Thermodynamics of Solid Formation in Cottonseed Oil

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The aim of this study is to establish thermodynamic relations which govern the equilibrium of solid formation during the cooling of cottonseed oil either when tripalmitin is added to it or when the oil is cooled in the presence of solvent with consequent enrichment of the solid phase in certain triacylglycerols. We have established analytical expressions of the functions and variables of state that can describe the experimental results obtained.

The effect of the addition of tripalmitin to refined cottonseed oil is well represented by simple expressions.

KEY WORDS: Cottonseed oil, solid deposition, thermodynamics, tripalmitin.

Cottonseed oil which has been classically refined goes cloudy during cold seasons. This handicap affects its presentation and reduces its trading value.

Several authors (1–5) have tried to extract the high melting point triacylglycerols which cause the cloudiness. The aim of the supplementary treatment applied is to make the oil retain perfect clarity. Thus, two fractions of oil are obtained, *viz.*, a liquid fraction used as table oil and a solid fraction destined for the margarine industry.

The technique consists in cooling the oil until crystallization, preferably in the presence of solvent which reduces viscosity, and then separating the solid and liquid phases. The solid-liquid equilibrium involved has not been studied from a thermodynamic standpoint.

We intend to cool refined cottonseed oil and to study the thermodynamic equilibrium of solid formation in various conditions. First we studied the variation of the cloud point of refined cottonseed oil upon addition of tripalmitin (PPP).

EXPERIMENTAL PROCEDURES

Effect of tripalmitin on the solidification temperature of cottonseed oil. The cottonseed oil used (RCO) was supplied by the Societé de Développement du Coton of North Cameroon (Sodecoton). Tripalmitin (99%) was purchased from Sigma Chemical Co. (St. Louis, MO) and was used without further purification.

Apparatus. The apparatus used to determine the temperature of solid formation in oil solutions is that set up by Belaadi (6). It is of simple thermal analysis type.

The apparatus is mainly composed of a cryogenic unit, a crystallizer and a potentiometric assembly for detecting phase change and registering temperature. In fact the cooling effect brought about by the cryogenic unit through a mixture of water and ethylene glycol (52%, v/v), helps to lower the temperature of the oil solution placed in a cell inside the crystallizer. The rate of cooling can be controlled by adjusting the temperature of the water/ethyleneglycol mixture from the cryorgenic unit. It is usually 0.02 degree/min when determining the temperature of the cloud point.

A thermometer, made with a platinum resistance (100 ohms at 0°C) connected to the potentiometric assembly enables registration of temperature and detection of the cloud point, which is visualised by a change of slope on the cooling curve produced by the recorder.

We have chosen a differential system which ought to give rise to a recording. Thus, the resistance probe through which a constant current is passed is connected to the terminals of a potentiometer whose deflection is recorded with high sensitivity. This is such that full scale deflection on the recording paper (25 cm) corresponds to a change in resistance of 1.5% or 4°C.

Method. A known amount of cottonseed oil and tripalmitin are placed in the sample cell and the mixture is gently heated to dissolve the tripalmitin. Thereafter the cell is allowed to cool to room temperature and is then placed in the crystallizer. The oil solution is slowly cooled while being agitated until solidification occurs and the temperature is determined. Details are available in reference (7).

RESULTS

The solidification temperature of cottonseed oil alone was determined five times and gave 0.1 ± 0.2°C. Measurements made upon adding tripalmitin to the oil were duplicates.

The above results for cottonseed oil from Cameroon is in very good agreement with that published by Ronzone (8) for cottonseed oil from China.

