Determination of Mixture Miscibility in Binary and Quaternary Systems of Liquid-Liquid Reactions by Thermodynamics

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Abstract

An industrial chemical process commonly involves two types of chemical reation systems: homogeneous and heterogeneous systems. Identification of mixing state is important in detail modeling of the system. This work focuses on determination of equilibrium mixing state for 3 liquid-liquid reaction systems: 2 types of amidation and transesterification. Each experimental system is binary with two components of reactants at the initial reaction time. As the reactions proceed, each system becomes quaternary with 4 components of 2 reactants and 2 products. The state of mixing of the systems was examined based on the change in dimensionless Gibbs free energy of mixing which was related to liquid activity coefficients. The coefficients were obtained from the UNIFAC method. The results show that the binary mixture of amidation is immiscible in almost all composition ranges except at low reactant concentrations while that of transesterification is immiscible for all compositions of mixture. The mole fraction values used in all systems at the initial reaction time indicate that the binary mixtures are immiscible. As the reactions proceed, the quaternary mixture of amidation is converted to miscible within a short reaction time period due to existing of surfactant produced from the reaction. On the other hand, the quaternary mixture of transesterification is still immiscible throughout the reaction time. At higher reaction temperature, the quaternary mixture of amidation requires a shorter time to convert from immiscible to miscible because of increased rate of surfactant production. The information of mixing state is important for choosing appropriate models in process analysis and design.

Keywords: Phase equilibrium; Binary system; Quaternary system; Amidation; Transesterification

1. Introduction

An industrial chemical process commonly involves two types of chemical reaction systems: homogeneous and heterogeneous systems. A homogeneous system consists of only one uniform phase. Although, the system consists of more than one component, the mixture is still in the form of a single phase. On the other hand, a heterogeneous system consists of two or more phases separated by interfacial boundaries. In a homogeneous reaction system, modeling of any phenomena in a uniform phase is simple. However, in a heterogeneous system consisting of more than one phase, modeling is more complex. Identification of the nature of a mixture therefore is important in process analysis and design.

In this research, two liquid-liquid reaction systems namely, amidation and transesterification are studied in identifying homogeneous and heterogeneous systems. Amidation is the reaction between fatty acid methyl ester and ethanolamine to produce ethanolamide as seen in Figures 1(a) and 1(b). Transesterification is the reaction of triglyceride with methanol to form fatty acid methyl ester which is commonly referred to as biodiesel. Transesterification reaction is shown in Figure 1(c).

These two reactions are the reactions between oil and aqueous phases which are immiscible due to the non-polar and polar nature of oil and aqueous phases, respectively. The products of these two reactions can be immiscible or miscible in the mixture depend on their polar nature.

In this work, the mixture of oil and aqueous phases in the condition of liquid-liquid equilibrium is focused. In initial condition for each reaction of liquid-liquid equilibrium, the system is binary with two components while as the reaction progressed, the system becomes quaternary with 4 components of 2 reactants and 2 products.

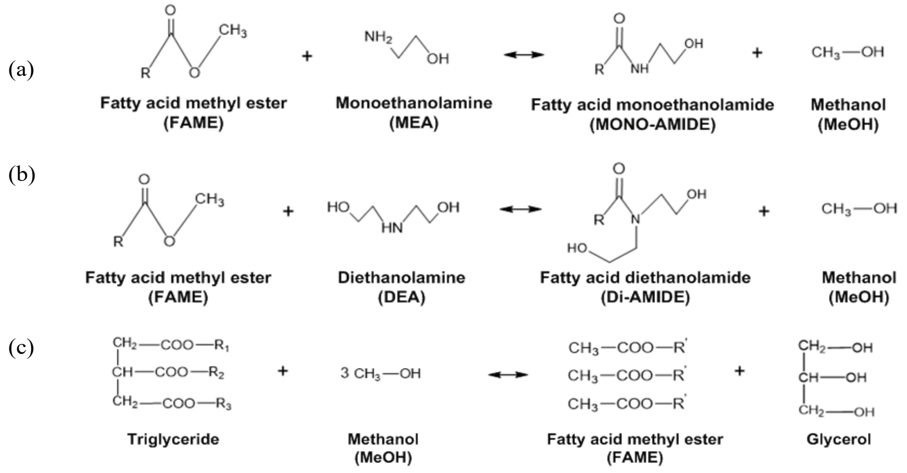

Figure 1 Schematic of amidation and tranesterification: (a) monoethanolamide, (b) diethanolamide and (c) tranesterification

