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Liquid-Liquid Phase Equilibrium in Glycerol-Methanol-Fatty Acids Systems

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The liquid-liquid phase equilibrium data for glycerol-fatty acids systems were first experimentally investigated in this work, and then compared with predictions of UNIFAC model. For these binary systems we have calculated the UNIQUAC coefficients, unknown in literature. Fatty acids studied are oleic, palmitic and stearic acids because they are the main components of vegetable oils used for the production of biodiesel starting from palm-oil. For ternary systems composed by glycerol-methanol-fatty acids, we have compared in the graphs of miscibility curve experimental values and predictions of UNIFAC model. The reliability of the solubility data has been proved in Othmer-Tobias plot.

1. Introduction

The process of synthesis of methylester (biodiesel) starting from triglycerides (vegetable oils), involves a series of problems, which are not directly linked to the main transesterification reaction, that are determining to obtain an appreciable product and co-products that can be industrially used. In fact, the purification from eventual dissolved or dispersed substances play a fundamental role in the economization of the global process. In the present work, the purification of glycerine from free fatty acid has been studied. In fact, multi-component system constituted by methylester and glycerine, in presence of small amounts of methyl alcohol, water and, as a function of the reactants, other substances like free fatty acids or soaps, can represent an important starting point for the understanding of the separation phenomena. In the first part of this study the liquid-liquid phase equilibrium for the glycerine-oleic acid binary system was determined experimentally and compared with predictions of the UNIFAC model. For this binary system equilibrium analysis has been performed at different temperature (from 20 to 80 °C) and mostly, we found that the predictions of UNIFAC are in good agreement with the experimental results. After that it has been studied other binary systems composed by different fatty acids both saturated and unsaturated with the aim to compare the different equilibrium of these binary systems as a function of the aliphatic chain length and the number of carbon-carbon double bond present. Finally it has been studied the effects of the presence of methanol in the same equilibrium systems in order to estimate the possibility of increasing the degree of purity of the glycerine formed as a co-product in the biodiesel production.

2. Experimental values of solubility of some fatty acids in glycerol

2.1 Experimental setup and procedure

The experiments with glycerol-fatty acids systems were performed in glass test-tubes of 20 ml volume. The two immiscible components were added into the test-tubes in some specific volume ratios: for example, 10 ml of glycerol and 1 ml of fatty acid. The test-tubes were manually mixed for a lot of minutes until to obtain an homogeneous colloidal phase. After reaching the thermodynamical equilibrium, the two phases were separated in a centrifugal device. 5 ml samples of heavy phase were collected in beckers for titration with a NaOH solution or alternatively with iodine method. All our experimental tests followed this procedure.

2.2 Oleic acid-glycerol system

Oleic acid is surely one of the most present components in triglycerides of vegetable oils (e.g. palm oil). Here, we have first experimentally investigated the solubility of oleic acid inside pure glycerol phase, at room temperature; the result obtained is a solubility of 0.06-0.07%. We have tried also to inquire into the importance of temperature: our experimental data do not change in the range between 20 °C and 80 °C. Other significant variables for this phase equilibrium, after the production and separation of biodiesel, should be the presence of relevant quantities of water and small percentage of unreacted methanol. Tests of solubility of oleic acid in glycerol with an addiction of 30-50% in weight of water, or with the presence of 1-2% in weight of methanol do not change the previous determined solubility (0.06-0.07%).

2.3 Stearic acid-glycerol system

Moreover we have experimentally investigated stearic acid-glycerol phase equilibrium. Our data show a great decline in the value of solubility of fatty acid: stearic acid is soluble inside the pure glycerol phase for a percentage of 0.007-0.010%. This was reasonably and qualitatively predictable because of the absence of hydrophilic double-bond group that increases in the oleic acid its affinity to glycerol .

2.4 Palmitic acid-glycerol system

In order to understand all the trends inside the family of fatty acids we have tested at last the system palmitic acid-glycerol. The value of solubility obtained is 0.013-0.015%. This fatty acid show an higher solubility than the staric acid. Palmitic and stearic acids are both without double-bond groups, but palmitic acid is two-carbon-atoms smaller than steraic acid; this feature involves an higher solubility in glycerol.

3. Results And Discussion

3.1 LLE-UNIFAC model

UNIFAC method (UNIQUAC Functional-group Activity Coefficients) is a significant development based on UNIQUAC equation and in detail treated by Fredenslund, Gmehling and Rasmussen (1977). It provides for the calculation of activity coefficients from contributions of the various groups making up the molecules of a solution.

UNIFAC is a complex predictive equation for γ_i^L that involves binary-interaction parameters for each pair of components in the mixture. We have compared our results with the predictions of UNIFAC model. In order to evaluate the activity coefficients and the value of solubility, we have used the coefficients found in literature and we have developed a programme in MATLAB to solve numerically UNIFAC equations. Two liquid phases at equilibrium can be described by the expression:

$$x_A \gamma_A(x_A,x_G) = y_A \gamma_A (y_A,y_G) \tag{1}$$
$$x_G \gamma_G(x_A,x_G) = y_G \gamma_G(y_A, y_G) \tag{2}$$
$$x_A+x_G = 1 \tag{3}$$
$$y_A+y_G = 1 \tag{4}$$

where A stands for fatty acid, G for glycerol, x for molar fraction in heavy phase and y for molar fraction in light phase.

