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Solid−Liquid Equilibria in Fatty Acid/Triglycerol Systems

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ABSTRACT: Used for biofuel production, fatty acids and their corresponding triglycerols are stored in most plants. At room temperature, saturated fatty acids and their triglycerols are solid, whereas unsaturated fatty acids and their triglycerols are liquid. Solid−liquid equilibrium data were measured for various binary systems of fatty acids and their triglycerols by differential scanning calorimetry. The freezing temperatures from liquidus curves for the binary systems containing tripalmitine were higher than those for systems containing palmitic acid. At the eutectic point, the melting temperatures for binary systems containing tripalmitine or palmitic acid were similar. The liquidus curves from the solid−liquid equilibrium data were compared with the predicted values obtained by using the LLE-UNIFAC model, and good agreement between the experimental and calculated results was found.

INTRODUCTION

Plant oils are expected to be a green source of fuel, recycling carbon over a very short time. In order to address the problems of global warming and the diminishing reserves of fossil fuels, new methods for producing alternatives to fossil fuels are now required. Originating from plants, biomass resources in general, and biodiesel fuel (BDF) in particular, are renewable and carbon neutral and thus are expected to be suitable energy sources for the reduction of carbon emissions. Most plants store triglycerols as fats, which are broken down into small molecules such as free fatty acids and esters for food, fuel, and other uses. BDF is a useful energy source for many industries. In general, BDF can be generated by the transesterification of triolein and methanol using a base catalyst. Several effective methods for generating fatty acid methyl ester have been proposed. Boocock et al.[1] have suggested that the use of tetrahydrofuran (THF) solubilizes triolein and methanol with the use of a base catalyst, and induces the rapid formation of the methyl ester from vegetable oils. Also, He et al.[2] have reported a catalyst-free transesterification process using supercritical methanol, an approach that shortened the transesterification time. We have reported that the transesterification with dimethyl ether (DME) is 100 times faster than that without DME.[3] We have also investigated the complex phase equilibria of the triolein/palmitic acid/methanol system containing DME[4] and considered novel applications of phase equilibria to BDF production.[5]

As an alternative approach, hydrodeoxygenation using metal catalysts can be used to generate BFD from fats, and the BFD composition is similar to that of crude oil. Therefore, current diesel engines would be compatible with the new fuels. A critical property of the continuous hydrodeoxygenation method is the freezing temperature of the feed mixture, which should be in a completely liquid state. The properties of BDF depend on the waste oils or fats from which it is made. Accordingly, it is important to understand the properties of these crude materials. In this study, we construct a model of two-component mixtures, which serve as the starting material in BDF production.

The objective of this study was to determine the freezing properties of various binary mixtures of triglycerols and fatty acids. The component having high melting temperature was tripalmitin or palmitic acid, and the other component having low melting temperature was triolein, trilinolein, oleic acid, or linoleic acid. Differential scanning calorimetry (DSC) was used to measure both melting temperature and freezing temperature for different compositions of the various binary systems. The DSC heating curve is very convenient to determine the solid−liquid phase equilibrium.[6] The UNIFAC mode has been most convenient method to predict activity coefficient without experimental data for any organic mixtures.[7] The LLE-UNIFAC model[9] was used to reproduce the solid−liquid equilibrium data for all liquidus curves from our previous work.[4]

EXPERIMENTAL SECTION

Materials. Oleic acid, triolein, linoleic acid, and trilinolein were used as the liquid components, and palmitic acid and tripalmitin were used as the solid components. All substances were purchased from Sigma-Aldrich, and their mass purities were certified as being greater than 0.99. Physical properties of the pure substances are listed in Table 1. They are measured by DSC in this study. The melting temperatures (T_m/K) of all components and the heats of fusion (ΔH_m) of solid components are used to calculate the solid−liquid equilibrium data. The eight binary mixtures of solid and liquid components were used as the model waste oils or fats. The mole fraction of the solid

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Table 1. Physical Properties of Triglycerols and Fatty Acids

name	formula	melting temperature T_m/K	molecular weight/g·mol^{-1}	heat of fusion ΔH_m/J·mol^{-1}
liquid component				
oleic acid	C18H34O2	286.7	282.5	
triolein	C57H104O6	278.7	885.46	
linoleic acid	C18H32O2	268.2	280.45	
trilinolein	C57H98O6	256.0	879.4	
solid component				
palmitic acid	C16H32O2	336.7	256.4	53500
tripalmitin	C51H98O6	339.0	807.35	607700

