

## Phase Equilibria in Triacylglycerols – Ethanol – Oleic Acid – Ethyl Oleate Quasi-Quaternary System

I.A. Permyakova<sup>1</sup>, V.V. Vol'khin<sup>1</sup>, D.A. Kazakov<sup>1\*</sup>, K. Kaczmariski<sup>2</sup>,  
O.S. Kudryashova<sup>3</sup>, E.A. Sukhoplecheva<sup>1</sup>

<sup>1</sup>Perm National Research Polytechnic University, Russia, 614990, Perm, Komsomolsky Ave., 29

<sup>2</sup>Rzeszów University of Technology, Poland, 35-959, Rzeszów, Str. W. Pola, 2

<sup>3</sup>Natural Science Institute of Perm State National Research University, Russia, 614990, Perm, Str. Genkelya, 4

### Abstract

In order to use waste vegetable oils to produce biodiesel a possibility of reagents (sunflower oil and ethanol) mixture homogenization under the simultaneous effect of two cosolvents (oleic acid and ethyl oleate) was investigated.

The possibility of action of oleic acid and ethyl oleate as cosolvents was analyzed with GSP model. For qualitative assessment of the intermolecular interaction parameter  $\zeta$  was used. This parameter is a measure of the ratio between cross-association (solvation) energy A–B and self-association (association) energies A–A and B–B. It was shown that most important role at intermolecular interactions of oleic acid and ethyl oleate with triglycerides belonged to dispersion forces. Predominant contribution of hydrogen bonds in the interaction of oleic acid and ethyl oleate with ethanol was shown. The prediction of improving the effect of the cosolvents with temperature increasing was done, and it was confirmed by experimental results.

The effect of oleic acid and ethyl oleate as cosolvents for homogenization of mixtures of sunflower oil and ethanol was investigated experimentally by studying the phase equilibria in the quasi-quaternary system triacylglycerols (sunflower oil) – ethanol – oleic acid – ethyl oleate at 30, 40, 50, 60 and 70 °C. The results of the experiments are presented in the form of phase diagrams of quasi-ternary boundary systems: triacylglycerols – oleic acid – ethanol and triacylglycerols – ethyl oleate – ethanol, and the phase diagrams of composition tetrahedron sections with five different ratios of components oleic acid: ethyl oleate. Generalization of the research results is presented in the form of polythermal phase diagram for the system triacylglycerols – ethanol – oleic acid – ethyl oleate.

Solubility polytherms (from 30 to 70 °C) for the system triacylglycerols – ethanol – mixed cosolvent with different ratios of oleic acid and ethyl oleate were plotted.

**Keywords:** biodiesel, waste vegetable oils, cosolvents, oleic acid, ethyl oleate, phase equilibrium, homogenization.

### Nomenclature

$\Delta G_{mix}$  Gibbs energy of mixing, J;  
 $n$  total amount of substances A and B, mole;  
 $R$  universal gas constant, J·mole<sup>-1</sup>·K<sup>-1</sup>;  
 $T$  absolute temperature, K;  
 $x_A$  molar fraction of component A;  
 $x_B$  molar fraction of components B;  
 $\Delta H_{mix}$  enthalpy of mixing, J;  
 $H^E$  excess enthalpy, J;  
 $\zeta$  energetic measure of ratio between intermolecular cross-bonds A–B (solvation) and intrinsic intermolecular links of individual non-electrolytes

A–A and B–B (association);  
 $S^E$  excess entropy, J·K<sup>-1</sup>;  
 $G^E$  excess Gibbs energy, J;  
 $G_C^E$  combinatorial contribution of excess Gibbs energy, J;  
 $G_r^E$  residual contribution of excess Gibbs energy, J;  
 $u_{ji}$  energy of interaction between  $i$ - and  $j$ -groups, J;  
 $\delta_d$  group parameter related to dispersion forces;  
 $\delta_p$  group parameter related to polar forces;  
 $\delta_a$  group parameter related to ability to function as proton donor;  
 $\delta_b$  group parameter related to ability to function as proton acceptor.

