

Measurements and Prediction of Melting Temperature and Eutectic Point of Binary Fatty Acids Based on Wilson Activity Model

S.M. Mirpoorian^a, M.H. Vakili^b, S.H. Noie^{b,*} and P. Roohi^c

^aChemical Engineering Department, Ferdowsi University of Mashhad, Mashhad, Iran

^bDepartment of Chemical Engineering, Shahreza Branch, Islamic Azad University, Shahreza, Iran

^cPhd of Chemical Engineering, National Iranian Gas Company

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There is a great technical interest in solid-liquid equilibrium (SLE) of binary fatty acids. Mainly, these substances are used for the design, development, and operation of many industrial processes because of their application in many manufacturing fields such as the cosmetic, pharmaceutical and biotechnology industries. In this study, a technique is proposed for binary fatty acid mixtures to estimate the melting temperatures as a function of mole fraction in the solid-liquid phase equilibrium. Derivation of the Wilson model was developed to predict the melting temperatures and latent heat to achieve eutectic points of capric acid, undecylic acid, pentadecylic acid, and margaric acid binary mixtures. The results showed that in the all binary mixtures, the eutectic point is near to a lighter compound except capric+undecylic acid because of the lower melting temperature of undecylic acid compared to capric acid. Comparison of experimental and thermodynamic studies revealed the low deviations between measured and calculated values obtained in this study.

Keywords: Fatty acid, Wilson model, Melting temperature, Eutectic point

INTRODUCTION

The prediction of equilibrium in solid-liquid phase is important to characterize the composition and the phase formation of many industrial processes. Despite the long history of merits of using solid-liquid phase experimental data in separation processes, the practical and theoretical interest in this area is still growing [1]. The solid-liquid equilibrium, especially fatty acids is important for the biofuel separation process. So, it is necessary to improve the thermodynamic models to predict thermophysical and phase equilibrium properties [2-6].

The complicated phase diagrams of fatty acid mixtures contain eutectic and pre-eutectic points, where a new solid substance forms in solid phase because of differences in the molecular interactions between similar or different molecules [7]. Furthermore, since the majority of fatty acids

in biodiesel fuels are made of natural vegetable oils, they attract many interests in renewable energy fields as an alternative for the fossil fuel [5].

The trustworthy determination of phase equilibrium properties is necessary for the correct estimation of phase formation and their compositions [5]. So, it is essential to improve the thermodynamic models which represent both the behavior of liquid and solid phases. The solid phase is of particular importance because it contains the pre-eutectic point [8,9]; most of the available literature models have focused on the eutectic point [10,11]. One interesting approach to estimate the pre-eutectic point was developed by Slaughter and Doherty [12], in which the component is formed in a solid phase.

The system of Capric + Lauric acids were investigated by Grondal and Rogers [13] and by Müller and Stage [14], the mixture of Lauric + Myristic acids were studied by Müller and Stage [14] and also by Heintz [15], and the mixtures lauric + palmitic and lauric + stearic acids were

*Corresponding author. E-mail: noie@um.ac.ir

investigated by Heintz [15]. Finally, the experimental results of the ten binary mixtures were correlated with the Wilson [16], NRTL [17] and UNIQUAC [18] models.

In this work, we study the experimental solid-liquid phase equilibrium of the six fatty acid binary mixtures using the DSC technique. The mixtures are composed of the following pairs of fatty acids: Capric + undecylic, capric + pentadecylic, capric + margaric, undecylic + pentadecylic, undecylic + margaric, and pentadecylic + margaric. Based on our literature survey, the mixtures of binary mixtures considered in this study are not evaluated yet and also Wilson model (studied for the 6 pairs of fatty acids in this study) has been employed only for myristic, palmitic and capric acid mixtures in Rocha *et al.* work [4]. Consequently, this is for first time which melting temperature and eutectic point of the ten binary mixtures listed are considered by experimental measurements and predicted by Wilson activity model.

EXPERIMENTAL

Capric acid, undecylic acid, pentadecylic acid and margaric acid were purchased from Merck pharmaceutical company. The purity, melting points and the latent heat of fatty acids are given in Table 1.

The melting temperatures and latent heat of the materials are in good agreement with the literature values [19-23]. A schematic of the differential scanning calorimetry (DSC) is depicted in Fig. 1. The apparatus was operated for estimation of the equilibrium eutectic and freezing points from the cooling temperature curve. Additionally, the measuring system has a source of laser light with a light detector to observe the solid formation at the melting point from the variation of light scattering intensity.

The experimental setup in Fig. 1 consists of an equilibrium cell with the capacity of about 9 cm³. A prepared sample at a specified composition was loaded on the equilibrium cell and heated to melt at a higher melting temperature of every fatty acid. The final melted mixture was homogenized by a magnetic stirrer, vigorously. Then, the melting mixture was cooled to temperatures below the lowest melting temperature of each fatty acids with cooling rate of 1.0 K min⁻¹. The temperature change rate in the

proximity of phase transition was controlled within 0.1 K min⁻¹ by a control system.