Table 2. Solid–Liquid Equilibrium Data for the Binary Palmitic Acid/Liquid Component Systems

mole fraction of palmitic acid	freezing temperature	eutectic temperature
$x(1)$/-	T_l/K	T_e/K
Liquid Component = Oleic Acid		
0.108	298.0	283.1
0.301	315.3	283.7
0.519	324.5	283.7
0.725	331.0	283.4
0.894	334.8	283.2
Liquid Component = Triolein		
0.047	290.7	275.6
0.101	306.3	275.7
0.290	316.9	276.1
0.501	327.6	275.8
0.707	331.8	276.1
0.888	335.0	275.6
Liquid Component = Linoleic Acid		
0.095	300.7	264.8
0.305	315.6	264.6
0.497	325.3	264.5
0.687	332.4	264.7
0.901	335.0	263.9
Liquid Component = Trilinolein		
0.105	307.3	
0.291	317.3	257.7
0.500	326.5	255.6
0.702	331.2	256.0
0.900	334.7	

Table 3. Solid–Liquid Equilibrium Data for the Binary Tripalmitin/Liquid Component Systems

mole fraction of tripalmitin	freezing temperature	eutectic temperature
$x(1)$/-	T_l/K	T_e/K
Liquid Component = Oleic Acid		
0.095	328.5	284.2
0.291	333.5	284.1
0.509	336.6	284.0
0.736	338.7	283.6
0.885	339.4	283.4
Liquid Component = Triolein		
0.157	328.3	279.3
0.255	331.7	278.7
0.497	335.3	278.7
0.702	336.8	277.4
0.862	338.1	275.4
Liquid Component = Linoleic Acid		
0.101	327.6	263.2
0.297	333.2	262.7
0.507	336.0	262.8
0.717	337.7	262.8
0.812	337.9	
Liquid Component = Trilinolein		
0.097	325.5	254.3
0.297	332.2	
0.472	334.4	251.4
0.653	336.7	252.4
0.885	338.0	

component ($x(1)$) for each binary mixture was set at about 0.1, 0.3, 0.5, 0.7, or 0.9 in mole fraction. The uncertainties for preparing each concentration were less than 0.001 in mole fraction.

DSC Measurement. The weight and mole fraction of the binary mixture in the DSC cell were carefully measured on an analytical balance (Mettler-Toledo Co.). The sample was quick-frozen at less than 200 K and was then heated up to 370 K on the DSC apparatus (SII, DSC6200). The rate of heating was fixed at 3 K·min^{-1}. The typical DSC of curve shows two endothermic peaks corresponding to the eutectic temperature and freezing temperature, respectively. The onset point of the first peak was determined as the eutectic temperature (T_e/K) (solidus line), and the temperature of the second peak was determined as the freezing temperature (T_l/K) (liquidus curve).[6] In order to obtain the melting temperature and freezing temperature, DSC measurement should be done by heating process to avoid the supercooling phenomena. The heating curves of DSC were measured more than three times, and the onset point and peak temperatures were reproduced in within about 0.5 K. The average values for the eutectic temperature and freezing temperature were listed in Tables 2 and 3. The uncertainties of the determined mole fraction of palmitic acid or tripalmitin for each binary mixture were less than 0.001.

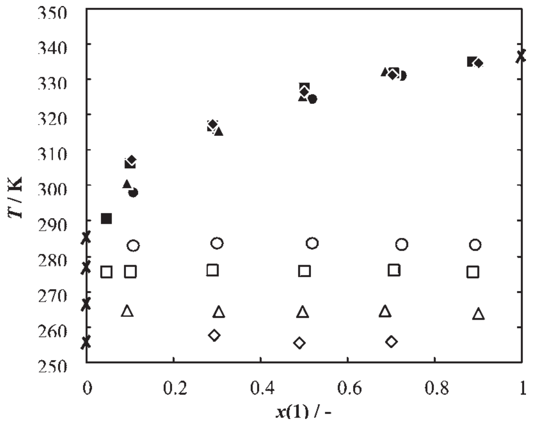

Figure 1. Temperature−composition phase diagrams at ambient pressure of the binary systems of palmitic acid and liquid component. Black symbols represent freezing temperature of mixtures, and white symbols represent eutectic; ●, ○, oleic acid; ■, □, triolein; ▲, △, linoleic acid; ♦, ◇, trilinolein; ×, pure components.