The dimensionless Gibbs free energy of mixing is the chemical potential that indicates the miscibility of a liquid- liquid mixture. This parameter is used to distinguish between homogeneous and heterogeneous systems. During the reaction, the heterogeneous phase of oil and aqueous can be transformed to homogeneous phase, and the phase transition is examined using the dimensionless Gibbs free energy of mixing. Denes and co-workers published a paper on the liquid-liquid-liquid equilibrium (LLLE) calculations based on the change in dimensionless Gibbs free energy of mixing [1]. When the dimensionless Gibbs free energy of mixing has negative value, the system is miscible. Furthermore, the liquid activity coefficients are needed to relate the dimensionless Gibbs free energy of mixing with the compositions of each species for non-ideality system. This coefficient can be evaluated using various models, including Wilson, NRTL, UNIQUAC and UNIFAC [2-4]. Wilson, NRTL and UNIQUAC thermodynamic models requires intermolecular interaction parameters that can only be obtained from experimental data. Only UNIFAC model does not require experimental data as applied in calculations. In the publication published by Fredenslund and colleagues [5], the UNIFAC model was presented to estimate model parameters using group contribution method of the chemical structure of each molecule. The group contribution method is a reliable and fast method for predicting liquid phase activity coefficients in nonelectrolyte mixtures at low to moderate pressures and a temperature. Steen and co-worker applied the UNIFAC method to estimate liquid phase activity coefficients for phase equilibrium calculation in a range of temperature from 300 to 425 K [6]. In this present work, the UNIFAC method is applied for determining the liquid activity coefficient for liquid-liquid systems in the temperature range of 343 to 393 K with a pressure of 1 bar.

Several researches have studied liquid-liquid equilibrium for binary and ternary mixtures of biodiesel [7-13]. In addition, a paper by Cintia and Antonio reported the equilibrium for quaternary system of transesterification of palm oil with ethanol [14]. However, the quaternary equilibrium study for transesterification of palm oil and methanol has not been reported. No prior research has studied the liquid-liquid equilibrium of amidation reaction. This work will study the liquid-liquid equilibrium of binary and quaternary systems for transesterification and amidation reactions.

The miscible of mixture will be also examined based on the change in dimensionless Gibbs free energy of mixing. The liquid activity coefficients are required to relate dimensionless Gibbs free energy of mixing with the compositions of each species. The coefficients will be obtained from the UNIFAC method. Furthermore, the effect of

2. Experimental methods

Two experimental systems were set up for 2 types of reactions: 1) The system for amidation of fatty acid methyl ester and ethanolamide 2) The system for transesterification of palm oil for biodiesel production.

2.1 Experimental set up for amidation

Amidation of fatty acid methyl ester is divided into 2 reactions: the reaction with monoethanolamine and the reaction with diethanolamine. Amidation experiments were carried out in a batch reactor with 500 rpm anchor agitator speed. The temperature of the reactor was controlled by a heater and jacket cooling equipped with a controller. Pressure and temperature data were monitored and collected using an acquisition system. The pressure in a closed batch reactor was initially at 1 bar and increased over time as the reaction proceeded due to increasing of methanol partial pressure. The batch reactor contained a reactant mixture of 100 milliliters. Sodium methoxide (CH_3ONa) was used as catalyst. The average molecular weight of FAME used in this work is 242.403 g/mol which corresponds to C_{14} fatty acid. The chemical composition analysis of fatty acid methyl ester was carried out by a high-performance liquid chromatography (HPLC) (Model 6320 ION trap LC/MS). The change of concentration and pressure over time were measured until they no longer change, when the steady state was reached. Compositions of monoethanolamide and diethanolamide were obtained from mass balance calculation. The experiments were reliably repeated for each condition. The information of compositions of all components is used to calculate the change in dimensionless Gibbs free energy of mixing for identifying the state of mixing of the systems.

In amidation of fatty acid methyl ester and monoethanolamine, the mixture at a mole ratio for fatty acid methyl ester to monoethanolamine of 1.0:1.03 and sodium methoxide catalyst at a concentration of 1.7% w/w are fed into a closed batch reactor. A reaction temperature of 110 °C was used to study a miscibility of liquid phase system. The reaction was operated for 6 hrs. The fatty acid methyl ester composition was analyzed by a high-performance liquid chromatography (HPLC).

In amidation of fatty acid methyl ester and diethanolamine, the mole ratio for fatty acid methyl ester to diethanolamine of 1.0:1.06 with the concentration sodium methoxide catalyst of 1.0% w/w was used.

The reaction was operated at a temperature of 75 °C. The composition of fatty acid methyl ester composition was analyzed by a high – performance liquid chromatography (HPLC).

