Solid-liquid Equilibrium Modelling and Stability Tests for Triacylglycerols Mixtures

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Abstract

Computer-Aided Mixture Design for product development can take advantage from equilibrium modelling. Systems composed by triacylglycerols (TAG) mixtures are widely used for many applications (foods, cosmetics, pharmaceutical and lubricants) and their end-use properties are very close related to phase behaviour (melting and crystallization). Such molecules can have different polymorphisms in solid state, leading to a lack of intersolubility and consequently formation of multiple solid phases. This work has implemented the solid-liquid equilibrium for TAG mixtures in a two step approach: stability tests and equilibrium compositions computations for two phase mixtures. The Michelsen's method for stability analysis was adapted to cope with polymorphisms and was successful for phase-split detection. Melting curves for mixtures composed by 9 TAGs in different compositions and molecular structures were simulated revealing good agreement with physical background for such systems. Further implementations of other initialization independents stability tests and robust optimization techniques show, therefore, a great potential for use as auxiliary computational framework for match improved mixtures in structured lipids research.

Keywords: triacylglycerols, polymorphisms, solid-liquid equilibrium, CAMD.

1. Introduction

Knowledge of phase equilibrium calculations has been widely applied in chemical process design, simulation and optimization. However, equilibrium calculations have also a great potential to be applied in product design, as many products have their properties directly related to phase behaviour in multi-component mixtures.

In chemical industry, phase behaviour plays an important role in the product functionality of many products: paints, rubber, plastic composites, agglomerated powders, extruded products, foams and foods (Bruin; Jongen, 2003). Phase equilibrium calculations are very useful in food industry for product design and fat-based foods are particular examples where phase behavior directly affects product requirements. The solid fat content and melting profile of such products influences the texture; the mouthfeel related to this texture and to its destruction during mastication is the key factor to final product quality and appreciation by the consumer (Bruin, 1999).

Vegetable oils and fats (natural or modified) are the main raw materials for these fat-based foods. Control of melting and solidification behaviour of such systems is therefore essential for manufacturing these products (Bruin; Jongen, 2003). Despite its importance for the design of fat-based foods with improved chemical, physical and nutritional properties, the use of phase equilibrium calculations remains still unsolved in

such systems, due to its complex nature. In fact, fats and oils are lipids systems composed mainly by triacylglycerols (TAG) molecules. For computing solid fat content, up to 1990, mainly empirical calculation methods were available (Wesdorp, 1990). Such empirical approach limits the application range and provides no fundamental understanding of phase behaviour of TAG systems. After 1990, experimental data on fatty systems (Liang *et al*., 2003; Inoue *et al*., 2004; Zhou and Hartel, 2006; Zhang *et al*., 2007) were published along with some discussions about general TAG phase equilibrium modelling (Wesdorp, 1990; Won, 1993; Himawan *et al*., 2006).

However, a robust and general methodology to cope with the complexity of the problem is still unsolved. One reason is that fats and oils are multi-component mixtures of different triacylglycerols that can crystallize in 3 different polymorphisms (α, β' and β). At these solid states, such molecules have limited miscibility, leading to the formation of several solid phases.

2. Molecular Structures and Polymorphisms

2.1. Triacylglycerol structure and fatty acids

Triacylglycerol molecules (TAGs) are responsible for more than 95% of vegetable oils composition. They are made by three fatty acids sterified to a glycerol backbone, as illustrate in Figure 1.

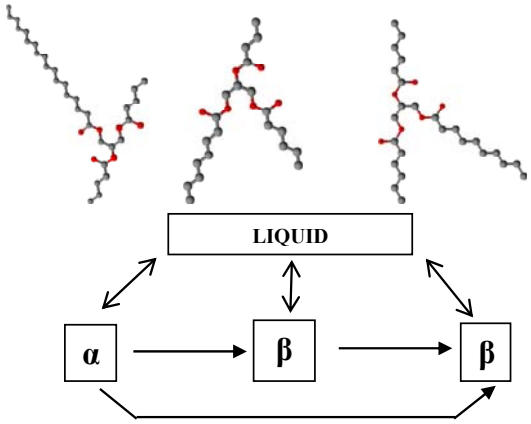

Figure 1: Triacylglycerol structures and state transitions.

Figure 1 shows a large variety of molecules according to the type of 3 fatty acids attached to the glycerol. The carbon chain length, the number of double bounds and even the position of fatty acid in the three possible positions directly affect melting point, melting enthalpy, viscosity and solid miscibility in mixtures. As a consequence, equilibrium between different species in liquid multi-solid phases is directly affected by these molecular issues.

2.2. Polymorphisms

TAG molecules present basically three different polymorphisms (Figure 1): unstable α, metastable β' and stable β, each one corresponding to a solid crystalline arrangement (Sato, 2001). Differences in molecular packing affect important properties related to solidification and melting behaviour, such as melting points and enthalpy of fusion

(molecule level), melting ranges and solid content (mixture level) as well as subjective properties related to fat crystal networks in edible products, as texture and spreadability.