\* Corresponding author. E-mail: kazakovbiotech@mail.ru

## Introduction

Biodiesel is a mixture of methyl or ethyl higher fatty-acid esters. The relevant process is based on triacylglycerols being transesterified by lower alcohols (methanol or ethanol) and by an alkaline catalyst. Triacylglycerols are derived from vegetable oils: rape oil, sunflower oil, palm oil, etc. The last century demonstrates a trend towards producing biodiesel from non-food raw materials, such as substandard vegetable oils or food processing wastes. Over 20% of the total edible vegetable oil output was shown [1] to be rejected. Almost 10% of vegetable oils are not reusable once used in thermal food processing.

However, waste vegetable oils are difficult to be used in biodiesel production. They include free fatty acids, sometimes at levels as high as 20 to 40% [2]. In presence of an alkaline catalyst, they are saponified, which complicates the process appreciably, thus requiring a less efficient acid catalyst to be substituted for the alkaline one. This justifies a two-stage process: the first stage includes mostly free fatty acid esterification using acid catalysis, the second one involves triacylglycerols transesterification using alkaline catalysis.

Vegetable oil and alcohol form heterogeneous mixtures, the soluble catalyst being present mostly in the alcoholic phase which acts as the reaction space. The process rate is controlled by oil mass transfer through the interface. The reaction can be appreciably accelerated by a cosolvent homogenizing the system. Ability to act as cosolvents was found in fatty acid esters which result in fatty acid being esterified and triacylglycerols (vegetable oils, animal fats) transesterified by lower alcohols [3]. However, the system may be homogenized only if the mixture contains esters above a certain level. Therewith, we showed [4] that free fatty acids (oleic acid and stearic acid) also could homogenize vegetable oil–ethanol mixtures and therefore act as cosolvents at the first process stage. Esterification must involve relevant esters substituting the free fatty acids sequentially which is likely to maintain the system homogeneity.

Since co-action of two cosolvents in one system, furthermore at their various ratios in the system and at various temperatures, was not studied previously, it became the objective of this research. The particular task was to examine phase equilibria in TAG–EtOH–OIA–EtOIA quasi-quaternary system at 30, 40, 50, 60 and 70 °C, where TAG are triacylglycerols (sunflower oil), EtOH is ethanol, OIA is oleic acid, EtOIA is ethyl oleate, and boundary TAG–EtOH–OIA and TAG–EtOH–EtOIA quasi-ternary systems.

## Experimental

Oleic acid (*Merck*), ethyl oleate (*Sigma-Aldrich*), ethyl alcohol predried by distilling with calcinated calcium oxide excess, and refined sunflower oil (GOST (State Standard of the Russian Federation) 52462-2005) were used. Sunflower oil triacylglycerols contained fatty acids at the following levels (wt.%): palmitic acid (C16:0) at 8.4; stearic acid (C18:0) at 3.6; oleic acid (C18:1) at 25.3; linoleic acid (C18:2) at 60.1; others at 2.6.

Fatty acids in the oil samples were determined after converting them to methyl esters by gas chromatography according to GOST R 51483-99. The test used gas chromatograph Kristall 5000.2 (SKB Khromatek CJSC, Russia) equipped with HP FFAP 50 m × 0.32 mm × 0.5 μm capillary column and a flame ionization detector (FID), carrier gas: helium. Methyl and ethyl esters of fatty acids were used as standards.

Free oleic acid was determined from acid number (GOST R 52110-2003).

Phase equilibria in ternary and quaternary systems were studied by visual polythermal technique [5].

## Results and Discussion

Review of phase equilibria in non-electrolyte systems, appraisal of stability and reasons of their split necessitates accounting for excess thermodynamic functions of the component mixing and intermolecular interactions as the reason of differences in properties of perfect and actual solutions [6].