The effect of tripalmitin on the solidification temperature of cottonseed oil is shown in Figures 1 and 2. Figure 2 presents the variation of the solidification temperature with the total tripalmitin (added plus that normally present in the oil); while Figure 1 shows the variation in terms of added tripalmitin only. It can be seen from both Figures 1 and 2 that the solidification temperature of cottonseed oil varies linearly with the amount of tripalmitin present. The amount of tripalmitin normally present in the cottonseed oil was determined as described by Balesdent *et al.* (9). In Figure 2 the intercept at zero added

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Abbreviations: c, Number of components (TAG) in the oil (RCO); GL_i, chemical potential of i in the liquid; GS_i, chemical potential of i in the solid; GL_{oi}, HL_{oi}, SL_{oi}, chemical potential, enthalpy and entropy of pure liquid i; GS_{oi}, HS_{oi}, SS_{oi}, chemical potential, enthalpy and entropy of pure solid i; $\Delta H_i = HL_{oi} - HS_{oi}$, melting enthalpy of pure i; i, each component of oil (RCO) $1 \leqslant i \leqslant c$; L, O, P, P', S, linoleic, oleic, palmitic, palmitoleic, stearic acid (PPP = tripalmitin; etc.); γL_i, activity coefficient of i in liquid solution; γL_o, activity coefficient of tripalmitin in liquid solution; N_i, number of mole of each i in an initial sample of oil (RCO) in the mixture (PPP + RCO); R, perfect gas constant; RCO, refined cottonseed oil; ΔS, common value of ΔS_i if they are equal; $\Delta S = SL_{oi} - SS_{oi}$, melting entropy of pure i; ΔS_o, melting entropy of tripalmitin; γS_i, activity coefficient of i in solid solution; γS_o, activity coefficient of tripalmitin in solid solution; T_A, cryoscopic constant; T_o, melting temperature of pure oil (RCO) without tripalmitin; TF_i, melting temperature of i; TF_o, melting temperature of tripalmitin; TAG, triacylglycerol; X, mole fraction of tripalmitin (PPP) in the initial mixture (PPP + RCO); X_i, mole fraction of i in the oil without PPP; Y, mole fraction of tripalmitin in the solid deposit; Y_i, mole fraction of i in the solid deposit; Z_i, mole fraction of i in the initial mixture (PPP + RCO).
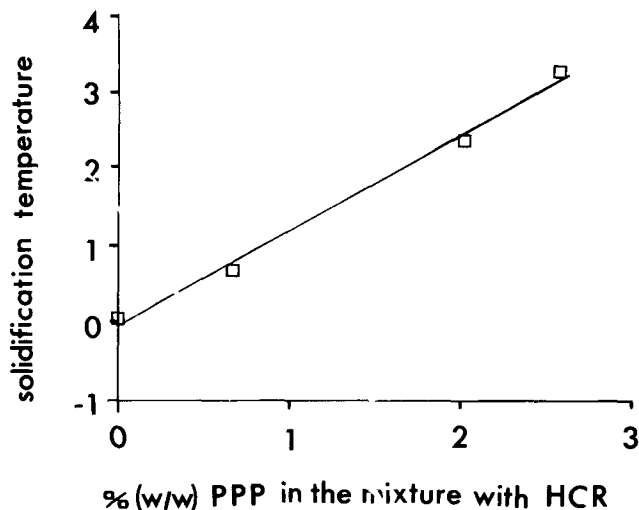
FIG. 1. Temperature of solidification of mixtures of RCO + PPP as a function of the amount of PPP in the mixture.
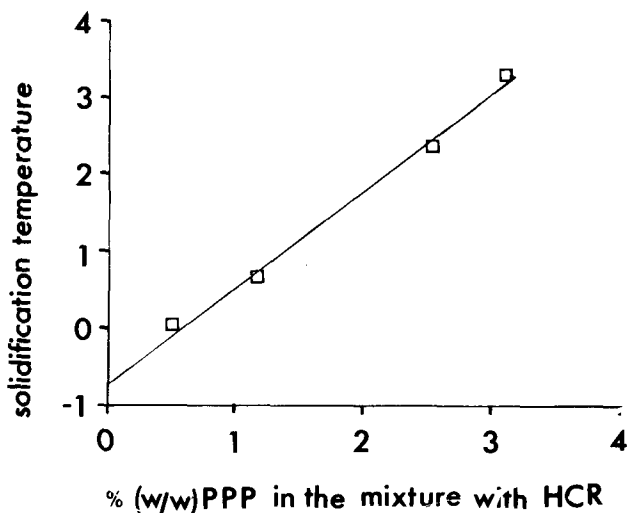