3. Multi-phase Multi-Component Solid Liquid Equilibrium

3.1. General Modelling

Computing phase equilibrium corresponds to the solution of a nonlinear programming (NLP) problem searching for the global minimization of the total Gibbs energy subject to material balance constraints that can be also represented as an equivalent set of nonlinear equations. Experimental and theoretical backgrounds allow to consider liquid and alpha solid phases as ideal (Wesdorp, 1990; Bruin, 1999; Himawan *et al*., 2006). Thus, only β' and β solid phases need description with an excess Gibbs free-energy model, the Margules equations is used in this work. Interaction parameters for the model were obtained by using the isomorphism based correlations, as illustrated by Wesdorp (90).

3.2. Stability Analysis

As the number of phases coexisting in equilibrium is not known *a priori*, the flash calculation is performed in two steps: stability analysis and calculation of phase fraction and equilibrium compositions. McDonald and Floudas (1997) demonstrated that while one can use global optimization to solve the NLP problem, it is computationally more efficient to use a two-stage approach, since the dimensionality of the global optimization problem in phase stability is less than that of the full equilibrium problem.

Stability tests concern the evaluation if a phase can be split in two other phases, given T, P and overall composition. In this work, we use the tangent plane criterion for stability problem as presented by Michelsen (1982a,b): a necessary and sufficient condition for stability of a mixture at fixed temperature, pressure and overall composition (**z**) is that the Gibbs energy surface be at no point below the plane tangent to the surface at **z**. This condition for n components mixture is expressed as follows:

$$D(x) = m(x) - m_0 - \sum_{i=1}^{n} \left(\frac{\partial m}{\partial x_i} \right)_0 (x_i - z_i) \geq 0 \quad \forall x_i \tag{1}$$

Where $m(x) = \sum_{i=1}^{n} x_i \ln x_i + g^E(x)$ and $g^E(x) = G^E / RT$ is the reduced molar excess Gibbs energy. The subscript zero indicates evaluation at $x = z$. D(x) is the tangent plane distance function, which represents that if there is any possible trial phase with composition x to be added which negative value of D(x), it is possible to have a negative variation of Gibbs free energy (initial phase is unstable and splits). As all of the minima in D(x) are located in the interior of the permissible region ($x_i \geq 0$, $\sum x_i = 1$) (Michelsen, 1982a), the value of D(x) will be nonnegative if it is nonnegative at all stationary points.

For achieving stationary points, Michelsen proposed an iteration procedure from a several initial guesses. The adaptation of this method to cope with polymorphisms is done by increasing the number of initial guesses: one pure phase of each component in each polymorphism and mixtures with compositions evaluated as an average of the mixtures already present (Wesdorp, 1990), leading to a 3n+4 initial guesses.

4. Results

Table 1 shows some stability tests performed in a mixture composed by 4 mono-Tags formed by the fatty acids Palmitic, Stearic, Myristic and Oleic. The overall composition (Z) and its physical state, temperature, stationary points and tangent plane distance are

shown together with the physical state of the new phase that will be formed in case of instability (most negative value of tangent plane distance).

Table 1: Stability tests in a four component TAG systems.

Feed (Z1,Z2,Z3,Z4)	Temperature (°C)	Stationary Points (x1,x2,x3,x4)	D(x)/RT	Phase Split
β' (0.25,0.25,0.25,0.25)	80	(0.1135, 0.1713, 0.5438, 0.1713)	-0.9610	Liquid
		(0.1598, 0.0441, 0.7520, 0.0441)	-0.3044	beta'
		(0.1369, 0.4103, 0.0424, 0.4103)	-0.0417	beta'
		(0.0546, 0.0058, 0.9338, 0.0058)	-0.4127	beta'
		(0.9170, 0.0227, 0.0376, 0.0227)	1.1466	Beta
		(0.0035, 0.4980, 0.0005, 0.4980)	0.1060	Beta
		(0.0011, 0.0001, 0.9986, 0.0001)	-0.3533	Beta
β' (0.1, 0.1, 0.1, 0.7)	35	(0.0555, 0.0330, 0.6802, 0.2313)	-1.2008	Liqud
		(0.0223, 0.0010, 0.9701, 0.0067)	-0.8398	beta'
		(0.0880, 0.1049, 0.0728, 0.7343)	0.0012	beta'
		(0.0196, 0.0008, 0.9743, 0.0053)	-0.8402	beta'
		(0.6140, 0.0110, 0.2983, 0.0768)	1.3439	beta
		(0.0022, 0.1246, 0.0009, 0.8723)	0.1268	beta
		(0.0004, 0.0000, 0.9994, 0.0001)	-0.8160	beta

Systems composed by 9 triacylglycerols were used to simulate melting curves. They contain saturated as well as unsaturated molecules with different chain lengths. Mixture 1 is composed by the followings TAGs: MMM, PPP, SSS, OOO, PPS, PSP, SSM, MMP and MMS. Figure 2 shows the melting curve for mixture 1 in the three solid states. It can be noticed that as molecules in α state have the lowest melting points, the α curve lies below the two other curves. For β' and β curves, there is a region (between 20°C and 55°C) where the behavior is inverted (β curves below β' curve), highlighting that solid liquid equilibrium can clarify different behaviors in TAG systems. For β' and β equilibrium, initial compositions given by stability analysis were used.