When a perfect solution is formed, the dependence of Gibbs energy of mixing,  $\Delta G_{mix}$ , from solution composition is determined as follows:

$$\Delta G_{mix} = nRT(x_A \ln x_A + x_B \ln x_B) \quad (1)$$

where  $n$  is total amount of substances A and B, mole;  $R$  is universal gas constant, J·mole<sup>-1</sup>·K<sup>-1</sup>;  $T$  is absolute temperature, K;  $x_A$ ,  $x_B$  are molar fractions of components A and B (binary solution), respectively. Since only the entropic component changes (number of possible configurations increases) as components are mixed when perfect solutions are formed, and enthalpy of mixing  $\Delta H_{mix} = 0$ , average A–B interaction energy of the mixture must remain equal to average A–A and B–B interaction energy in pure liquids.

In actual solutions, interactions A–A, A–B and B–B are quite different, and a change in enthalpy becomes an important factor in their formation. The change in enthalpy is also possibly accompanied by further increase in entropy when free mixing of molecules is complicated by clustering. Thermodynam-

ic properties of actual solutions are described using excess functions, for example, excess enthalpy  $H^E$ . Negative  $H^E$  value means that interaction A–B in the mixture is stronger than A–A and B–B in pure liquids. Reverse correlation is also possible. Generally, this relationship may be quantified as follows:

$$H^E = n\zeta RTx_Ax_B \quad (2)$$

where  $\zeta$  is energetic measure of ratio between intermolecular cross-bonds A–B (solvation) and intrinsic intermolecular links of individual non-electrolytes A–A and B–B (association).

If  $\zeta < 0$ , the mixing process is exothermal and interaction A–B (solvent-to-solute) must be more energy-efficient than pure-liquid interactions A–A and B–B, while reverse correlation,  $\zeta > 0$ , is related to an endothermal process.

For regular solutions ( $H^E \neq 0$ ,  $S^E = 0$ ), excess Gibbs energy is related to excess mixing enthalpy, which is expressed as follows:

$$\Delta G_{mix} = nRT(x_A \ln x_A + x_B \ln x_B + \zeta x_Ax_B) \quad (3)$$

Therefore,  $\zeta < 0$  favours homogeneous mixture formation while  $\zeta > 0$  facilitates phase split. This causes interest in research of intermolecular interactions in non-electrolyte solutions [7–8].

However, this does not consider the entropic factor, so Eq. (3) is qualitatively valid for actual solutions, if the enthalpic contribution in the solution formation prevails over the entropic factor. For non-electrolyte solutions, this condition is likely to be met in case of strong intermolecular interactions. The concept of intermolecular interactions involving structural groups of non-electrolyte molecules, contributing to formation and split of their solutions evolved due to development of phase equilibrium modeling techniques. The best known one is UNIFAC model using UNIQUAC equation [9–11]. The model expresses the excess Gibbs energy as a sum of the combinatorial contribution and the residual one:

$$G^E = G_C^E + G_r^E \quad (4)$$

The combinatorial term considers the molecule shape and size, the residual one takes account of the intermolecular interaction energy.

At present, the values required for calculations [10] have been calculated for low-molecular organic compounds only. The UNIFAC-based calculation results provide a good fit of the experimental data. However, high-molecular compounds demonstrate significant discrepancies of estimated and experimental data [12]. Modeling difficulties also occur when the solution comprises non-electrolytes of largely varying molecular weights and intermolecular interactions are strong. This is particularly pronounced in such systems as oil–methanol–methyl oleate [13].

The system component number also matters. Although calculations are possible, in principle, for multi-component systems of any complexity, only a few researchers studied equilibria in quaternary systems using UNIFAC model [14]. Further difficulties may arise when the system includes two cosolvents. Therefore, tentative forecast and explanation of the findings from intermolecular interactions in non-electrolyte solutions or mixtures in the course of experimental study of TAG–EtOH–OIA–EtOIA system in this paper are limited to qualitative assessment of  $\zeta$ .

