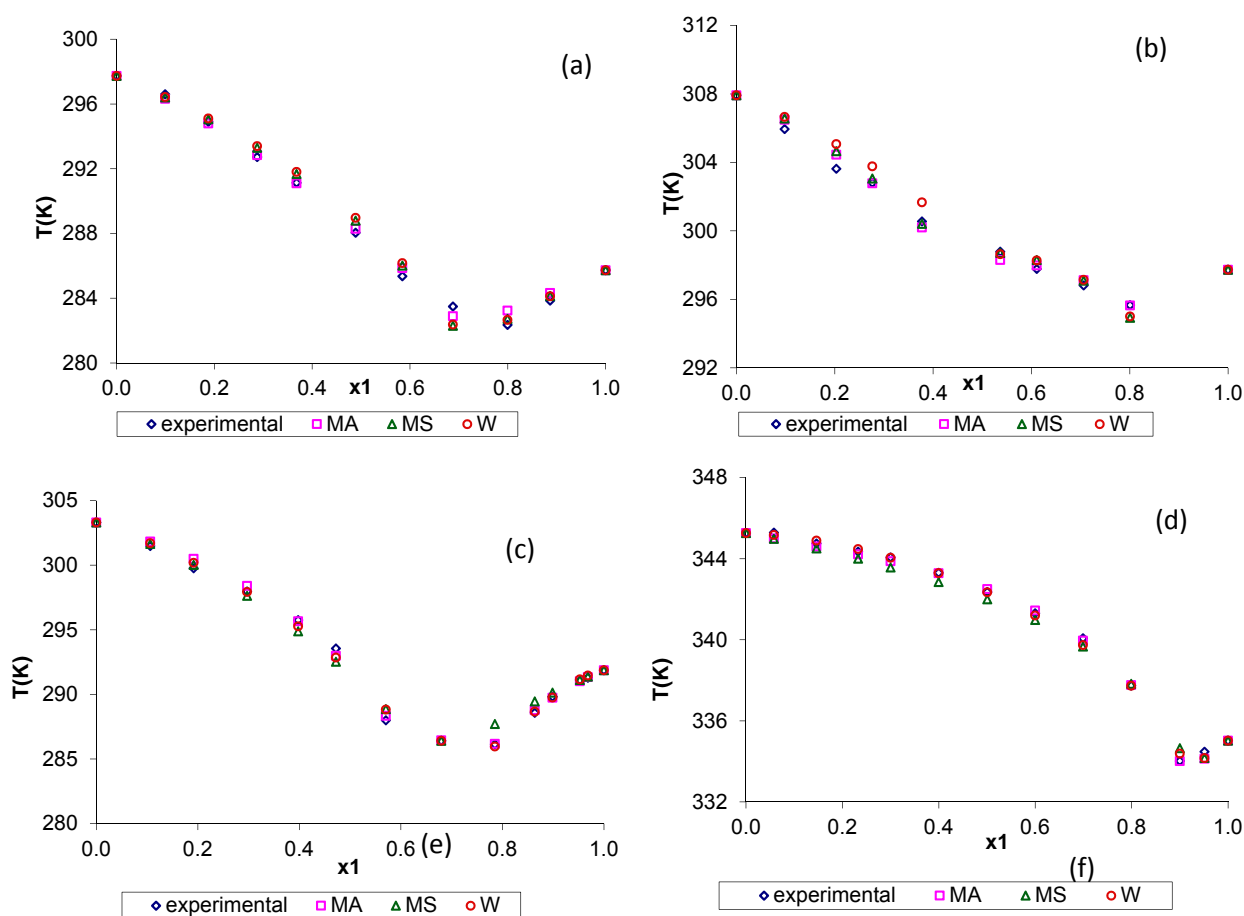


Figure 1: Solid-liquid equilibrium diagram for ethyl miristate (1) ethyl palmitate (2)(a), ethyl palmitate (1) ethyl stearate (2)(b), methyl miristate (1) methyl palmitate (2)(c) and palmitic acid (1) tristearin (2)(d) with Margules Asymmetric (MA); Margules Symmetric (MS) and Wilson (W) models .

The methodology based on phase diagrams obtained by solid-liquid phase calculation was capable to represent the presence or not of solids compounds, using thermodynamics' models compared with experimental data obtained by DSC technique. The curve fitting was done by the sum of squared errors, as described in the previous section.

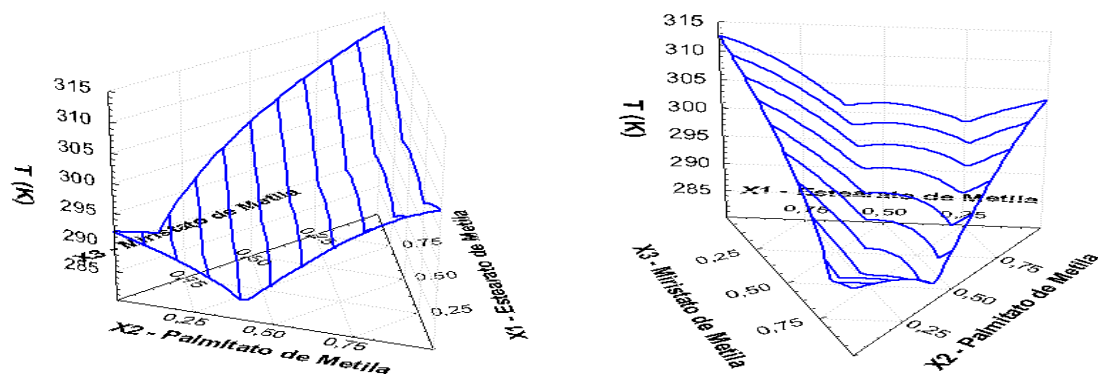


Figure 2: Two visions of solid-liquid equilibrium surface for methyl stearate (1) methyl palmitate (2) methyl miristate (3)

5. Conclusions

In this work, equations for the temperature as a function of molar fraction were used to calculate the phase diagram for solid–liquid equilibrium, including the presence of both peritectic and eutectic points. The models developed showed strong and efficient to obtain phenomenon on liquidus line by both the two models Margules and Wilson. The ternary surface show the big applicability and diversity possibilities for composition of oils and fatties. Five case studies were considered. The method was very easy to apply. The results are satisfactory in agreement with experimental data, including all types mixtures studied in this work, with strong interests in biofuel industry.

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