Liquid–liquid equilibrium constant for acetic acid in an olive oil–epoxidized olive oil–acetic acid–hydrogen peroxide–water system

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Abstract

The liquid–liquid equilibrium constant for acetic acid in a quinary system olive oil–epoxidized olive oil–acetic acid–hydrogen peroxide–water was experimentally determined for temperatures and component ratios relevant for *in situ* epoxidation of plant oils. The values have the constant range from 1.52 to 2.73. To predict the equilibrium constant for acetic acid, the experimental data were correlated with UNIQUAC (universal quasi chemical) and NRTL (non-random two liquid) activity coefficient models. For simplified calculation of the phase equilibrium the insolubility of olive oil and epoxidized olive oil in the water, as well as insolubility of water and hydrogen peroxide in the olive oil and epoxidized olive oil, was assumed. The root mean square deviation (*RMSD*) of the experimental and calculated values of the liquid–liquid equilibrium constant for acetic acid is 0.1910 for the UNIQUAC model and 0.1815 for the NRTL model. For rigorous flash calculation, when the partitioning of all components between the phases was assumed, the *RMSD* for the NRTL model is 0.1749.

Keywords: Liquid–liquid equilibrium, acetic acid, plant oil, epoxidation.

Available online at the Journal website: http://www.ache.org.rs/HI/

SCIENTIFIC PAPER

UDC 66.094.39:665.3:547.292:544.35

Hem. Ind. **70** (2) 165–175 (2016)

doi: 10.2298/HEMIND141210024J

Percarboxylic acid, such as performic or peracetic acid, is a common oxidizing agent in a large scale production of epoxidized plant oils. The percarboxylic acid is generated *in situ* through the acid catalyzed reaction of corresponding organic acid with hydrogen peroxide in an aqueous solution. A soluble mineral acid, usually sulfuric acid, or an acidic cation exchange resin can be used as a catalyst for this reaction [1,2]. Depending on applied catalyst, the reaction system of epoxidation is either two- (oil–water) or three-phase (oil–water–ion exchange resin) system. Thus, it is important to obtain the liquid-liquid equilibrium data for modeling and optimization of the epoxidation process. A rigorous two- or three-phase model of the epoxidation reaction system should include a partition coefficient for organic acid [3–6]. The coefficient is dependent on a liquid–liquid equilibrium constant for organic acid and molar densities of the phases [7–9]. A few authors investigated partitioning of formic acid or acetic acid between the oil and water phases of the epoxidation reaction system. Rangarajan *et al*. determined experimentally the partition coefficient for acetic acid in a soybean oil-acetic acid-water system at 313 and 333 K [3]. On the basis of experimental data for the liquid-liquid equilibrium constant for acetic acid, Sinadinović-Fišer and Janković calculated the partition coefficient for acetic acid in the soybean oil–acetic acid–water system at temperature range of 293–353 K [7]. Campanella *et al*. determined the partition coefficient for formic acid/acetic acid in the soybean oil–formic acid/acetic acid–water system at 313 K [8]. A presence of epoxidized plant oil in the system was taken into account when the liquid-liquid equilibrium constant for acetic acid was investigated for the epoxidized soybean oil–acetic acid–water system [9]. In aforementioned works, neither the changing of the oil phase composition during the reaction of epoxidation, *i.e*., different ratios of plant oil and epoxidized plant oil, nor the presence of hydrogen peroxide in the system was considered. In this work, however, the temperature and composition dependency of the liquid-liquid equilibrium constant for acetic acid (K_A) in a system containing five reaction components was investigated. To predict the liquid–liquid equilibrium constant for acetic acid in an olive oil (OO)–epoxidized olive oil (EOO)–acetic acid (A)–hydrogen peroxide (HP)–water (W) system, the interaction parameters of the UNIQUAC (universal quasi chemical) [10] and NRTL (non-random two liquid) [11] models for the activity coefficient were determined by fitting the experimental data obtained for the equilibrium constant at different temperatures and compositions. The results of simplified and rigorous calculation of the phase equilibrium were compared.

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Paper received: 10 December, 2014
Paper accepted: 3 March, 2015

Determination of the liquid–liquid equilibrium constant

For the same reference state in two phases, L_1 and L_2, the liquid–liquid equilibrium condition for component *j* is:

$$\gamma_j^{L_1} x_j^{L_1} = \gamma_j^{L_2} x_j^{L_2} \tag{1}$$

where γ_j^L is the activity coefficient of component *j* in phase L; and x_j^L is the mole fraction of component *j* in phase L.

The mole fraction of component *j* in the phase *L* can be expressed by the following equation:

$$x_j^L = \frac{m_j^L / M_j}{\sum_{k=1}^{NC} m_k^L / M_k} \tag{2}$$

where m_j^L and m_k^L (g) are the masses of component *j* and *k*, respectively, in phase L; M_j and M_k (g/mol) are molecular masses of component *j* and *k*, respectively; and NC is the number of components in the system.