Intermolecular interaction-related structural groups in the compounds involved in the system under study are given in Table 1. We estimated the solvation energy and the association energy separately, in each case a GSP-model based between-group interaction energy equation [7] was used:

$$-u_{ji} = \delta_{aj}\delta_{d,i} + \delta_{pj}\delta_{p,i} + \delta_{aj}\delta_{b,i} + \delta_{bj}\delta_{a,i} \quad (5)$$

where  $u_{ji}$  is energy of interaction between  $i$ - and  $j$ -groups,  $J$ ;  $\delta_d$  and  $\delta_p$  are group parameters related to dispersion forces and polar forces, respectively;  $\delta_a$  and  $\delta_b$  are group parameters related to ability to function as proton donors and acceptors, respectively. Generally,  $\delta_{aj}\delta_{b,i} + \delta_{bj}\delta_{a,i}$  reflects hydrogen bonds contribution to the interaction.

**Table 1**  
Structural Groups in Molecules of TAG, EtOH, EtOIA and OIA

Organic compound	Number of structural groups in the molecule						
	CH <sub>3</sub>	CH <sub>2</sub>	CH	C <sub>2</sub> H <sub>2</sub>	CH <sub>2</sub> OH	COO	COOH
Triacylglycerol (triolein) <sup>a</sup>	3	44	1	3	0	3	0
Ethanol	1	0	0	0	1	0	0
Ethyl oleate	2	15	0	1	0	1	0
Oleic acid	1	14	0	1	0	0	1

<sup>a</sup> Triolein is the model component

Numerical values of  $\delta_d$ ,  $\delta_p$ ,  $\delta_a$  and  $\delta_b$  for the low-molecular electrolyte structural series are given in [7]. However, they are not intended for calculating  $u_{ji}$  in high-molecular non-electrolyte systems but may be useful to assess qualitatively the sign and value of  $\zeta$ . Thus, if  $\zeta < 0$ , stable non-electrolyte solutions are more likely to be formed since in this case cross-association (solvation) energy A–B must exceed the sum of self-association (association) energies A–A and B–B.

According to [7–8], structural group properties important for non-electrolyte solutions to form can be distinguished. Paraffinic groups, CH, CH<sub>2</sub> and CH<sub>3</sub>, provide intermolecular interactions via dispersion force. The double bond also results in some polarity of the molecules. The main group of aliphatic alcohols, COH, displays two-centre behaviour in solutions: it can form hydrogen bonds both as a proton donor and as a proton acceptor. It also contributes to the molecule polarity. An alcohol molecule also comprises paraffinic groups. The carboxylic group, COOH, can also form all four kinds of intermolecular bonds, as does the hydroxylic group, but is quantitatively different: the carboxylic group is much more of a proton donor but less of a proton acceptor than the alcoholic hydroxylic group [7]. The ester group, COO, is classified as an one-centre unit, its centre behaves as an electron donor on account of one of free electron pairs of the oxygen atom.

Well-known ability of vegetable oils and low-molecular alcohols to produce heterogeneous mixtures is due mostly to pronounced difference in their polarities. According to [15], mutual dissolution of two non-electrolytes may be facilitated by an additional non-electrolyte (cosolvent) which dissolves both of the layering non-electrolyte pair. Solvency of a non-electrolyte may also change when an additional substance is dissolved in it. By the way, when liquid non-electrolytes are mixed to produce a solution, either of them may be taken either as the solvent or as the solute.

When evaluating the ability of OIA and EtOIA to dissolve in TAG and EtOH, their polarity must be considered. TAG is a weakly polar substance, EtOIA somewhat polar due to the COO group, OIA moderately polar due to the COO and HC=CH groups, EtOH rather highly polar due to the COH group. Similarity of OIA, EtOIA and TAG as low-polarity substances favours their mutual dissolution, while EtOH as a polar substance drops out of this series as to this attribute. The dispersion force of intermolecular attraction gains in importance for high-molecular fatty acids and their derivatives. Molecules of TAG, OIA and EtOIA have high content of paraffinic groups (see Table 1), which must facilitate

mutual dissolution in binary TAG–OIA and TAG–EtOIA systems. EtOH may not dissolve TAG appreciably on account of the dispersion force, due to low number of paraffinic groups in the alcohol molecule. Therefore, only in binary TAG–OIA and TAG–EtOIA interactions the dispersion force may result in  $\zeta < 0$ .

