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Fluid Phase Equilibria

An approach to calculate solid–liquid phase equilibrium for binary mixtures

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ABSTRACT

An approach is presented to calculate solid–liquid phase equilibrium for binary mixtures, using expressions for the temperature as a function of the molar fraction. For Margules model the expression gives explicitly the temperature, while for other liquid phase activity models an iterative procedure is required to calculate the temperature. The method is very easy to apply and it can be used for mixtures that have peritectic and eutectic points, or just a eutectic point. The approach was applied to five case studies with binary mixtures of fatty acids and triglycerides. The results were in good agreement with experimental data.

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1. Introduction

Oils and fats are composed of mixtures of fatty acids [1]. The calculation of solid–liquid equilibrium for these mixtures has a relevant application in many manufacturing areas, such as foods, pharmaceutics, cosmetic, and, more recently, bio-diesel industries [1–6]. The calculation of this equilibrium state is important for all process where there exists interaction between solid and liquid phases, such as extraction, distillation, absorption, and others [6–9].

The reliable determination of phase equilibrium is necessary for the correct prediction of phase formation and their composition [9]. So, it is important to improve the thermodynamic models that could represent both the behavior of the solid and liquid phases, particularly the solid phase, due to the existence of the peritectic point [6,7] and most of the available models are able to represent only the eutectic point [10,11]. One interesting approach to calculate the peritectic point is presented by Slaughter and Doherty [3], where the formation of a compound is considered in the solid phase.

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 if found [8,12].

The general approach in this work applies the same assumptions used by Slaughter and Doherty [3], 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 [3], using a mathematical limit. The liquid phase was modeled using Margules 2-sufix equation [6], 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.

The Kuhn–Tucker conditions [13] were applied to find the solution for the phase diagrams. For the general liquid model, the expressions for the temperature require an iterative procedure, while for Margules model explicit expressions for the temperature as a function of molar fraction were determined. These equations are capable to represent the peritectic point, if it exists. A convexity analysis of the model was done using Margules model [13,14], indicating that the problem with this model has only one minimum. The approach was tested with five case studies from the literature, with binary mixtures of fatty acids and triglycerides.

2. Thermodynamic model

In this work, it is used the approach of minimizing the Gibbs free energy, with respect to the number of moles of each component in each phase, at constant temperature and pressure.

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2.1. Gibbs free energy

The Gibbs free energy is given by

$$G = \sum_{k=1}^{NP} \sum_{i=1}^{NC} n_i^k \cdot \mu_i^k \tag{1}$$

where the chemical potential and the fugacities are given by

$$\mu_i^k = \mu_i^{k,\circ} + R \cdot T \cdot \ln \frac{\hat{f}_i^k}{f_i^{k,\circ}} \tag{2}$$

$$\hat{f}_i^k = f_i^{k,\circ} \cdot x_i^k \cdot \gamma_i^k \tag{3}$$

Since in this work solid-phase equilibrium is considered, the reference state was chosen to be the solid phase ($f_i^{k,\circ} = f_i^{s,\circ}$ and $\mu_i^{k,\circ} = \mu_i^{s,\circ}$). The following relation then is important:

$$\ln \frac{f_i^{l,\circ}}{f_i^{s,\circ}} = \frac{\Delta h_{fi}}{R \cdot T_{ti}} \cdot \left(\frac{T_{ti}}{T} - 1 \right) - \frac{\Delta c_{pi}}{R} \cdot \left(\frac{T_{ti}}{T} - 1 \right) + \frac{\Delta c_{pi}}{R} \cdot \ln \frac{T_{ti}}{T} \tag{4}$$

Defining the parameter B_i as

$$B_i = \ln \frac{f_i^{l,\circ}}{f_i^{s,\circ}} \tag{5}$$

the Gibbs free energy for a solid–liquid mixture can be written as

$$G = \sum_{i=1}^{NC} (n_i^l + n_i^s) \cdot \mu_i^{s,\circ} + R \cdot T$$
$$\cdot \left[\sum_{i=1}^{NC} n_i^l \cdot (B_i + \ln x_i^l + \ln \gamma_i^l) + n_i^s \cdot (\ln x_i^s + \ln \gamma_i^s) \right] \tag{6}$$

2.2. Model for the solid phase

The solid phase was modeled considering a modification of the model used by Slaughter and Doherty [3].

2.2.1. Considerations about modeling the solid phase

Slaughter and Doherty [3] have used a model for activity coefficient in the solid phase given by

$$\gamma_i^s = \frac{1}{x_i^s + \varepsilon} \tag{7}$$

Although this model does not obey the Gibbs–Duhem equation exactly, as pointed out by those authors [3], it keeps the solid phases nearly immiscible. The parameter ε is set to a small value ($\varepsilon = 0.001$).