The temperature in the equilibrium cell was measured every moment by a sensing probe within ±0.01 K. The measurements were duplicated to the assurance of reproducibility in estimation of the mixture melting temperature. It showed that the uncertainties of temperature in experiments were not larger than 0.5 K.

THERMODYNAMIC MODEL

Model for Solid Phase

The Gibbs free energy for a solid-liquid mixture can be written as:

$$G = \sum_{i=1}^{NC} (n_i^l + n_i^s) \cdot \mu_i^{s,0} + RT \cdot \left[\sum_{i=1}^{NC} n_i^l \cdot (B_i + \ln X_i^l + \ln \gamma_i^l) + n_i^s \cdot (\ln X_i^s + \ln \gamma_i^s) \right] \quad (1)$$

In order to modeling the mixture melting point, the formation of a compound in the solid phase was considered. The mole balance in the system is then given by:

$$n_i = n_i^0 + v_i \cdot \xi \quad i = 1, \dots, NC \quad (2)$$

where NC is the number of components. For reactants $v_i < 0$, for products $v_i > 0$, and for inert species $v_i = 0$.

Considering that the product p has $v_p = 1$, we have:

$$n_p = n_p^0 + \xi \quad (3)$$

The mole balance must include both phases, since there is a mass transfer between them in order to reach equilibrium, even if the compound is formed only in the solid phase. Therefore, the first term in Eq. (1) can be written as:

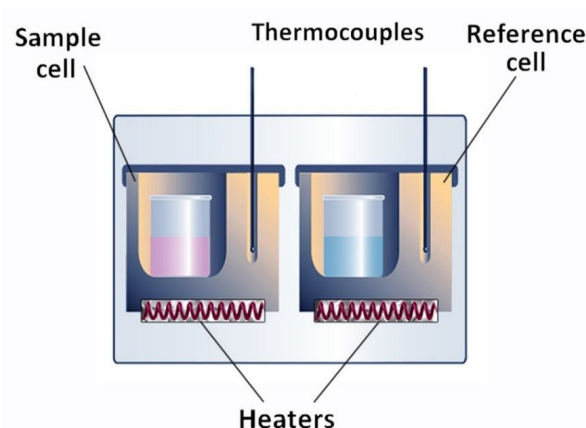
$$\sum_{i=1}^{NC} (n_i^l + n_i^s) \cdot \mu_i^{s,0} = \sum_{i=1}^{NC} n_i \cdot \mu_i^{s,0} \quad (4)$$

Applying Eq. (2) in Eq. (4):

$$\sum_{i=1}^{NC} n_i \cdot \mu_i^{s,0} = \sum_{i=0}^{NC} (n_i^0 + v_i \cdot \xi) \cdot \mu_i^{s,0} \quad (5)$$

Table 1. Purity, Melting Temperatures and the Latent Heat of Fatty Acids

Compound	Formula	Purity (%wt)	T _m (K)	Δ _{fus} H (J g ⁻¹)
Capric acid	C ₁₀ H ₂₀ O ₂	≥ 98%	304.8	27.79
Undecylic acid	C ₁₁ H ₂₂ O ₂	≥ 98%	301.7	25.98
Pentadecylic acid	C ₁₅ H ₃₀ O ₂	≥ 98%	325.7	41.53
Margaric acid	C ₁₇ H ₃₄ O ₂	≥ 98%	334.2	51.33


Fig. 1. DSC experimental setup.

Applying Eq. (3) in Eq. (5):

$$\sum_{i=0}^{NC} (n_i^0 + v_i \cdot \xi) \cdot \mu_i^{s,0} = \sum_{i=1}^{NC} n_i^0 \cdot \mu_i^{s,0} + (n_p - n_p^0) \cdot \sum_{i=0}^{NC} v_i \cdot \mu_i^{s,0} \quad (6)$$

The change in the Gibbs free energy in a reaction is defined as:

$$\Delta G_R^0 = \sum_{i=1}^{NC} v_i \cdot \mu_i^{s,0} \quad (7)$$

It is also considered that the product only is formed in the solid phase [3] and does not exist in the liquid phase:

$$n_p^l = 0 \quad (8)$$

$$n_p = n_p^s \quad (9)$$

Therefore, the first part of Eq. (1) can be written as:

$$\sum_{k=1}^{MP} \sum_{i=1}^{NC} n_i^k \cdot \mu_i^{s,0} = \sum_{i=1}^{NC} n_i^0 \cdot \mu_i^{s,0} - n_p^0 \cdot \Delta G_R^0 + n_p^s \cdot \Delta G_R^0 \quad (10)$$