3.1.1 Comparison with phase equilibrium data

In this work we have modelled liquid-liquid equilibria with UNIFAC equations at room temperature. For the case of oleic acid-glycerol the result is a solubility for the fatty acid of 0.22%, three times higher than the experimental data. Very important to underline are also the results calculated with UNIFAC model about stearic and palmitic acid inside pure glycerol phase. In fact for stearic acid the model has foreseen a solubility of 0.27%, higher than the one predicted for oleic acid. Moreover UNIFAC has given palmitic acid soluble in glycerol for a percentage of 0.64%, value higher than the previous ones. We have concluded that UNIFAC model overestimates the solubility of fatty acids and doesn't consider the influence of double-bond group.

3.1.2 Temperature dependence in UNIFAC model

For the case of oleic acid-glycerol system, we have tested the sensibility of UNIFAC equation with light changes in the variable temperature. The data of the model are as it follows: at 25 °C oleic acid is 0.22% soluble in glycerol; at 50 °C the result is 0.24 %, and at 80 °C it becomes 0.27%. It's a very slow increase of solubility with temperature, even if in the experimental samples we haven't noticed any influence in this range of temperature.

3.2 UNIQUAC model

UNIQUAC (UNIversal QUAsi Chemical) equation is based on the same principles of UNIFAC model and it calculates activity coefficients as function of binary-interaction parameters τ_{ij} and τ_{ji}, as described by Abrams and Prausnitz (1975). In literature, for fatty acids-glycerol systems, nobody has published these parameters; thus, we have put our experimental solubility data (or similarly the molar fraction x) in UNIQUAC equation and we have calculated for each pair fatty acid-glycerol the interaction parameters τ_{AG} and τ_{GA}. We have solved the following system in the unknowns τ_{AG}, τ_{GA}, y_A, y_G :

$$x_A \gamma_A(\tau_{AG},\tau_{GA}) = y_A \gamma_A (\tau_{AG},\tau_{GA}) \tag{5}$$
$$x_G \gamma_G(\tau_{AG},\tau_{GA}) = y_G \gamma_G(\tau_{AG},\tau_{GA}) \tag{6}$$

$x_A + x_G = 1$ (7)
$y_A + y_G = 1$ (8)

In the case of oleic acid we have obtained: $\tau_{AG} = -0.3364$ and $\tau_{GA} = 1.7967$. For stearic acid: $\tau_{AG} = -0.4254$ and $\tau_{GA} = 1.6649$. Furthermore for palmitic acid: $\tau_{AG} = -0.4381$ and $\tau_{GA} = 1.6100$.

3.3 Fatty acids-glycerol-methanol ternary systems

The last important section of this work is about the graphs of glycerol-methanol-fatty acids ternary systems (G stands for glycerol, M for methanol and A for fatty acid). For the points of the miscibility curve obtained through UNIFAC model, we have numerically solved this system:

$x_A \gamma_A(x_A, x_G, x_M) = y_A \gamma_A(y_A, y_G, y_M)$ (9)
$x_G \gamma_G(x_A, x_G, x_M) = y_G \gamma_G(y_A, y_G, y_M)$ (10)
$x_M \gamma_M(x_A, x_G, x_M) = y_M \gamma_M(y_A, y_G, y_M)$ (11)
$x_A + x_G + x_M = 1$ (12)
$y_A + y_G + y_M = 1$ (13)
$Fx_A = Hx_A + Ly_A$ (14)
$Fx_G = Hx_G + Ly_G$ (15)
$Fx_M = Hx_M + Ly_M$ (16)

where F is the initial total molar quantity, H heavy phase molar quantity and L light phase molar quantity. In Figures 1 and 2 ternary diagrams for glycerol-methanol-oleic acid system at 25 °C are reported.

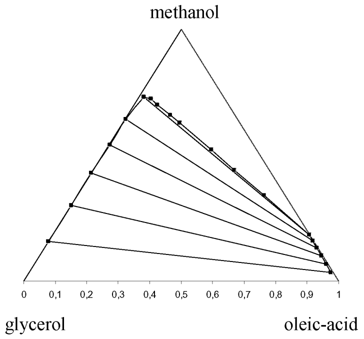

Figure 1. Ternary diagram for glycerol-methanol-oleic acid system at 25 °C. Data obtained with the UNIFAC model.

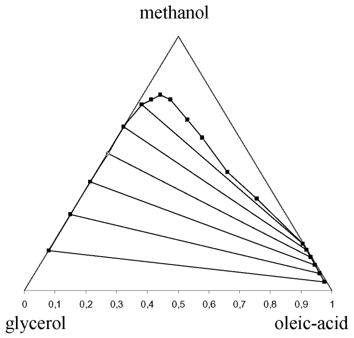

Figure 2. Ternary diagram for glycerol-methanol-oleic acid system at 25 °C. Experimental data.