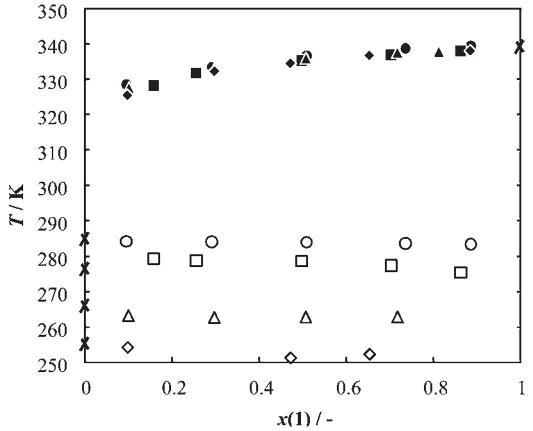

Figure 2. Temperature−composition phase diagrams at ambient pressure of the binary systems of tripalmitin and liquid component. Black symbols represent freezing temperature, and white symbols represent eutectic; ●, ○, oleic acid; ■, □, triolein; ▲, △, linoleic acid; ♦, ◇, trilinolein; ×, pure components.

■ RESULTS AND DISCUSSION

The solid−liquid equilibrium data for eight binary mixtures are listed in Tables 2 and 3.

The freezing temperatures and eutectic temperatures for the binary mixtures containing palmitic acid (Table 2) and tripalmitin (Table 3) are plotted in Figures 1 and 2, respectively. Each two-component mixture was a eutectic system. The eutectic temperature of each mixture should be constant regardless of the concentration of the solid component. For a given solid component of either palmitic acid or tripalmitin, the eutectic temperature was largely unchanged if the liquid component of the binary mixture was same. The freezing temperatures of palmitic acid or tripalmitin did not change much with the liquid components. However, the eutectic temperatures for binary systems changed much with the liquid components, and they were found to be similar values to the melting temperatures of pure liquid components. This means that the eutectic composition was very close to the liquid component and the eutectic temperature of the mixture was very close to the melting temperature of the pure liquid component. Thus, the eutectic composition depends strongly on the identity of the liquid component. In the case where the solid component was palmitic acid, the freezing temperature decreased considerably with decreasing concentration of the solid component, whereas little decrease was found in the case of tripalmitin.

Table 4. UNIFAC Groups for Triglycerols and Fatty Acids

compound	UNIFAC group assignment
palmitic acid	3 1 ’CH3′ 14 ’CH2’ 1 ’COOH’
tripalmitin	4 1 'CH' 3 'CH3' 41 'CH2' 3 'CH2COO'
oleic acid	4 1 'CH3′ 14 'CH2' 1 'CH═CH' 1 'COOH'
triolein	5 1 'CH' 3 'CH3′ 41 'CH2' 3 'CH2COO' 3 'CH═CH'
linoleic acid	4 1 'CH3' 12 'CH2' 2 'CH═CH' 1 'COOH'
trilinolein	5 1 'CH' 3 'CH3' 35 'CH2' 3 'CH2COO' 6 'CH═CH'

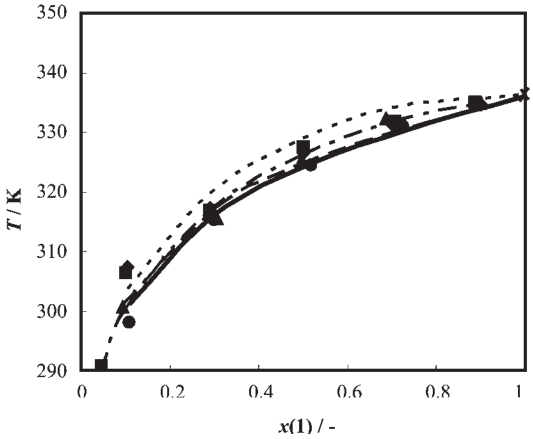

Figure 3. Predicted solid−liquid equilibria for systems of palmitic acid and various fats. Symbols are identical with Figures 1 and 2, and lines indicate calculated values by UNIFAC model. Solid line, oleic acid; dash-dotted line, triolein; broken line, linoleic acid; dotted line, trilinolein.