Using the thermodynamic models presented in the previous sections, the Gibbs free energy can be written as:

$$G = \sum_{i=1}^{NC} n_i^0 \cdot \mu_i^{s,0} - n_p^0 \cdot \Delta G_R^0 + n_p^s \cdot \Delta G_R^0 + R \cdot T \cdot \sum_{i=1}^{NC} n_i^l \cdot \left[B_i + \ln n_i^l - \ln \sum_{j=1}^{NC} n_j^l \right] + R \cdot T \cdot \sum_{i=1}^{NC} n_i^l \cdot \ln \gamma_i^l \quad (11)$$

and satisfying the restrictions:

$$n_i^s + n_i^l = n_i^0 + v_i \cdot (n_p^s - n_p^0) \quad i=1, \dots, NC \quad i \neq p \quad (12)$$

$$n_i^s \geq 0 \quad i=1,\dots,NC \quad (13)$$

$$n_i^l \geq 0 \quad i=1,\dots,NC \quad i \neq p \quad (14)$$

$$n_p^l = 0 \quad (15)$$

The equilibrium composition is then calculated by minimizing G , given by Eq. (11), with respect to the variables n_i^S and n_i^L , satisfying the restrictions (12)-(14), at constant T and P . Other quantities kept constant during the minimization are n_i^0 , v_i , B_i , ΔG_R^0 , and $\mu_i^{S,0}$. The liquid activity coefficients γ_i^l depend on n_i^l and T , and therefore, they are also variables in the minimization.

The solid-liquid phase diagram for binary mixtures can be found by the minimization of the Gibbs free energy mentioned above. The approach to calculate the solid-liquid phase diagram can also be extended to include any number of components and any number of products. However, in this work the model was restricted to binary fatty acid mixtures.

General Model for Liquid Phase

The thermodynamic analysis illustrates three possible solid-liquid equilibrium regions in the T - x_l diagrams as a function of the molar fraction. Accordingly, Region I is represented by liquid line beginning from $x_l = 0$ until the peritectic point, Region II is one where solid phase is component 1 (from eutectic point to $x_l = 1$), and Region III, if exists, is the region where the solid phase is the compound. In this study, there is no any interval between peritectic and eutectic points (Region III)

Rocha and Guirardello [1] described solid-liquid phase equilibrium for fatty acid binary mixtures as follow:

Region I

$$T = \frac{\Delta h_{f2}}{\frac{\Delta h_{f2}}{T_{f2}} - R \cdot \ln[(1-x_1) \cdot \gamma_1^l]} \quad (16)$$

which is limited by:

$$-R.T.[B_1 + \ln x_1] - R.T. \ln \gamma_1^l \geq \max \left\{ 0, \frac{1}{v_1} \cdot \Delta G_R^0 \right\} \quad (17)$$

Region II

$$T = \frac{\Delta h_{f1}}{\frac{\Delta h_{f1}}{T_{f1}} - R \cdot \ln[x_1 \cdot \gamma_1^l]} \quad (18)$$

which is limited by:

$$-R.T.[B_2 + \ln(1-x_1)] - R.T. \ln \gamma_2^l \geq \max \left\{ 0, \frac{1}{v_2} \cdot \Delta G_R^0 \right\} \quad (19)$$

The temperature in Eqs. (1) and (2) is not explicit because γ_i^l is a function for either of T and x_i^l . So, the value of temperature should be found by using an iterative procedure.

Latent heat of binary mixtures. A formula was developed by Zhang *et al.* to calculate the latent heat of fatty acid mixtures [24]. For binary mixtures, the formula for liquid phase is as follows:

$$H_m = T_m \sum_{i=1}^n \left[\frac{X_i H_i}{T_i} + X_i (C_{PLi} - C_{PSi}) \ln \frac{T_m}{T_i} \right] \quad (20)$$

where H_m is the latent heat of mixture in J mol^{-1} , C_{PLi} is the specific heat at constant pressure of component i at liquid and C_{PSi} is the specific heat at constant pressure of component i at solid.

If the molecular weight of every component is big enough, the error of the formula for latent heat is rather small due to ignoring the sensible heat. As for the long-chain organic compounds, the error is very low.

$$H_m = T_m \sum_{i=1}^n \frac{X_i H_i}{T_i} \quad (21)$$

For binary mixtures, Eq. (20) is:

$$H_m = T_m \left[\frac{X_1 \Delta h_{f1}}{T_{f1}} + \frac{(1-X_1) \Delta h_{f2}}{T_{f2}} \right] \quad (22)$$

where Δh_{f1} and Δh_{f2} are the latent heat of pure substance 1 and pure substance 2, respectively.