2.2 Transesterification experiment

Transesterification experiment in a batch reactor with 200 rpm magnetic stirrer speed reported by Kaewchada and co-workers [15] will be used in studying the state of mixing of the system. The experiments were carried out under a reaction temperature of 60 °C with the mole ratio of methanol and triglyceride of 6:1. The potassium hydroxide (KOH) concentration of 1% w/w is used as the catalyst. The reaction time of 6 hours was used. The fatty acid methyl ester composition was analyzed by a gas chromatograph, using a column (DB-Wax) and equipped with a flame ionization detector (FID).

3. Mathematical models

3.1 Study of the miscibility using dimensionless Gibbs free energy of mixing

In thermodynamics, the change in dimensionless Gibbs free energy of mixing is the chemical potential that is minimized when a system at constant pressure and temperature reaches equilibrium. The minimization of dimensionless Gibbs free energy of mixing is used to examine the miscibility of binary and multicomponent. The details are shown below.

3.1.1 Binary mixture

In the initial condition of the reaction, two reactants exist in the system making a binary reacting mixture. Once the reaction started, another two product components are formed resulting in a multicomponent reacting mixture. The dimensionless Gibbs free energy of mixing is considered for binary mixture as shown in eq 1.

$$\Delta g_{\text{mix}} = x_1 \ln(\gamma_1 x_1) + x_2 \ln(\gamma_2 x_2) \qquad (1)$$

where Δg_{mix} is the dimensionless Gibbs free energy of mixing, x the mole fraction of component 1 varied in the range of 0 to 1 and the subscripts of 1, 2 the species of components 1 and 2, respectively. Note that for amidation reaction the subscripts 1 is the species either monoethanolamine or diethanolamine. The subscripts 2 is fatty acid methyl ester. While, transesterification reaction, the subscripts 1 and 2, are the species methanol and triglyceride, respectively.

The function of eq 1 is used to determine the local minima of change in Gibbs free energy of mixing for binary mixtures. The change in Gibbs free energy can have just one local minimum or two local minima with a local maximum between them. In the latter case the two components are partially miscible. Mixtures with only one local minimum are stable miscibility at any composition.

If there are two local minima, a tangent line can be fitted to the function as shown in Figure 2. The tangency points (T_{I}, T_{II}) assign the boundaries (x_{I}, x_{II}) between the stable and unstable liquid phase. If the overall composition of the mixture is found in the opened composition-interval between these two points then the mixture splits into two equilibrium liquid phases with the composition corresponding to the tangent values ($\Delta g_{\text{mix}}>0$). Outside the immiscible regions, where the change in Gibbs free energy of mixing is less and equal to zero (Δg_{mix} mix≤ 0), the system is miscible.

3.1.2 Multicomponent mixture

As the reaction proceeds, a binary liquid mixture changed to be a quaternary liquid mixture. The function of dimensionless Gibbs free energy of mixing for a binary system (eq 1) is changed to be eq (2) for a quaternary system.

$$\begin{aligned}\Delta g_{\text{mix}} = x_1 \ln(\gamma_1 x_1) + x_2(\ln\gamma_2 x_2) \\ + x_3(\ln\gamma_3 x_3) \\ + x_4(\ln\gamma_4 x_4)\end{aligned} \qquad (2)$$

where the subscripts of 1, 2, 3 and 4 represent the species of components 1, 2, 3 and 4, respectively. Note that the subscripts 1, 2, 3 and 4 are ethanolamine, fatty acid methyl ester, ethanolamide and methanol, respectively for amidation reaction. Subscripts 1, 2, 3 and 4 for transesterification reaction, represent methanol, triglyceride, fatty acid methyl ester and glycerol, respectively.

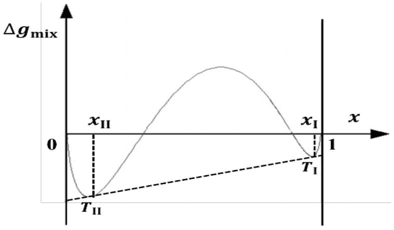

Figure 2 Change in dimensionless Gibbs free energy of mixing with a tangent line between two minima.