Mutual non-electrolyte solubility in OIA–EtOH and EtOIA–EtOH pairs may be appreciably influenced by hydrogen bonding. Since proton-donor and proton-acceptor sites are combined in molecules of low-molecular alcohols, their molecules are capable both of association and solvation. Oleic acid also has sites to form two types of hydrogen bonds but it is more of a proton donor than of a proton acceptor [7], and is capable of solvation in EtOH phase. Hydrogen bonding facilitates solubility of carboxylic acids in alcohols but the latter is reduced as the carbon atom number in the hydrocarbon radical is increased. However, due to rather high hydrogen bond energy [7], summation of forces is likely to result in  $\zeta < 0$ . Fatty acid esters comprise an electron-donor site only, so they do not tend to self-associate or solvate triacylglycerols but they form a hydrogen bond with the proton-donor site in alcohols. Hydrogen bonding facilitates mutual solubility of EtOIA and EtOH, although a large hydrocarbon radical in esters of higher fatty acids impedes dissolution.  $\zeta < 0$  may persist in esters but its absolute value is lower than in OIA.

By appraising relative solubility of OIA and EtOIA in TAG from the intermolecular interactions discussed above, we can conclude that, so far as the interaction is primarily due to the dispersion force, this factor has approximately the same effect on solubility of both substances. Nevertheless, some preference as to solubility in TAG may be given to OIA, on account of the double bond contribution.

Therefore, given very low mutual solubility of TAG and EtOH at low temperatures (25 °C), OIA and EtOIA are soluble in them due to dispersion force (in TAG) and hydrogen bonds (in EtOH). As cosolvents, OIA and EtOIA can increase solubility of TAG in EtOH, OIA being somewhat more efficient. Quantitatively, however, cosolvency of OIA and EtOIA is to be clarified experimentally.  $\zeta < 0$  is likely to be increasable in absolute value due to solubility of TAG in EtOH rising as temperature increases. This may decrease the A–A and B–B association energy, which favours solutions to form according to Eqs. (2) and (3).

The first stage of the experiment considers the binary TAG (sunflower oil) – EtOH system at 30 to 70 °C. The component level measurements are shown in Table 2.



**Table 2**  
Equilibrium Phase Composition in TAG–EtOH System

Temperature, °C	TAG-enriched phase composition		EtOH-enriched phase composition	
	TAG, wt. %	EtOH, wt. %	TAG, wt. %	EtOH, wt. %
30	99.09	0.91	0.45	99.55
40	98.88	1.12	0.45	99.55
50	98.13	1.87	0.47	99.53
60	96.40	3.60	0.45	99.55
70	94.37	5.63	0.60	99.40

Increase in temperature has a relatively weak effect on solubility of EtOH in TAG and, particularly, of TAG in EtOH, and mutual solubility of EtOH and TAG remains low. Presence of cosolvents may have significantly higher impact on solubility.

When determining the cosolvency of OIA and EtOIA, ternary systems were studied first. The phase equilibrium data for TAG–EtOH–OIA (Fig. 1a) and TAG–EtOH–EtOIA (Fig. 1b) systems at 30 to 70 °C, on the one hand, demonstrate that OIA and EtOIA can homogenize the TAG + EtOH mixture and, on the other hand, allow to detect differences in effects

of these cosolvents if used separately. Complete homogenization of a mixture requires the following cosolvent content (wt.%): 25.7 (30 °C) to 16.5 (70 °C) for OIA and 54.3 (30 °C) to 32.0 (70 °C) for EtOIA. Thus, OIA as a cosolvent is needed in a smaller amount than EtOIA, and, furthermore, at 30 °C OIA has effect almost as high as at 70 °C while the effect of EtOIA is much more temperature-dependent. At 70 °C, OIA and EtOIA are considerably closer to each other in effect than at 30 °C. The experimental findings are qualitatively in line with the predictions.