FIG. 2. Temperature of solidification of mixtures of RCO + PPP as a function of the total amount of PPP in the mixture with RCO from which constituent PPP has been removed.

tripalmitin corresponds to $-0.8\,^{\circ}C$, which is slightly lower than that obtained for the solidification of the initial cottonseed oil and confirms the general trend that tripalmitin raises the solidification temperature

Hence, this study shows that the presence of a high melting point triacylglycerol, such as tripalmitin, in cottonseed oil raises the cloud point of the oil.

Study of the thermodynamic equilibrium: Theoretical. The principle of determining the thermodynamic relations between variables of interest in solid formation from a complex liquid is simple—it consists of writing down the equations for the equality of chemical potential of each chemical species in the two phases, solid and liquid. It is essential, first of all, to clearly define the variables in question.

Let us consider a complex liquid of composition defined by mole fractions X_1, X_2, ... X_i, ... X_c of the c constituents, which forms a complex solid phase at temperature

(T) of composition defined by the mole fractions Y_1, Y_2, ... Y_i, ... Y_c of the same constituents. (We have here a liquid solution and a solid solution).

The chemical potential of each species, i, in a given phase (liquid or solid) GL_i or GS_i is split into two parts, *viz.*, that for the pure substance in the same state (liquid or solid) GL_{oi} or GS_{oi} and that for the mixing where we introduce the coefficients of activity γL_i and γS_i, so that we have:

$$GL_i = GL_{oi} + RT \ln \gamma L_i \cdot X_i$$

$$GS_i = GS_{oi} + RT \ln \gamma S_i \cdot Y_i$$

Given the equality of chemical potential at the temperature of solid formation, we have:

$$GL_{oi} + RT \ln \gamma L_i \cdot X_i = GS_{oi} + RT \ln \gamma S_i \cdot Y_i$$

Hence:

$$RT \ln (\gamma S_i \cdot Y_i / \gamma L_i \cdot X_i) = GL_{oi} - GS_{oi} \qquad [1]$$

The difference between the chemical potential of each pure substance in the liquid state and in the solid state can be written as a function of temperature through the enthalpy of fusion, $\Delta H_i = HL_{oi} - HS_{oi}$, or the entropy of fusion, $\Delta S_i = SL_{oi} - SS_{oi}$ since:

$$GL_{oi} = HL_{oi} - T \cdot SL_{oi}$$

$$GS_{oi} = HS_{oi} - T \cdot SS_{oi}$$

Thus:

$$GL_{oi} - GS_{oi} = H_{oi} - S_{oi} - T (SL_{oi} - SS_{oi}) = \Delta H_i - T \cdot \Delta S_i$$

Since this quantity is zero at the temperature of fusion (melting) TF_i of the pure substance i, we have $\Delta H_i = TF_i \cdot \Delta S_i$ when

$$GL_{oi} - GS_{oi} = \Delta S_i (TF_i - T)$$

Equation [1] can then be written as:

$$RT \ln (\gamma S_i \cdot Y_i / \gamma L_i \cdot X_i) = \Delta S_i (TF_i - T)$$

thus

$$Y_i = \frac{\gamma L_i}{\gamma S_i} X_i \cdot \exp [\Delta S_i (TF_i - T)/RT] \qquad [2]$$

The (2c + 1) variables X_i, Y_i, T are thus linked by the (c + 2) relations:

$$\sum_{i=1}^{c} X_i = 1 \qquad \sum_{i=1}^{c} Y_i = 1$$

and the c relations [2] giving c-1 independent variables.