3.2 Estimation of liquid activity coefficient using UNIFAC method

The UNIFAC group contribution method is based on the concept of functional groups comprise of the molecules where no experimental thermodynamic data are available. The liquid activity coefficient, γ_i, is expressed as a function of molar composition and temperature. The UNIFAC method is similar to that described in the book of Smith and co- worker book [16] which is summarized below. The UNIFAC equation of activity coefficients is comprised of two parts: a combinatorial term (γ^{C}) to account for molecular size and shape differences, and a residual term (γ^{R}) to account for molecular interactions, as seen in eq 3.

$$\ln\gamma_i = \ln\gamma_i^{C} + \ln\gamma_i^{R} \qquad (3)$$

3.2.1 Combinatorial part

The combinatorial part accounts for molecular size and shape differences between molecules and affects the entropy of mixture and is based on the lattice theory, as shown below.

$$\ln\gamma_i^{C} = 1 - J_i + \ln J_i - 5q_i\left(1 - \frac{J_i}{L_i} + \ln\frac{J_i}{L_i}\right) \qquad (4)$$

where

$$L_i = \frac{q_i}{\sum_j q_j x_j} \quad ; \quad J_i = \frac{r_i}{\sum_j r_j x_j} \qquad (5)$$

The pure component parameters, r_i, and q_i, can be calculated from the sum of the van der Waals subgroup volume and surface area, respectively as follows:

$$r_i = \sum_k v_k^{(i)} R_k \qquad (6)$$

$$q_i = \sum_k v_k^{(i)} Q_k \qquad (7)$$

where R_k and Q_k are the van der Waals volume and surface area of subgroups k, respectively.

3.2.2 Residual part

The residual contribution part accounts for the molecular interactions of groups in the mixture. It can be defined as:

$$\ln\gamma_i^{R} = q_i\left[1 - \sum_k \theta_k \frac{\beta_{ik}}{s_k} - e_{ki}\ln\frac{\beta_{ik}}{s_k}\right] \qquad (8)$$

where

$$e_{ki} = \frac{v_k^{(i)} Q_k}{q_i} \qquad (9)$$

$$\beta_{ik} = \sum_m e_{mi}\tau_{mk} \qquad (10)$$

$$\theta_k = \frac{\sum_i x_i q_i e_{ki}}{\sum_j x_j q_j} \qquad (11)$$

$$s_k = \sum_m \theta_m \tau_{mk} \qquad (12)$$

and $$\tau_{mk} = \exp\frac{-a_{mk}}{T} \qquad (13)$$

where $v_k^{(i)}$ is the number of subgroups of type k in a molecule of species ***i***, x_i the mole fraction of component *i* and a_{mk} the group interaction parameter. The subscripts of i stands for the species, *j* the dummy index running over all species, *k* the subgroups identifier and m the dummy index running over all subgroups. $a_{mk} \neq a_{mk}$ for each group. *T* is the absolute temperature, q_i the molecular surface areas, θ_m the area fraction, τ_{mk} the group distribution parameter, a_{mk} the net energy of interaction between groups ***m*** and ***k***. The details are explained in Smith and coauthors [16].

The UNIFAC parameters of each subgroup—volume, surface area, and the number of subgroups in each molecule of species i—are reported by the Dortmund Data Bank (DDB) as shown in Tables 1, 2, and 3 for the systems of monoethanolamide, diethanolamide, and biodiesel, respectively

Table 1 UNIFAC parameters of each subgroup k: volume (R_k), surface area (Q_k) and the numbers of each subgroup k each molecule of species i $v_k^{(i)}$ of monoethanolamide system. The concerned species are monoethanolamine (1), fatty acid methyl ester (2), monoethanolamide (3), and methanol (4).

Subgroup	k	R_k	Q_k	$v_k^{(1)}$	$v_k^{(2)}$	$v_k^{(3)}$	$v_k^{(4)}$
CH_3	1	0.9011	0.8480	0	2	1	0
CH_2	2	0.6744	0.5400	1	11	13	0
OH	14	1.0000	1.2000	1	0	1	0
CH_3OH	15	1.4311	1.4320	0	0	0	1
CH_2COO	22	1.6764	1.4200	0	1	0	0
CH_2NH_2	29	1.3692	1.2360	1	0	1	0
$CONHCH_2$	96	1.9637	1.4880	0	0	1	0

Table 2 UNIFAC parameters of each subgroup k: volume (R_k), surface area (Q_k) and the numbers of each subgroup k in each molecule of species i ($v_k^{(i)}$) of diethanolamide system. The concerned species are diethanolamine (1), fatty acid methyl ester (2), diethanolamide (3), and methanol (4).