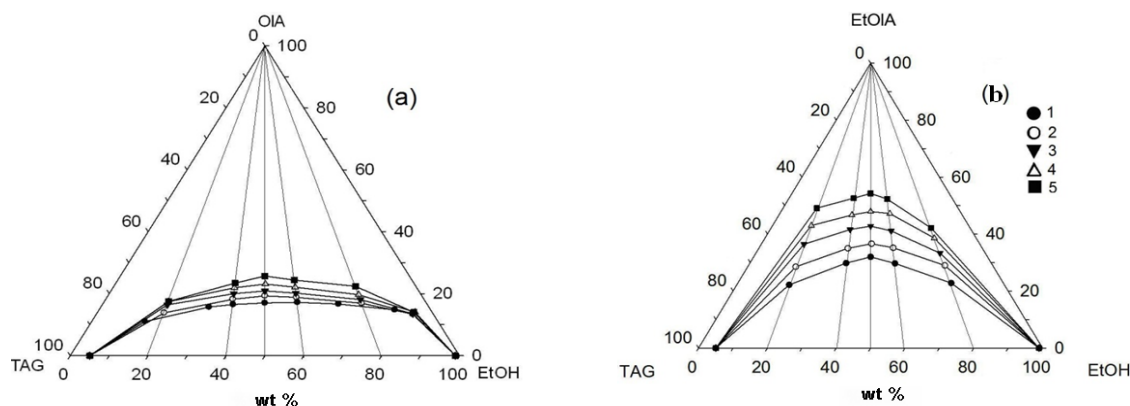


Fig. 1. Phase diagrams for quasi-ternary systems: a) TAG–OIA–EtOH, b) TAG–EtOIA–EtOH, at 70 °C (1), 60 °C (2), 50 °C (3), 40 °C (4), 30 °C (5).

The shape of binodal curves demonstrates that solubility of EtOH in TAG phase (at the lower left in the diagram) is higher than in EtOH phase (at the lower right in the diagram). Areas of the relevant homogeneous phases expand as OIA increases in the system. Approximately the same picture is observed with EtOIA as a cosolvent but homogenizing a mixture takes more of it than of OIA which is in line with the prediction. As to OIA and EtOIA cosolvents themselves, they can dissolve both in TAG and in EtOH phases. The ternary TAG–EtOH–EtOIA

system diagram also shows a certain asymmetry in binodal curves at 30 to 50 °C. To homogenize a TAG-enriched mixture, several times more of EtOIA cosolvent is required than for an EtOH-enriched mixture.

The experimental findings are consistent with the qualitative sign assessment of  $\zeta$  as the solvation-to-association energy ratio. Since the hydrogen-bonding solvation process between OIA (the proton donor) and EtOH (the proton acceptor) may be more energy-efficient than the association pro-

cess in EtOH phase, OIA displays considerable cosolvency at temperature as low as 30 °C. Unlike OIA, EtOIA can be a proton acceptor only while EtOH acts as a proton donor, and a weaker one than oleic acid [7]. In these conditions, association competitiveness of alcohol as a solvent may be more marked with respect to the solvation process based on cross hydrogen bonding between EtOH and EtOIA. Increase in temperature appears to reduce the association process in the alcoholic phase and facilitates EtOIA dissolving in it. The observation, when OIA and EtOIA are redistributed during dissolution between TAG and EtOH in favour of the latter as their content as cosolvents in the mixture

increases, may be attributed to enhanced competitiveness of the solvation process as compared to association in EtOH phase. A solute effect on the particle packing change in the TAG-enriched phase is also not ruled out.

To construct a phase diagram for the quasi-quaternary TAG–EtOH–OIA–EtOIA system, five sections of the composition tetrahedron were studied (Fig. 2). Each section shows a system of variable TAG-and-EtOH composition and constant OIA-to-EtOIA ratio. OIA-to-EtOIA ratios (wt.%) were 80:20, 60:40, 50:50, 40:60 and 20:80. The phase diagram for each section gives binodals for 30, 40, 50, 60 and 70 °C.