Wilson Model for Liquid Phase

Based on molecular consideration, Wilson [16] presented the following expression for the excess Gibbs free energy of binary solution:

$$\frac{g^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(x_2 + \Lambda_{21}x_1) \quad (23)$$

The activity coefficients derived from Wilson model are:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right) \quad (24)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) + x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right) \quad (25)$$

In this work, according to Eqs. (16), (17), (24) and (25), the liquid phase is modeled based on Wilson equation for two equilibrium regions.

Region I

$$T_1 = \frac{\Delta h_{f2}}{\frac{\Delta h_{f2}}{T_{f2}} - R \left[\ln(1-x_1) - \ln(x_2 + \Lambda_{21}x_1) - x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right) \right]} \quad (26)$$

Region II

$$T_2 = \frac{\Delta h_{f1}}{\frac{\Delta h_{f1}}{T_{f1}} - R \left[\ln x_1 - \ln(x_1 + \Lambda_{12}x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right) \right]} \quad (27)$$

Eutectic point. While Region III does not exist in the present mixtures ($v_1 < 0$, $v_2 < 0$ and $\Delta G_R^\circ \geq 0$), the composition of eutectic point can be calculated by Eq. (28).

$$\frac{\frac{\Delta h_{f1}}{T_{f1}} - R \left[\ln x_1 - \ln(x_1 + \Lambda_{12}(1-x_1)) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}(1-x_1)} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + (1-x_1)} \right) \right]}{\frac{\Delta h_{f2}}{T_{f2}} - R \left[\ln(1-x_1) - \ln(x_2 + \Lambda_{21}x_1) - x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}(1-x_1)} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + (1-x_1)} \right) \right]} = \quad (28)$$

RESULT AND DISCUSSION

As mentioned, in this work, six cases are considered, including capric + undecylic, capric + pentadecylic, capric + margaric, undecylic + pentadecylic, undecylic + margaric, and pentadecylic + margaric. The experiments were carried out using an apparatus depicted in Fig. 1.

According to experimental results, the Wilson activity model was used to estimate the phase transition of solid-liquid equilibrium by using Eqs. (26) and (27).

Experimental data are listed and added to the Sigmaplot Systate Software. For each binary mixture, experimental data (from $x_1 = 0$ to eutectic point) are fitted to Eq. (26) and other data (from eutectic point to $x_1 = 1$) are fitted to Eq. (27). After fitting by Sigmaplot software, the Wilson coefficients (Λ_{12} and Λ_{21}) for Eq. (26) and Eq. (27) are obtained (Table 2).

Figures 2-11 show the experimental and calculated melting temperature of capric + undecylic, capric + pentadecylic, capric + margaric, undecylic + pentadecylic, undecylic + margaric, and pentadecylic + margaric acid binary mixtures, respectively.

The T_1 and T_2 curves collide at the eutectic point. At this point, both solid 1 and solid 2 can coexist in equilibrium with a binary liquid mixture. The composition at this point is the eutectic composition, and the corresponding temperature is the eutectic temperature.

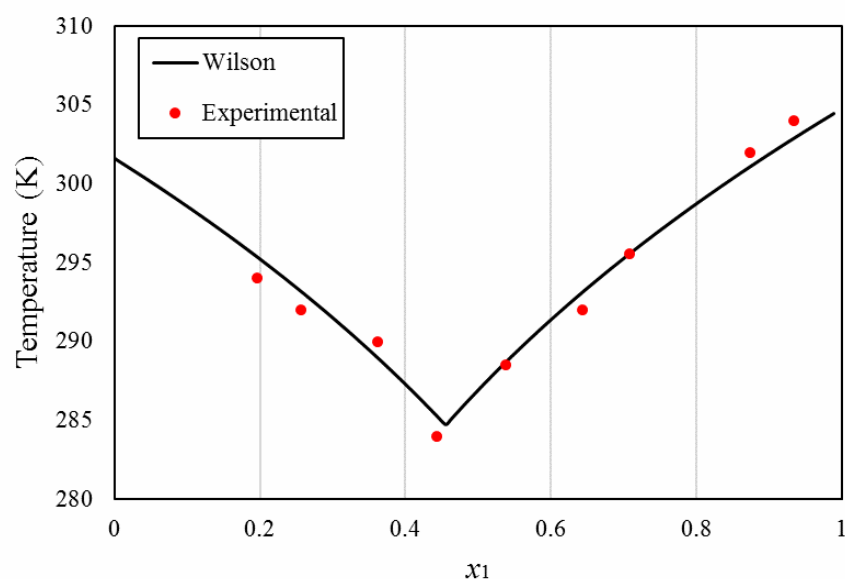
Figures 2-7 show the calculated results using Eqs. (26) and (27) for the binary carboxylic acid mixtures, taking into account that chemical equilibria in the solid phase are in well agreement with the experimental data in comparison with those calculated by the Wilson model.

These phase diagrams (Figs. 2-7) are given by a set of points (x_1, T), where T is melting temperature and x_1 is the molar fraction of the first compound of each binary mixture. It showed that there is a good agreement in all cases.