Subgroup	k	R_k	Q_k	$v_k^{(1)}$	$v_k^{(2)}$	$v_k^{(3)}$	$v_k^{(4)}$
CH_3	1	0.9011	0.8480	0	2	1	0
CH_2	2	0.6744	0.5400	3	11	14	0
OH	14	1.0000	1.2000	2	0	2	0
CH_3OH	15	1.4311	1.4320	0	0	0	1
CH_2COO	22	1.6764	1.4200	0	1	0	0
CH_2NH	32	1.2070	0.9360	1	0	0	0
$CON(CH_2)_2$	99	2.4054	1.8120	0	0	1	0

Table 3 UNIFAC parameters of each subgroup k: volume (R_k), surface area (Q_k) and the numbers of each subgroup k in each molecule of species i ($v_k^{(i)}$) of biodiesel system. The concerned species are methanol (1), triglyceride (2), fatty acid methyl ester (3), and glycerol (4).

Subgroup	k	R_k	Q_k	$v_k^{(1)}$	$v_k^{(2)}$	$v_k^{(3)}$	$v_k^{(4)}$
CH_3	1	0.9011	0.8480	0	2	1	0
CH_2	2	0.6744	0.5400	0	41	39	2
CH	3	0.4469	0.2280	0	1	0	1
OH	14	1.0000	1.2000	0	0	0	3
CH_3OH	15	1.4311	1.4320	0	0	0	1
CH_2COO	22	1.6764	1.4200	3	3	3	0

Table 4 Reaction systems with reactant and product components, and reaction temperature.

System	Reaction	Reactants	Products	Temperature (˚C)
1	Amidation	monoethanolamine and fatty acid methyl ester	monoethanolamide and methanol	100, 110, 120
2	Amidation	diethanolamine and fatty acid methyl ester	diethanolamide and methanol	70, 75, 80
3	Transesterification	methanol and triglyceride	glycerol and fatty acid methyl ester	50, 60, 70

4. Results and discussion

The liquid-liquid equilibrium of oil and aqueous mixture is focused. Three reaction systems of liquid-liquid mixtures are studied consisting of 1) amidation with monoethanolamine 2) amidation with diethanolamine 3) transesterification. The reactants and products in the liquid-liquid mixtures of each reaction system and the reaction temperature are shown in Table 4. In initial condition for each reaction of liquid-liquid equilibrium, the system is binary with two components. As the reactions proceed, the reaction systems become quaternary with 4 components of 2 reactants and 2 products. Table 4 shows the components of 2 reactants and 2 products for three systems.

4.1 Results of miscibility for binary system

This section examines the miscibility of binary mixture by using the change in dimensionless Gibbs free energy of mixing. The study of miscibility for binary mixture at initial time (t = 0) is carried out. Figure 3 shows the change in dimensionless Gibbs free energy of mixing in amidation of monoethanolamine and fatty acid methyl ester for the mole fraction of component varied in the range of 0 to 1. The results show that Δ_{gmix} has two local minima and one local maximum between those two minima points for all temperature conditions. Thus, the two components are partially miscible. The analysis of an equilibrium composition is described in the book of Smith and co-workers [16]. The tangency points (T_I, T_{II}) assign the boundaries at $x_{(MEA,I)}$=0.976 and $x_{(MEA,II)}$=0.075 at a temperature of 100 ˚C. The equilibrium compositions of the liquid phase I and liquid phase II at a temperature of 100 ˚C are 0.976 and 0.075. At different temperature conditions, the equilibrium composition of both liquid phases is shown in Table 5 The overall compositions of reactants used in amidation of monoethanolamine are listed in Table 5 and the location of these overall compositions at different temperature conditions are shown in Figure 3. The overall mole fraction is located in the opened mole fraction interval between the two tangency points. Thus, this system mixture is partial miscible.

Figure 4 shows the change in dimensionless Gibbs free energy of mixing in amidation of diethanolamine and fatty acid methyl ester with a diethanolamine mole fraction range of 0 to 1. The results show that Δgmix also has two local minima and one local maximum between those two minimum points at all temperature conditions. The overall mole fraction of DEA in the mixture (x_{DEA}=0.513) is found in the opened composition-interval between $x_{(DEA,I)}$=0.986 and $x_{(DEA,II)}$=0.0061 at a temperature of 70 °C. The mixture of this system splits into 2 equilibrium liquid phases with the mole fraction of diethanolamine 0.986 and 0.0061 for liquid phase 1 and liquid phase 2, respectively at 70 °C. At different temperature conditions, the equilibrium composition of both liquid phases is shown in Table 5.

Table 5 Equilibrium composition of liquid phase I and liquid phase II at different temperature.