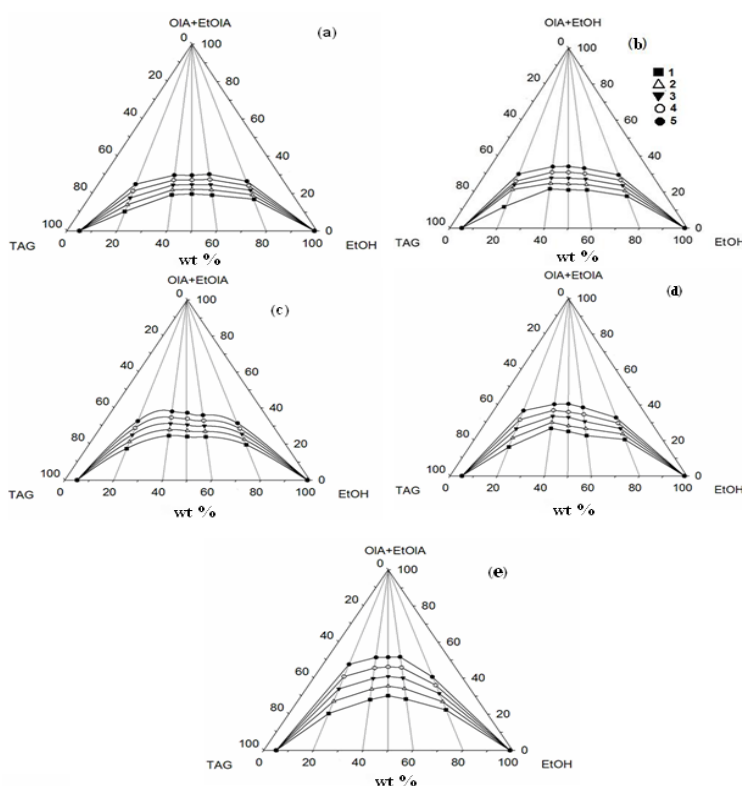


Fig. 2. Phase diagrams for composition tetrahedron sections at OIA-to-EtOIA ratios (wt.%): a) 80:20, b) 60:40, c) 50:50, d) 40:60, e) 20:80, at 70 °C (1), 60 °C (2), 50 °C (3), 40 °C (4), 30 °C (5).

The binodal curves in section diagrams are intermediate between TAG–EtOH–OIA and TAG–EtOH–EtOIA systems (Fig. 1a and 1b). It means that OIA and EtOIA, when present together as cosolvents in the TAG–EtOH–OIA–EtOIA system, produce total effect similar to the additivity-based one. As noted above, as to solubility in TAG, where dispersion force is important, and in EtOH where hydrogen bonding prevails, OIA is a somewhat better cosolvent than EtOIA. Appropriately, OIA also remains a more efficient cosolvent if mixed with EtOIA.

The phase diagrams for the quasi-quaternary

TAG–EtOH–OIA–EtOIA system were constructed for 30, 40, 50, 60 and 70 °C, diagrams for 30 and 70 °C are shown in Fig. 3 as an example. Each vertex of the tetrahedron designates a pure component, points in the edges show binary compositions, while points in the tetrahedron face reflect ternary compositions. The two-phase equilibrium area of the system is located in the tetrahedron portion which designates small contents of OIA and EtOIA cosolvents in the mixture. Most of the composition tetrahedron volume is occupied by a homogeneous region. As temperature rises, the two-phase volume decreases.

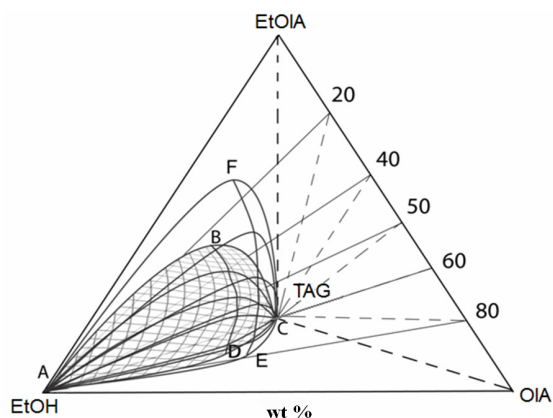


Fig. 3. Phase diagrams for quasi-quaternary TAG–EtOH–OIA–EtOIA system at 70 °C (surface ABCDA) and 30 °C (surface AFCEA).