UNIFAC Prediction. We used the following thermodynamic function for solid−liquid equilibria to estimate the freezing temperature T of waste oils and fats at any concentration

$$\ln x(1)\,\gamma(1) = \frac{\Delta H_{\mathrm{m}}}{R}\left(\frac{1}{T_{\mathrm{m}}} - \frac{1}{T_{\mathrm{l}}}\right) \qquad (1)$$

Here, T_{m} is the melting temperature of the solid component, ΔH_{m} is the heat of fusion, $x\,(1)$ is the mole fraction, and $\gamma(1)$ is the activity coefficient of the solid component. The UNIFAC model was used to determine the activity coefficient of a real solution. The calculations were done using eq 1 and UNIFAC model. In this approach, the components in the mixture are grouped according to functional group, and this method is applicable to almost all biodiesel related materials. The UNIFAC has been convenient model of activity coefficient in the most organic solutions. That was first proposed by Frendenslund et al.[8] for vapor−liquid equilibrium, and Magnussen et al.[9] had extended UNIFAC model for liquid−liquid equilibrium. The temperature range of solid−liquid equilibrium should be closed to that of liquid−liquid equilibrium. The UNIFAC groups used in this study are shown at Table 4. The parameters for the

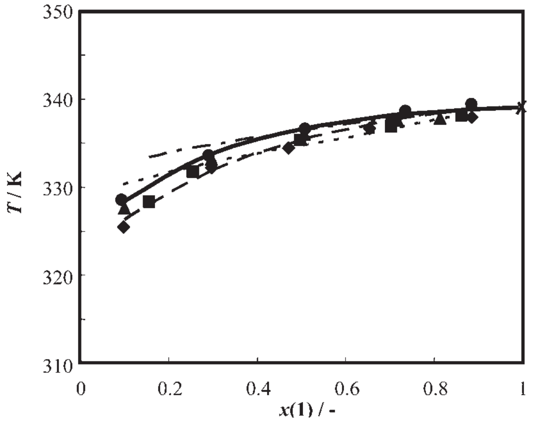

Figure 4. Predicted solid−liquid equilibria for the systems of tripalmitin and various fats. Symbols are identical with Figures 1 and 2, and lines indicate calculated values by UNIFAC model. Solid line, oleic acid; dash-dotted line, triolein; broken line, linoleic acid; dotted line, trilinolein.

Table 5. Mean Deviation between UNIFAC Prediction and Experimental Data

binary systems	mean deviation/K
palmitic acid/oleic acid	0.46
palmitic acid/linoleic acid	−0.46
palmitic acid/triolein	−1.55
palmitic acid/trilinolein	1.09
tripalmitin/oleic acid	−0.21
tripalmitin/linoleic acid	−0.55
tripalmitin/triolein	2.05
tripalmitin/trilinolein	1.03

UNIFAC model were taken from Magnussen's paper[9] as well as from our previous paper[4]

The predicted freezing temperatures obtained by using the UNIFAC model are shown in Figures 3 and 4. Here, we can see that the predicted values agree well with the experimental values with only slight error in the low concentration region. The changes in freezing temperature depending on the composition were considered to be estimated well. The value of the activity coefficients from UNIFAC model is not so far from unity that is the value of ideal solution. Therefore, those mixtures could be ideal. The small differences of freezing temperature for different binary systems could be represented by UNIFAC model. Thus, the UNIFAC model appears to be effective at estimating the freezing temperature of binary systems of waste oils and fats at any concentration. The mean deviations between the predicted values and experimental data are listed in Table 5.

■ CONCLUSION

We investigated binary mixtures containing saturated fatty acids and unsaturated fatty acids as a model of waste oils and fats, which are starting materials in BDF production. The solid−-liquid equilibria of the mixtures were measured by DSC. All binary mixtures were found to be eutectic systems, and the eutectic temperature of each mixture was constant regardless of the concentration and the identity of the solid component. The freezing temperature tended to decrease with decreasing concentration of the solid component. This decreasing trend differed depending on the identity of the solid component; specifically, the freezing temperature decreased considerably in the case of palmitic acid, but only slightly in the case of tripalmitin.

In addition, we estimated the solid−liquid equilibria through calculations using the UNIFAC model. As a result, the calculated values were found to correspond well to the experimental values. The differences due to the identity and concentration of oils and fats were considered to be estimated well. Therefore, the UNIFAC model is effective at estimating the solid−liquid equilibria of oils and fats at any composition.

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