System	Temperature (°C)	Overall mole fraction		$(x_{i,\mathrm{I}}, x_{i,\mathrm{II}})$
Amidation with monoethanolamine	100	x_{MEA}	0.507	(0.976, 0.075)
	110			(0.978, 0.078)
	120			(0.981, 0.081)
Amidation with diethanolamine	70	x_{DEA}	0.513	(0.986, 0.0061)
	75			(0.990, 0.0065)
	80			(0.991, 0.0073)
Transesterification	50	x_{MeOH}	0.960	(1,0)
	60			(1,0)
	70			(1,0)

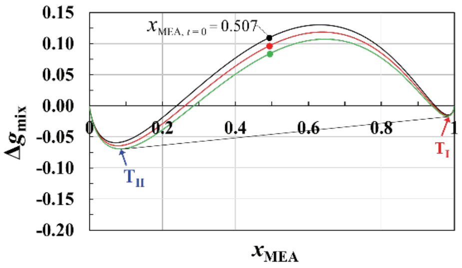

Figure 3 Change in dimensionless Gibbs free energy of mixing in the mixture of monoethanolamine and fatty acid methyl ester at initial time with different temperature conditions

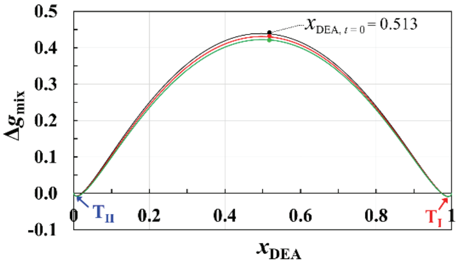

Figure 4 Change in dimensionless Gibbs free energy of mixing in the mixture of diethanolamine and fatty acid methyl ester at initial time with different temperature conditions

The binary mixture for amidation with monoethanolamine is more soluble than that of amidation with diethanolamine due to smaller intramolecular bonding forces of monoethanolamine [17].

In the system of transesterification, the results show that the mixture of this system splits into 2 liquid phases at all methanol compositions (see Figure 5). This system is heterogeneous at all methanol mole fraction and all temperature conditions. This is due to the nature of non-polarity of oil phase and polarity of methanol phase.

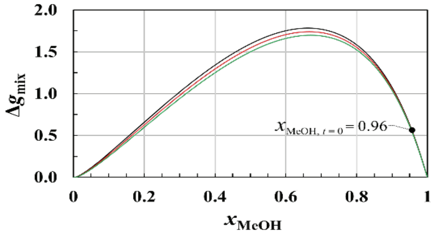

Figure 5 Change in dimensionless Gibbs free energy of mixing in the mixture of methanol and triglyceride at initial time with different temperature conditions

4.2 Results of miscibility for multicomponent mixture

As the reactions proceed, the binary systems change to quaternary systems with two additional product components. This section examines the miscibility of quaternary mixture by using the change in dimensionless Gibbs free energy of mixing. Three systems with 2 reactant and 2 product components as listed in Table 4 are studied. Table 6 shows the experimental compositions of components as a function of time for the system of amidation with monoethanolamine. With the compositions at each time of reaction, the change in dimensionless Gibbs free energy of mixing was calculated and the results are shown in Table 6. The results show that the system of amidation with monoethanolamine was transformed from an immiscible system at the initial time to a miscible system within a short reaction time (0.14 min) when the change in dimensionless Gibbs free energy of mixing is negative value as shown in Table 6. For a period of up to 0.13 min, the system mixture is immiscible with the positive value of the change in dimensionless Gibbs free energy of mixing (see Table 6 and Figure 6). The mixing behavior as less products produced, is similar to the binary system. As the reaction proceeds further, the mole fraction of monoethanolamide increases and the system becomes miscible. This is due to the nature of surfactant of the product (i.e., monoethanolamide) reducing the surface tension between monoethanolamine and fatty acid methyl ester.

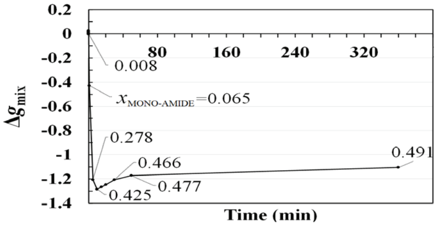

Figure 6 Change in dimensionless Gibbs free energy of mixing in the mixture of monoethanolamine, fatty acid methyl ester, monoethanolamide and MeOH over time at a temperature of 110 ˚C

Table 6 Change in Gibbs free energy over time for amidation with monoethanolamine.