If Eq. (7) is used in the expression for the Gibbs free energy, we have for the solid phase:

$$R \cdot T \cdot \sum_{i=1}^{NC} n_i^s \cdot (\ln x_i^s + \ln \gamma_i^s) = R \cdot T \cdot \sum_{i=1}^{NC} n_i^s \cdot \ln \frac{n_i^s}{n_i^s + \varepsilon \cdot \sum_{j=1}^{NC} n_j^s} \tag{8}$$

It is interesting to observe in Eq. (8) that, if we take the limit of $\varepsilon \to 0$, the right-hand side of Eq. (8) tends to zero. Even if $n_i^s \to 0$ for some i (but not all i), the right-hand side still tends to the limit zero. If all $n_i^s = 0$, the solid phase does not exist.

Considering the excess Gibbs free energy and its relation with the activity coefficient:

$$G_{ex}^k = R \cdot T \cdot \sum_{i=1}^{NC} n_i^k \cdot \ln \gamma_i^k \tag{9}$$

$$\ln \gamma_i^k = \frac{\partial}{\partial n_i^k} \left[\frac{G_{ex}^k}{R \cdot T} \right]_{T,P,n_j^k} \tag{10}$$

the result for the activity coefficient in the solid phase is

$$\ln \gamma_i^s = -\ln(x_i^s + \varepsilon) + \varepsilon \cdot \left[\frac{1}{x_i^s + \varepsilon} - \sum_{j=1}^{NC} \frac{x_j^s}{x_j^s + \varepsilon} \right] \tag{11}$$

$$\gamma_i^s = \frac{1}{x_i^s + \varepsilon} \cdot \exp \left[\varepsilon \cdot \left(\frac{1}{x_i^s + \varepsilon} - \sum_{j=1}^{NC} \frac{x_j^s}{x_j^s + \varepsilon} \right) \right] \tag{12}$$

Eq. (12) is close to Eq. (7) for small ε (except for $x_i^s \ll \varepsilon$). It obeys the Gibbs–Duhem equation and it keeps the solid phases nearly immiscible. However, in the limit $x_i^s \to 1$ we have that $\gamma_i^s \to 1/(1 + \varepsilon)$ instead of 1. Nevertheless, in the limit of $\varepsilon \to 0$ the result is $\gamma_i^s \to 1$.

The small value for ε was used by Slaughter and Doherty to avoid some numerical problems in the calculation of the equilibrium constant [3]. However, since in this work it is used a different approach for the equilibrium calculation, we can use the limit of $\varepsilon \to 0$ in the Gibbs free energy.

2.2.2. Model for the solid phase used in this work

In this work, the model for the solid phase was considered to be one that obeys the Gibbs–Duhem equation and that has the following properties:

$$\gamma_i^s \cdot x_i^s = 1 \quad \text{for } 0 < x_i^s \le 1 \tag{13}$$

$$\gamma_i^s \cdot x_i^s = 0 \quad \text{for } x_i^s = 0 \tag{14}$$

$$\lim_{x_i^s \to 0} (x_i^s \cdot \ln(\gamma_i^s \cdot x_i^s)) = 0 \tag{15}$$

As a result of these conditions, we have that

$$R \cdot T \cdot \sum_{i=1}^{NC} n_i^s \cdot (\ln x_i^s + \ln \gamma_i^s) = 0 \tag{16}$$

It is important to point out that this model does not consider an ideal mixture for the solid phase, but one with the excess Gibbs free energy given by

$$G_{ex}^s = -R \cdot T \cdot \sum_{i=1}^{NC} n_i^s \cdot \ln x_i^s \tag{17}$$

Since this model results in total immiscibility for the components in the solid phase, if more than one component i solidifies, then each n_i^s can be considered as a different solid phase.

2.3. Product formation in the solid phase

In order to model the peritectic point, it was considered the formation of a compound in the solid phase, with a stoichiometric proportion, as in a chemical reaction or in some kind of physical association [3]. The moles balance in the system is then given by

$$n_i = n_i^0 + \nu_i \cdot \xi \quad i = 1, \ldots, NC \tag{18}$$

For reactants $\nu_i < 0$, for products $\nu_i > 0$, and for inert species $\nu_i = 0$. Considering that the product p has $\nu_p = 1$, we have

$$n_p = n_p^0 + \xi \tag{19}$$

The moles balance must include both phases, since there is a mass transfer between them in order to reach equilibrium, even if