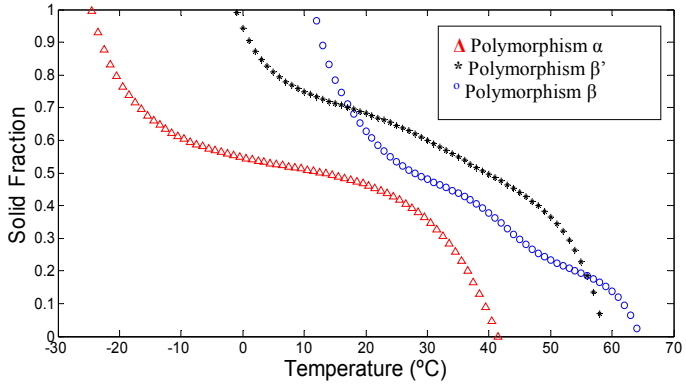

Figure 2: Melting curves for 3 polymorphic states (Mixture 1).

In Figure 3, mixture 1 was simulated using two different compositions, both in β form: Composition 1 is [0.05;0.05;0.2;0.3;0.06;0.1;0.05;0.05;0.14] while composition 2 is [0.1;0.1;0.1;0.5;0.05;0.05;0.03;0.03;0.03]; therefore, in composition 2 half of the system is made by TAG OOO (formed by three oleic acids), which is highly unsaturated (low melting points). Thus, it can be noticed the large influence of this unsaturations in the melting profile of the mixture (lower solid contents for all temperature range).
Resolution of solid-liquid equilibrium can also give useful information about the influence of TAG structures in the melting profile of the mixtures. In order to achieve this, mixture 1 was modified: TAG MMM (14:0) was substituted for LLL (12:0)-mixture 2 and for CCC (10:0)-mixture 3. As the carbon number decreases, the melting points are lower (for same degree of unsaturations); thus, a lower solid fraction for a given temperature is expected, which can be observed in Figure 4. This is true especially between 0°C and 20°C: in the final regions of solidification (more than 80 % of solid) and final region of melting (more than 70 % of liquid), the curves are very similar. Even in the middle regions, the difference is not large as the structure of there mixtures are quite similar. However, the curves reveal the sensitivity of the model even for small changes in molecular structures.

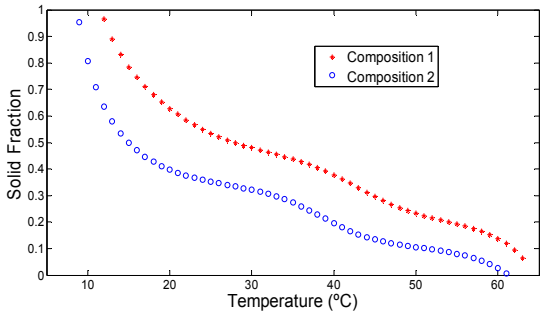

Figure 3: Influence of composition changes in melting curves (mixture 1; β state).

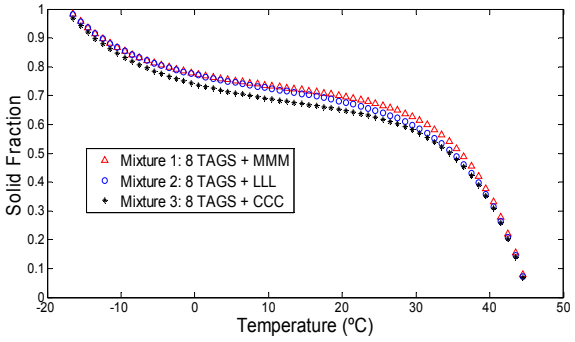

Figure 4: Melting curves for 3 mixtures differing of one TAG.

5. Conclusions

Melting and solidification behavior of triacylglycerol mixtures have a great importance for quality assessment of many products. The resolution of solid-liquid equilibrium with polymorphisms for triacylglycerol systems reveals useful information about melting and solidification profile of these complex mixtures. The effect of changes in mixture

composition or in small changes in molecular structures can be noticed by solid fractions in different temperatures. The technique has showed potential use for theoretical predictive capacity for new mixtures. However, the very large numbers of possible molecules that can be formed by fatty acids in a glycerol backbone requires the use of simulated melting curves coupled with optimization techniques in a Computer Aided Mixture Design environment for triacylglycerols. Besides this, other stability methods (as interval methods) must be tested in order to compare its robustness and the independence of phase split detection to initialization, for using in multi-phase solid problems. Further DSC curves simulations can also be assessed by SLE, and the use of experimental curves can be used as model validation.

The move towards the molecular level for product design is a major trend and challenge for Process System Engineering (PSE) in the future (Grossmann and Westerberg, 2000) and lipid-based products can take advantage of thermodynamic modelling for its phase behavior, allowing to achieve new products with improved functional properties and sustainability principles, as natural resources of triacylglycerols and fatty acids are renewable and provide alternative products using glycerol structure.

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