Time (min)	x_{MEA}	x_{FAME}	$x_{\mathrm{MONO-AMIDE}}$	x_{MeOH}	Δg_{mix}
0	0.507	0.493	-	-	0.100
0.1	0.502	0.487	0.006	0.006	0.026
0.11	0.501	0.486	0.006	0.006	0.019
0.12	0.500	0.485	0.007	0.007	0.011
0.13	0.500	0.485	0.008	0.008	0.004
0.14	0.499	0.484	0.008	0.008	-0.003
1	0.442	0.427	0.065	0.065	-0.429
5	0.229	0.214	0.278	0.278	-1.208
10	0.082	0.067	0.425	0.425	-1.286
15	0.068	0.053	0.439	0.439	-1.267
20	0.057	0.042	0.450	0.450	-1.247
30	0.041	0.026	0.466	0.466	-1.208
50	0.031	0.016	0.477	0.477	-1.173
360	0.017	0.002	0.491	0.491	-1.105

Table 7 Change in Gibbs free energy over time for amidation with diethanolamine.

Time (min)	x_{DEA}	x_{FAME}	$x_{\mathrm{DI-AMIDE}}$	x_{MeOH}	Δg_{mix}
0	0.514	0.486	-	-	0.430
1	0.493	0.466	0.020	0.020	0.200
2	0.474	0.446	0.040	0.040	0.033
2.1	0.472	0.444	0.042	0.042	0.018
2.2	0.470	0.442	0.044	0.044	0.003
2.3	0.468	0.440	0.046	0.046	-0.012
3	0.454	0.427	0.059	0.059	-0.108
4	0.436	0.408	0.078	0.078	-0.231
5	0.418	0.390	0.096	0.096	-0.340
20	0.200	0.172	0.314	0.314	-1.120
40	0.143	0.116	0.371	0.371	-1.185
60	0.118	0.090	0.396	0.396	-1.192
80	0.102	0.075	0.411	0.411	-1.188
100	0.096	0.069	0.418	0.418	-1.184
120	0.096	0.068	0.418	0.418	-1.184
180	0.095	0.068	0.418	0.418	-1.184
240	0.095	0.067	0.419	0.419	-1.184
480	0.094	0.066	0.420	0.420	-1.183

Table 7 shows the experimental results of the composition change over time as the amidation with diethanolamine proceeds. In addition, the change in dimensionless Gibbs free energy of mixing calculated from eq 2 is also shown in Table 7 and Figure 7. The results indicates that the reaction mixture in the amidation with diethanolamine takes longer reaction time to transform from immiscible to miscible (2.3 mins) compared to that in the amidation with monoethanolamine. During 2.2 min reaction, the change in Gibbs free energy of mixing is positive value indicating an immiscible mixture. After 2.2 min reaction, the system mixture becomes miscible because of a higher mole fraction of diethanolamide which is a surfactant (see Table 7). The amidation with monoethanolamine requires a shorter reaction time period to reach miscibility than the amidation with diethanolamine due to smaller intramolecular bonding forces of monoethanolamine.

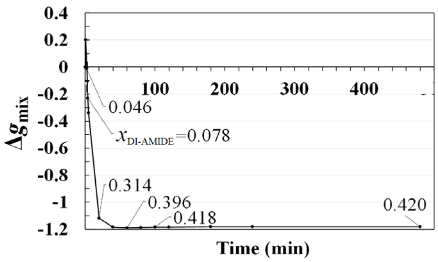

Figure 7 Change in dimensionless Gibbs free energy of mixing in the mixture of diethanolamine, fatty acid methyl ester, diethanolamide and MeOH over time at a temperature of 75°

Table 8 and Figure 8 shows that the change in Gibbs free energy for transesterification is positive at all reaction time. Thus, in the system of transesterification, the mixture is still heterogeneous throughout the reaction time due to existing of the non-polarity of oil phase and polarity of methanol phase. The products of this system have no property of surfactant.

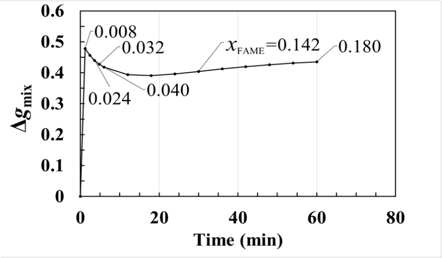

Figure 8 Change in dimensionless Gibbs free energy of mixing in the mixture of methanol, triglyceride, fatty acid methyl ester and glycerol over time at 60 °C

Table 8 Change in Gibbs free energy over time for transesterification.