The reliability of the solubility data in the ternary system glycerol-methanol-oleic acid has been proved in Othmer-Tobias plot, as described by the same Othmer and Tobias (1942) and reported in Figure 3.

$$x = \ln\left(\frac{1-b}{b}\right)$$

$$y = \ln\left(\frac{1-a}{a}\right)$$

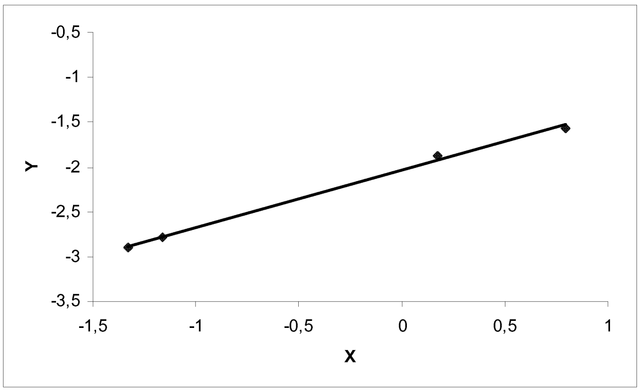

Figure 3. Othmer-Tobias plot for the experimental data from the glycerol-methanol-oleic acid system at 25 °C, where *a* is the mole fraction of oleic-acid in the fatty phase and *b* is the mole fraction of glycerol in the glycerol phase.

In Figures 4-7 ternary diagrams for glycerol-methanol and stearic acid or palmitic acid systems at 25 °C are reported.

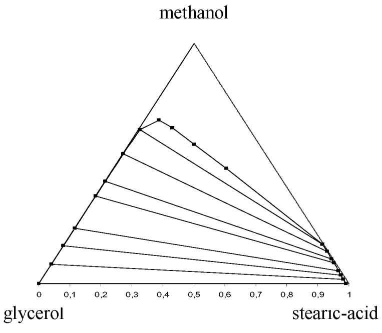

Figure 4. Ternary diagram for glycerol-methanol-stearic acid system at 25 °C. Data obtained with the UNIFAC model.

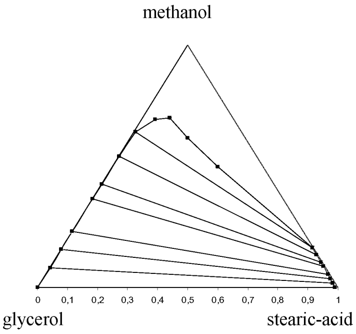

Figure 5. Ternary diagram for glycerol-methanol-stearic acid system at 25 °C. Experimental data.

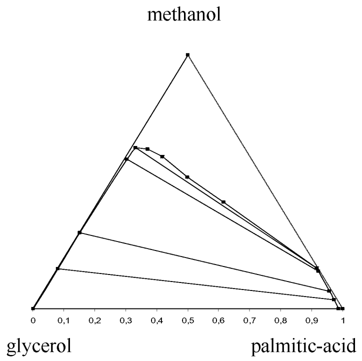

Figure 6. Ternary diagram for glycerol-methanol-palmitic acid system at 25 °C. Data obtained with the UNIFAC model.

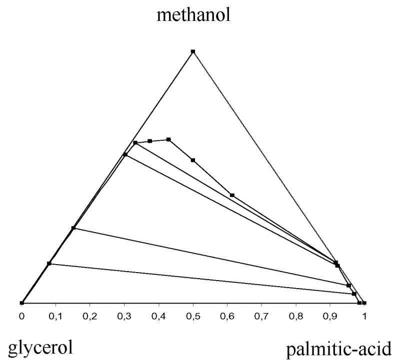

Figure 7. Ternary diagram for glycerol-methanol-palmitic acid system at 25 °C. Experimental data.

4. Conclusions

We have studied the purification of glycerol from fatty acids. For the binary systems glycerol-fatty acids, our experimental data show an increasing values of solubility with the number of double-carbon bonds, because of the polarity of this group. This trend is not predicted by UNIFAC model. On the other side, solubility increases with the reducing of fatty acids' molecular weight. Correctly UNIFAC provides for this tendency, although it overestimates all the solubilities. The values of solubility of our systems don't seem to be influenced by the presence of water or changes of temperature in the range 20-80 °C. Finally we have analyzed the influence of methanol in ternary systems glycerol-methanol-fatty acids. The points of the two branches of miscibility curves, obtained by UNIFAC model, show that the presence of methanol causes an increasing in the solubility in the glycerol phase. This is a predictable trend because methanol is completely soluble both in glycerol and in fatty acids. In accordance with overestimated values of solubility, UNIFAC points on the top of miscibility curves of ternary systems are lower than the experimental ones. We can conclude a good agreement for ternary systems equilibria between experimental and UNIFAC model data.

5. References

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