Therefore, if the values of the c-1 variables are defined, all the other c+2 are also defined. So, for example, given a liquid of known composition, (c-1) titers X_i are known, and the temperature T of solidification and the composition Y_i of the solid can be determined.

The foregoing expressions will be used to analyze the results of the variation of solidification temperature with the amount of added tripalmitin.

Variation of solidification temperature with added tripalmitin. We consider a cottonseed oil which contains no original tripalmitin, its composition is defined by the molar titers X_1, ... X_i, ... X_c in the c constituents, with $\sum_{i=1}^{c} X_i = 1$. Tripalmitin is then added to the oil so that its mole fraction in this triacylglycerol becomes X. The solid thus formed has the composition Y_1, ... Y_i, ... Y_c for triacylglycerols other than PPP and Y in tripalmitin.

The new composition of the oil after adding tripalmitin has become Z_1, ... Z_i, ... Z_c for the other triacylglycerols and X for tripalmitin, with

$$X + \sum_{i=1}^{c} Z_i = 1$$

In oil containing no initial tripalmitin, with N_1, ... N_i, ... N_c moles of c species, we add N moles of tripalmitin and the titers then become:

$$X_i = N_i / \sum_{i=1}^{c} N_i \qquad \text{for } i = 1 \text{ to } c$$

$$Z_i = N_i/(N + \sum_{i=1}^{c} N_i) \text{ for } i = 1 \text{ to } c \text{ and } X = N/(N + \sum_{i=1}^{c} N_i)$$

whence:

$$\frac{Z_1}{X_1} = \frac{Z_2}{X_2} = ... = \frac{Z_i}{X_i} = ... = \frac{Z_c}{X_c} = \frac{\sum_{i=1}^{c} Z_i}{\sum_{i=1}^{c} X_i} = \frac{1 - X}{1}$$

Hence:

$$Z_i = (1 - X)X_i \quad \text{for } i = 1 \text{ to } c$$

Equation [2] becomes:

$$Y_i = \frac{\gamma L_i}{\gamma S_i} X_i (1 - X) \exp [\Delta S_i(TF_i - T)/RT] \quad \text{for } i = 1 \text{ to } c$$

and for tripalmitin whose quantities γL, γS, ΔS and TF are subscripted by o,

$$Y = \frac{\gamma L_o}{\gamma S_o} \cdot X \exp [\Delta S_o(TF_o - T)/RT]$$

given that the sum of Y_i and Y must equal one, we have

$$1 = \sum_{i=1}^{c} \frac{\gamma L_i}{\gamma S_i} X_i(1 - X) \exp [\Delta S_i(TF_i - T)/RT]$$

$$+ \frac{\gamma L_o}{\gamma S_o} X \cdot \exp [\Delta S_o(TF_o - T)/RT]$$

which is the sought relation between X and T. Rearranging, we have:

$$X = \frac{1 - \sum_{i=1}^{c} \frac{\gamma L_i}{\gamma S_i} \exp [\frac{\Delta S_i}{RT} (TF_i - T)]}{\frac{\gamma L_o}{\gamma S_o} \exp [\frac{\Delta S_o}{RT} (TF_o - T)] - \sum_{i=1}^{c} \frac{\gamma L_i}{\gamma S_i} \exp [\frac{\Delta S_i}{RT} (TF_i - T)]}$$

We had seen earlier that X was a linear function of T, such that at $T = T_o$, $X = 0$. Also the term $T - T_o$ can be introduced as $TF_i - T = TF_i - To - (T - T_o)$.

If we make the reasonable assumption that the entropies of fusion of the triacylglycerols are close in value, we can write down that the various values of $\Delta S_i/R$ are all equal to $\Delta S/R$.