Time (min)	x_{MeOH}	x_{TG}	x_{FAME}	x_{GL}	Δg_{mix}
0	0.960	0.040	-	-	0.512
1.2	0.950	0.039	0.008	0.003	0.478
2.4	0.941	0.037	0.017	0.006	0.456
3.6	0.932	0.035	0.024	0.008	0.440
4.8	0.923	0.034	0.032	0.011	0.428
6	0.915	0.032	0.040	0.013	0.418
12	0.877	0.025	0.074	0.025	0.394
18	0.845	0.019	0.102	0.034	0.391
24	0.820	0.014	0.124	0.041	0.396
30	0.801	0.010	0.142	0.047	0.404
36	0.787	0.007	0.154	0.051	0.412

42	0.776	0.005	0.164	0.055	0.420
48	0.768	0.004	0.171	0.057	0.426
54	0.762	0.003	0.176	0.059	0.431
60	0.758	0.002	0.180	0.060	0.435

4.3 Effect of temperature on the mixing of the systems for amidation and transesterification reactions

This section examines the effect of temperature on the mixing for three reactions listed in Table 4. The temperatures for three reaction systems are varied as shown in Table 4.

A higher temperature required a shorter time to convert from heterogeneous to homogeneous because of increased rate of reactions, resulting in more surfactant product produced in the system (see Tables 9 and 10).

Table 9 Change in dimensionless Gibbs free energy at different temperatures for amidation with monoethanolamine.

Temp., (°C)	$x_{\text{MONO-AMID}}$	Δg_{mix}	Time to change phase (min)
100	0.009	-0.0001	0.15
110	0.008	-0.0029	0.14
120	0.007	-0.0021	0.10

Table 10 Change in dimensionless Gibbs free energy at different temperatures for amidation with diethanolamine.

Temp., (°C)	$x_{\text{DI-AMIDE}}$	Δg_{mix}	Time to change phase (min)
70	0.049	-0.025	4.0
75	0.046	-0.012	2.3
80	0.044	-0.006	1.9

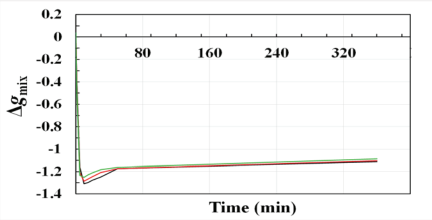

Figure 9 Change in dimensionless Gibbs free energy of mixing in the mixture of monoethanolamine, fatty acid methyl ester, monoethanolamide and MeOH at different temperatures

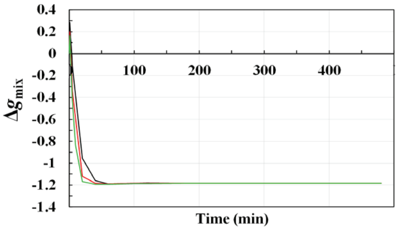

Figure 10 Change in dimensionless Gibbs free energy of mixing in the mixture of diethanolamine, fatty acid methyl ester, diethanolamide and MeOH at different temperatures

The system of transesterification is heterogeneous at all temperature. The effect of temperature on the mixing is not much significant on mixing of this system.

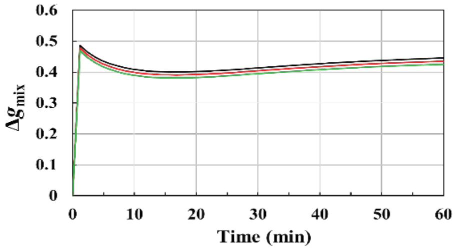

Figure 11 Change in dimensionless Gibbs free energy of mixing in the mixture of methanol, triglyceride, fatty acid methyl ester and glycerol at different temperatures

5. Conclusions

This work focuses on determination of equilibrium mixing state for three liquid-liquid reaction systems: 1) amidation with monoethanolamine 2) amidation with diethanolamine and 3) transesterification. At the initial time of reactions, the system is binary with two components of reactants. As the reactions proceed, the systems become quaternary with 4 components of 2 reactants and 2 products. The state of mixing of the systems was examine based on the change in dimensionless Gibbs free energy of mixing which was related to liquid activity coefficients. The coefficients were obtained from the UNIFAC method.

1. The calculation results show that in the system of amidation, the binary mixture is immiscible in almost all composition ranges except at low reactant concentrations. The mixture with overall composition used in this work at the initial time is immiscible. In the system of transesterification, the mixture of triglyceride and methanol is split into two phases for all composition ranges. Therefore, only a heterogeneous phase was found in the system.

2. As the reactions proceed, the quaternary mixture of amidation turns to be miscible within a short reaction time period while that of transesterification is still immiscible throughout the reaction time.

3. At higher reaction temperature, the quaternary mixture of amidation requires a shorter time to convert from immiscible to miscible because of increased rate of surfactant production. The effect of temperature on the mixing of transesterification system is not much significant.

6. Acknowledgement

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