Case study 1 is a binary mixture of saturated fatty acids, capric acid and undecylic acid. Eutectic point is shown in the phase diagram (Fig. 2), where the presence of the eutectic point occurs for x_1 in 0.457 (0.457 capric acid + 0.543 undecylic acid). A single eutectic in the melting temperature curve observed for the mixture (with $x_1 = 0.457$) would suggest the formation of the phase compound at this composition just as the case of capric/undecylic acid

Table 2. Calculated Wilson Parameters of Six Considered Fatty Acid Binary Mixtures

Binary mixture	Eq. (26)		Eq. (27)	
	Λ_{12}	Λ_{21}	Λ_{12}	Λ_{21}
Capric acid + undecylic acid	0.5982	1.5556	0.4523	1.6594
Capric acid + pentadecylic acid	0.4996	1.6992	1.2081	0.8277
Capric acid + margaric acid	0.3583	1.9761	4.5676	-0.0044
Undecylic acid + pentadecylic acid	0.4790	1.7394	1.3448	0.7436
Undecylic acid + margaric acid	1.3029	0.7675	1.2344	0.8100
Pentadecylic acid + margaric acid	0.5778	1.5595	1.3118	0.7371

**Fig. 2.** Solid-liquid equilibrium diagram for capric acid (1) and undecylic acid (2).

mixture.

Case study 2 is a mixture of binary saturated fatty acids, capric acid and pentadecylic acid. Eutectic point is shown in the phase diagram (Fig. 3), where the presence of the eutectic point occurs for x_1 in 0.764 (0.764 capric acid + 0.236 pentadecylic acid).

Case study 3 is a mixture of binary saturated fatty acids, capric acid and margaric acid. Eutectic point is shown in the phase diagram (Fig. 4), where the presence of the eutectic

point occurs for x_1 in 0.869 (0.869 capric acid + 0.131 margaric acid).

Case study 4 is a mixture of binary saturated fatty acids, undecylic acid and pentadecylic acid. Eutectic point is shown in the phase diagram (Fig. 5), where the presence of the eutectic point occurs for x_1 in 0.793 (0.793 undecylic acid + 0.207 pentadecylic acid).

Case study 5 is a mixture of binary saturated fatty acids, undecylic acid and margaric acid. Eutectic point is shown in

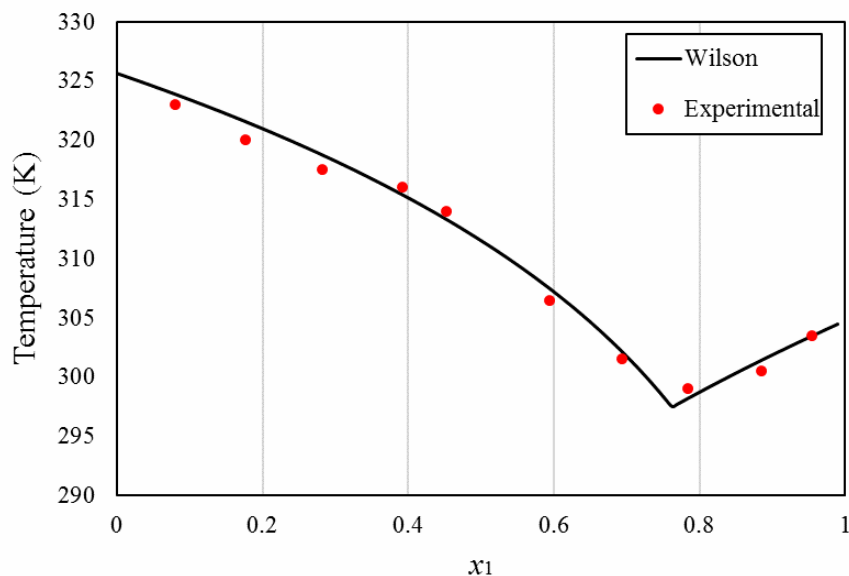


Fig. 3. Solid-liquid equilibrium diagram for capric acid (1) and pentadecylic acid (2).