The interface includes binodal curves: AEC, ADC and AFC, ABC, which pertain to ternary TAG–EtOH–OIA and TAG–EtOH–EtOIA systems for 30 and 70 °C, respectively. The heterogeneous region is restricted by surface AFCEA at 30 °C and ABCDA at 70 °C, and adjoins the tetrahedron faces showing the ternary compositions. The quasi-quaternary phase diagram (Fig. 3) gives five tetrahedron sections which were used to construct it. The relevant OIA values of the mixture are shown in the EtOIA–OIA edge.

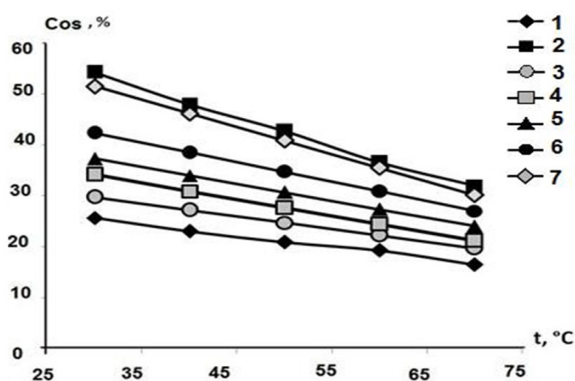


Fig. 4. Solubility polytherms at TAG-to-EtOH of 50:50 wt.% for TAG–EtOH–Cos system, where Cos: 1 – OIA, 2 – EtOIA, and OIA-plus-EtOIA, wt.%. 3 – 80:20, 4 – 60:40, 5 – 50:50, 6 – 40:60, 7 – 20:80.

For the experimental data to be conveniently usable in practice, Fig. 4 gives solubility polytherms (30 to 70 °C) for systems: TAG–EtOH–Cos, where Cos is cosolvent: OIA or EtOIA (one of two individual cosolvents) and OIA + EtOIA (mixed cosolvents at various OIA-to-EtOIA ratios which are related to five sections of the composition tetrahedron). The

polytherms show relationship to temperature of the minimum Cos amount required to homogenize the system completely. Such relationships were obtained for all relevant component ratios of the quasi-quaternary system but graphs related to sections and ternary boundary systems at TAG-to-EtOH of 50:50 wt.% are given as an example.

The section polytherms are seen to be individual between those for individual cosolvents. Thus, OIA + EtOIA cosolvent (50 + 50 wt.%) is required to homogenize the system completely at 38.1 and 23.2 wt.%, OIA at 25.7 and 16.5 wt.% and EtOIA at 54.3 and 32.0 wt.% at 30 and 70 °C, respectively.

## Conclusions

1. The experimental findings showed triacylglycerols-and-ethanol mixture could be homogenized using OIA and EtOIA as cosolvents. Oleic acid and ethyl oleate act as cosolvents if present in the system both individually or together. These cosolvents are interchangeable but, for the effect to be equal, EtOIA in the mixture must be somewhat higher than OIA. Since EtOIA is a biodiesel component, i.e. a product, while OIA is an impurity in waste vegetable oil and is converted to EtOIA via esterification, a cosolvent need imbalance may be covered by cyclic usage of some product biodiesel, including all higher fatty acid ethyl esters in the product.

2. Stability and split probability of non-electrolyte solutions as caused by cosolvents was evaluated using  $\zeta$  value which is an energetic measure of group interaction ratio in competing solvation and association processes.  $\zeta$  was assessed qualitatively with regard for dispersive and polar forces, and for proton-donor and proton-acceptor capacity of structural groups. According to the test data supported by the experimental findings, oleic acid as a cosolvent is a more efficient homogenizer in the oil-and-ethanol system as compared to ethyl oleate.

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