The expression $\exp[(\Delta S_i)/(RT) (TF_i - T)]$ can be split into a product of two terms:

$$\exp[\frac{\Delta S_i}{RT}(TF_i - T_o) - \frac{\Delta S_i}{RT}(T - T_o)] = \exp\frac{\Delta S}{RT}(TF_i - T_o) \cdot \exp\frac{\Delta S}{RT}(T_o - T)$$

whence

$$X = \frac{\exp [\frac{\Delta S}{RT} (T - T_o) - \sum_{i=1}^{c} \frac{\gamma L_i}{\gamma S_i} \exp [\frac{\Delta S_i}{RT} (TF_i - T_o)]}{\frac{\gamma L_o}{\gamma S_o} \exp [\frac{\Delta S_o}{RT} (TF_o - T_o)] - \sum_{i=1}^{c} \frac{\gamma L_i}{\gamma S_i} \exp [\frac{\Delta S_i}{RT} (TF_i - T_o)]}$$

But $\Delta S/R$ is of the order of 50, while $T - T_o$ is no higher than a few Kelvin, $\Delta S/RT (T - T_o)$ is no higher than 0.5 and $\exp [(\Delta S)/(RT) (T - T_o)] = \exp E$, can be reduced to $1 + E$; thus, with:

$$\Sigma = \sum_{i=1}^{c} \frac{\gamma L_i}{\gamma S_i} \exp [\frac{\gamma S_i}{RT} (TF_i - T_o)]$$

it turns out that:

$$X = \frac{1 + \frac{\Delta S}{RT} (T - T_o) - \Sigma}{\frac{\gamma L_o}{\gamma S_o} \exp \frac{\Delta S_o}{RT} (TF_o - T_o) - \Sigma}$$

but $X = 0$ for $T = T_o$, such that $\Sigma = 1$, so T_o is defined and we have:

$$X = \frac{\frac{\Delta S}{RT} (T - T_o)}{[\frac{\gamma L_o}{\gamma S_o} \exp \frac{\Delta S_o}{RT} (TF_o - T_o) - 1]}$$

$$X = \frac{T - T_o}{\frac{RT}{\Delta S} [\frac{\gamma L_o}{\gamma S_o} \exp \frac{\Delta S_o}{RT} (TF_o - T_o) - 1]}$$

Since T and T_o are quite close, the denominator of the above expression can be replaced by the term T_A, where:

$$T_A = \frac{RT_o}{\Delta S} [\frac{\gamma L_o}{\gamma S_o} \exp \frac{\Delta S}{R} (\frac{TF_o}{T_o} - 1) - 1]$$

and T_o is defined by:

$$\sum_{i=1}^{c} \frac{\gamma L_i}{\gamma S_i} \exp [\frac{\Delta S}{RT} (TF_i - T_o)] = 1$$

The required relation X(T) can be written as:

$$X = \frac{T - T_o}{T_A}$$

Figure 2 shows that the experimental points give a straight line whose equation is:

$$X(T) = \frac{T - 272,3}{130}$$

The value found of $T_A = 130$ K is quite plausible, it corresponds to that obtained through the definition of T_A, where:

$$\frac{\Delta S}{R} = 50 \text{ and } \frac{\gamma L_o}{\gamma S_o} = 1,3 \cdot 10^{-4}$$

The final relation is very similar to the classical one, $X(T) = \Delta T/K$, where K is the cryoscopic constant, valuable for the freezing depression of pure components. Here, the similar relation was demonstrated valuable for the deposition of solid solution from a multicomponent solution, upon particular conditions. These conditions are that the entropies of fusion of all components of the liquid solution are the same.

The agreement between theory and experimental results is good, which suggests that thermodynamic equilibrium has been attained in the system studied. Our work suggests that such analytical expressions can be established for other triacylglycerols regarding the variation of solidification temperature with the amount of added triacylglycerol.

Degree of enrichment of the solid fraction. The degree of enrichment of the solid fraction obtained when oil is cooled was also derivated (10) from general equation [2], but our experimental measures of this enrichment were not so reliable in light of difficulties of good separation of solid and liquid.

ACKNOWLEDGMENTS

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