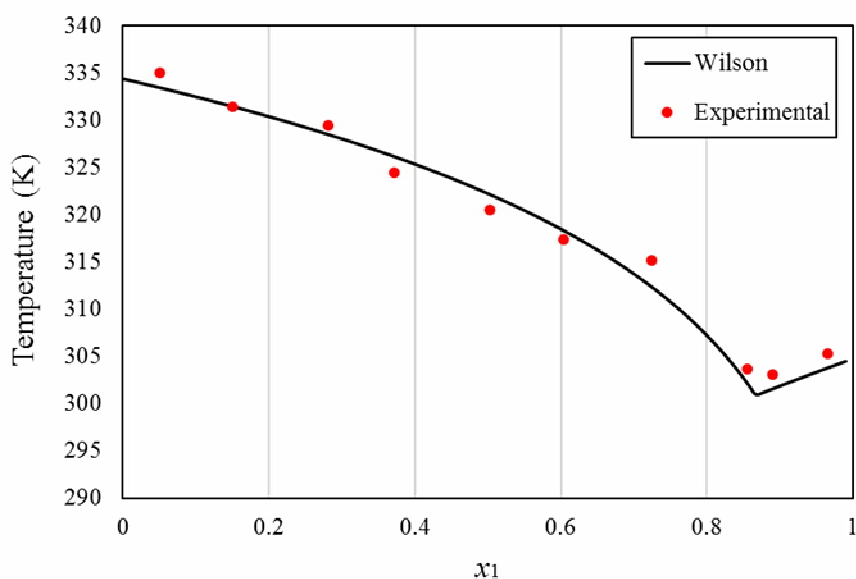


Fig. 4. Solid-liquid equilibrium diagram for capric acid (1) and margaric acid (2).

the phase diagram (Fig. 6), where the presence of the eutectic point occurs for x_1 in 0.894 (0.894 undecylic acid + 0.106 margaric acid).

Case study 6 is a mixture of binary saturated fatty acids, pentadecylic acid and margaric acid. Eutectic point is shown

in the phase diagram (Fig. 7), where the presence of the eutectic point occurs for x_1 in 0.643 (0.643 pentadecylic acid + 0.357 margaric acid).

As mentioned above, the experimental measurements in this work were correlated using Wilson model [16]. The

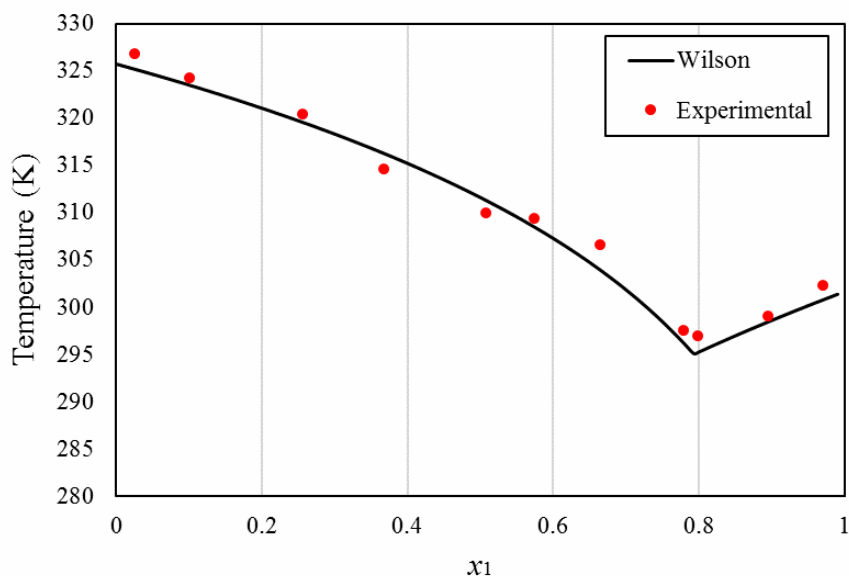


Fig. 5. Solid-liquid equilibrium diagram for undecylic acid (1) and pentadecylic acid (2).

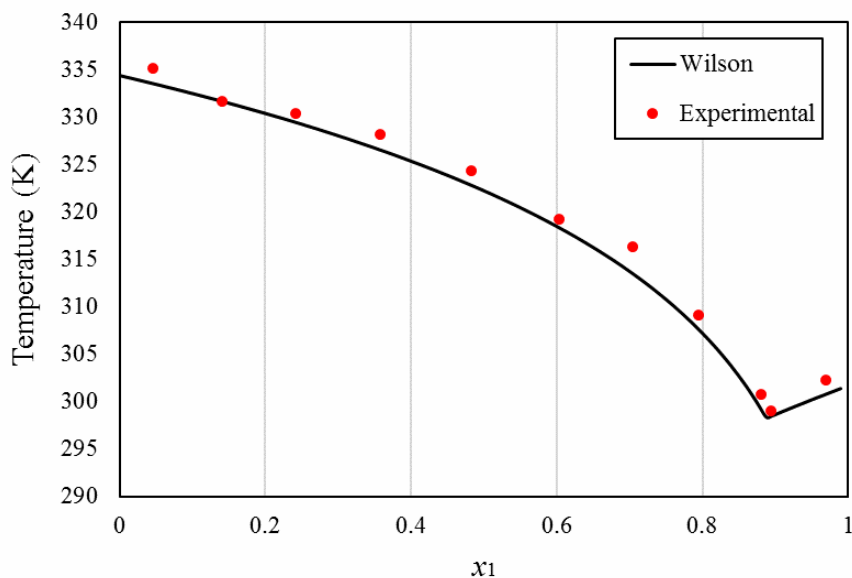


Fig. 6. Solid-liquid equilibrium diagram for undecylic acid (1) and margaric acid (2).

average relative deviation (ARD%) and the average absolute deviations (AAD%) of melting temperatures values obtained from Wilson model can be calculated by Eq. (29) and Eq. (30), respectively.

$$ARD = 100 \sum_{i=1}^N |T_{exp,i} - T_{calc,i}| / N \quad (29)$$

$$AAD = 100 \frac{1}{N} \sum_{i=1}^N |T_{exp,i} - T_{calc,i}| / T_{exp,i} \quad (30)$$

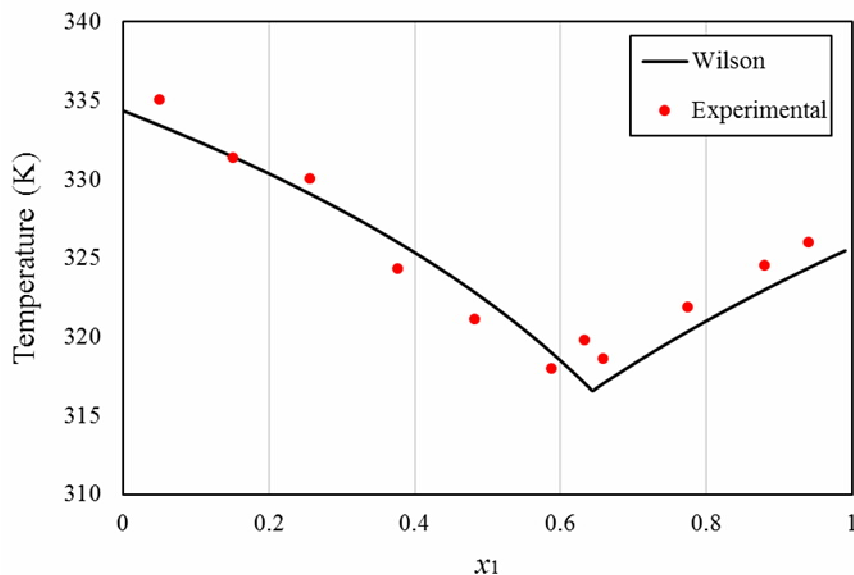


Fig. 7. Solid-liquid equilibrium diagram for pentadecylic acid (1) and margaric acid (2).

Where N is the number of experimental data, T_{exp} is the experimental temperature and T_{calc} is calculated temperature. Table 3 presents ARD and AAD between experimental and calculated values of six considered binary mixtures.

As indicated in Table 3, the higher AAD% of Wilson model equals to 0.58 in reproducing melting temperatures of six fatty acids binary mixtures are for capric acid + margaric acid equals.

It is interesting to compare the values of the calculated activity coefficients, using the parameters considered in this work, and some predictive methods for activity coefficients. The values of the infinite dilution activity coefficients can easily be calculated using the Wilson symmetric model by

$$\ln \gamma_1^\infty = -\ln(\Lambda_{12}) + (1 - \Lambda_{21}) \quad (31)$$

$$\ln \gamma_2^\infty = -\ln(\Lambda_{21}) + (\Lambda_{12} - 1) \quad (32)$$

The values for γ^∞ using Wilson models were calculated using the parameters presented in Table 2.

Considering that the main difference between some of the components in the case studies is the difference in their molecular sizes, the Flory-Huggins theory for fatty acid solutions can be used to estimate the infinite dilution

coefficient of the binary mixtures, given by [25]

$$\ln \gamma_1^\infty = \ln\left(\frac{v_i}{v_j}\right) - \left(1 - \frac{v_i}{v_j}\right) \quad (33)$$

where v_i and v_j are the molar volumes of components i and j , respectively.

In Table 4, the values of the activity coefficients at infinite dilution of each binary mixtures are presented. The molar volumes were calculated using the molar mass and the densities at some temperatures. The values for the densities were estimated from literature values [26,27]. As shown in Table 4, there is a good agreement between Flory-Huggins and Wilson models. The lowest and highest deviation is for mixtures pentadecylic/margaric acid and capric/margaric acid, respectively.

CONCLUSIONS

In this study, we developed an apparatus to consider the phase equilibria of six fatty acid binary mixtures for solid-liquid phase equilibrium. The melting and eutectic temperatures were estimated from curves. The phase equilibrium data and eutectic points of capric + undecylic

Table 3. ARD% and AAD% of Six Binary Mixtures

x_1	T_{exp}	T_{calc}	ARD %	AAD %	x_1	T_{exp}	T_{calc}	ARD %	AAD %
Capric + undecylic					Undecylic + pentadecylic				
0.196	294.12	295.38	0.43	-1.26	0.025	326.77	325.14	0.50	1.63
0.256	292.32	293.19	0.30	-0.87	0.101	324.21	323.44	0.24	0.77
0.362	290.41	288.96	0.50	1.45	0.256	320.46	319.50	0.30	0.96
0.442	284.76	285.32	0.20	-0.56	0.367	314.65	316.23	0.50	-1.58
0.537	288.52	288.62	0.03	-0.10	0.508	309.98	311.24	0.41	-1.26
0.643	292.93	293.07	0.05	-0.14	0.573	309.39	308.46	0.30	0.93
0.708	295.56	295.54	0.01	0.02	0.664	306.65	303.91	0.89	2.74
0.874	302.32	301.08	0.41	1.24	0.779	297.58	296.10	0.50	1.48
0.935	304.32	302.89	0.47	1.43	0.799	297.01	295.20	0.61	1.81
Average			0.27	0.13	0.894	299.00	298.41	0.20	0.59
Capric + pentadecylic					Undecylic + margaric				
0.080	323.01	323.91	0.28	-0.90	0.045	335.18	333.51	0.50	1.67
0.176	320.12	321.62	0.47	-1.50	0.141	333.34	331.62	0.52	1.72
0.282	317.52	318.80	0.40	-1.28	0.241	330.40	329.41	0.30	0.99
0.392	316.23	315.42	0.26	0.81	0.357	329.23	326.52	0.82	2.71
0.452	314.09	313.34	0.24	0.75	0.483	324.01	322.78	0.38	1.23
0.593	306.53	307.53	0.33	-1.00	0.603	319.26	318.30	0.30	0.96
0.694	301.56	302.14	0.19	-0.58	0.704	316.30	313.48	0.89	2.82
0.784	299.76	298.17	0.53	1.59	0.794	309.16	307.62	0.50	1.54
0.884	300.59	301.38	0.26	-0.79	0.880	301.11	299.25	0.62	1.86
0.955	303.22	303.47	0.08	-0.25	0.894	299.00	298.41	0.20	0.59
Average			0.30	-0.32	0.970	302.59	300.74	0.61	1.85
Pentadecylic + margaric					Capric + margaric				
0.050	335.09	334.26	0.25	0.83	0.050	335.09	334.26	0.25	0.83
0.151	333.59	331.41	0.65	2.18	0.151	331.41	334.07	0.80	-2.66
0.256	330.05	329.06	0.30	0.99	0.282	329.44	328.46	0.30	0.98
0.377	323.98	325.97	0.61	-1.99	0.372	324.48	326.11	0.50	-1.63
0.483	321.17	322.78	0.50	-1.61	0.503	320.01	322.10	0.65	-2.09
0.588	317.97	318.93	0.30	-0.96	0.603	317.35	318.30	0.30	-0.95
0.633	319.84	316.99	0.89	2.85	0.724	315.15	312.34	0.89	2.81
0.658	318.91	317.02	0.59	1.89	0.855	303.68	302.17	0.50	1.51
0.774	322.13	320.32	0.56	1.81	0.889	303.95	301.54	0.79	2.41
0.879	324.87	322.97	0.58	1.90	0.965	306.28	303.76	0.82	2.52
0.940	325.87	324.36	0.46	1.51	Average			0.58	0.37
Average			0.52	0.85					

Table 4. Infinite Dilution Activity Coefficient and Relative Deviations

No.	Mixture	T_{eutectic}	γ_1^{∞}		Dev. %	γ_2^{∞}		Dev. %
			Flory-huggins	Wilson		Flory-huggins	Wilson	
1	Capric + undecylic acid	284.7	0.959	0.996	3.78	1.042	0.996	4.57
2	Capric + pentadecylic acid	297.5	0.995	0.932	6.74	0.981	0.912	7.58
3	Capric + margaric acid	300.9	0.965	0.901	7.24	0.943	0.864	9.24
4	Undecylic + Pentadecylic acid	295.2	0.996	0.955	4.33	0.953	0.945	0.81
5	Undecylic + margaric acid	298.2	0.968	0.927	4.42	0.976	0.905	7.88
6	Pentadecylic + margaric acid	316.5	0.989	0.995	0.64	0.993	0.995	0.19

acid, capric + pentadecylic acid, capric + margaric acid, undecylic + pentadecylic acid, undecylic + pentadecylic acid, and pentadecylic + margaric acid binary mixtures were measured and considered. The experimental data of six binary mixtures were correlated by Wilson activity model without any intermediate compound. Derivations of Wilson model for melting temperature of mixtures as a function of mole fraction were used to estimate the melting points and eutectic point in solid-liquid equilibrium. Based on the results, the thermodynamic investigation of phase equilibrium in the solid phase can improve accuracy of eutectic points in binary mixtures. This study approach can be developed to estimate phase equilibrium for other binary mixtures of fatty acids.

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