According to Eq. (1), the liquid–liquid equilibrium constant for acetic acid (K_A) in investigated oil-water system is defined as:

$$K_A = \frac{\gamma_A^w}{\gamma_A^o} = \frac{x_A^o}{x_A^w} \tag{3}$$

where used superscripts are for water (w) and oil (o) phases.

The experimental value of the liquid-liquid equilibrium constant for acetic acid can be calculated *via* Eq. (3) using mole fractions (x_A^L).

The predicted value of the equilibrium constant for acetic acid can be obtained also *via* Eq. (3) using activity coefficients (γ_A^L). The activity coefficient of component *j* is the function of phase composition (x_j^L) and temperature (*T*). For investigated system, the coefficients are defined as:

$$\gamma_j^o = f\left(x_{OO}^o, x_{EOO}^o, x_A^o, x_{HP}^o, x_W^o, T\right) \tag{4}$$

$$\gamma_j^w = f\left(x_{OO}^w, x_{EOO}^w, x_A^w, x_{HP}^w, x_W^w, T\right) \tag{5}$$

For the calculation of the equilibrium constant, in this work the UNIQUAC and NRTL models for the activity coefficient were used. Their interaction parameters were determined by fitting the experimental data for the liquid-liquid equilibrium.

The UNIQUAC binary interaction parameter ($\tau_{j,k}$) is expressed as [10]:

$$\tau_{j,k} = e^{\frac{-u_{j,k}}{RT}} \tag{6}$$

where $u_{j,k}$ (J/mol) indicates an adjustable binary parameter for components *j* and *k* in the mixture; and *R* is the universal gas constant.

The NRTL binary interaction parameter ($G_{j,k}$) is given as [11]:

$$G_{j,k} = e^{-\alpha \frac{u_{j,k}}{RT}} \tag{7}$$

A value of the non-randomness parameter (α) of 0.2, which was used in this work, is recommended for the partially miscible liquids [11].

EXPERIMENTAL

Materials and chemicals

Olive oil, product of the Urzante, S.L., Spain, was purchased in supermarket. Glacial acetic acid (>99.8%) was bought from Sigma-Aldrich, Germany, while 30 wt.% aqueous hydrogen peroxide solution, hydrobromic acid and isopropyl alcohol (min 99.5%) were ordered from J.T. Backer, Netherlands. An acid form of sulfonated polystyrene-type cation exchange resin Amberlite IR-120H from Sigma-Aldrich, USA, was used as a catalyst. Alfapanon, Serbia, was a supplier of the aqueous solutions of potassium permanganate (0.1 N), sodium hydroxide (0.1 N) and sodium thiosulfate (0.1 N), while sulfuric acid (p.a.), iodine (p.a.) and bromine (p.a.) were purchased from Centrohem, Serbia. Potassium iodide (extra pure), benzene (p.a.) and chloroform (min 98.5%) were purchased from LachNer, Czech Republic.

Epoxidation procedure

The epoxidation of olive oil was carried out in bulk with peracetic acid formed *in situ* according to the method reported in the literature [12]. Mole ratio of oil unsaturation:acetic acid:hydrogen peroxide was 1:0.5:1.5. The amount of cationic ion exchange resin Amberlite IR-120H used as catalyst was 20 wt.% of acetic acid and hydrogen peroxide solution weight. Olive oil (250 g), glacial acetic acid and catalyst were introduced into a 500 mL three-neck round-bottom flask placed in a water bath and equipped with magnetic stirrer, thermometer, reflux condenser and dropping funnel. The 30% aqueous hydrogen peroxide was dropwise charged into the reaction mixture at temperature of 323±1 K within half an hour. The stirring speed of 1000 rpm was constant. After addition, the temperature of the reaction mixture was increased to 348 K and maintained within ±1 K next 8 h. After removing of the ion exchange resin by filtration, cooled product was centrifuged. Separated oil phase was washed with water (313 K) until pH 7. Water was evaporated at 323 K under the vacuum (about 30 kPa). Stock of epoxidized

olive oil was obtained by blending products of 8 epoxidation runs.

Equilibration procedure

The liquid–liquid equilibrium constant for acetic acid in the system olive oil–epoxidized olive oil–acetic acid–hydrogen peroxide–water was experimentally determined by equilibrating the system components at four temperatures employing seven compositions. A 500 mL three-neck round-bottom flask with weighed masses of olive oil (m_{OO}), epoxidized olive oil (m_{EOO}), acetic acid (m_A), 30% aqueous solution of hydrogen peroxide (m_{aqHP}) and water (m_W) was equipped with condenser, thermometer and magnetic stirrer. Compositions of investigated mixtures are given in Table 1. The mixtures were equilibrated in a thermostatic water bath at 293, 308, 323 and 338 (±1) K for an hour under the constant stirring of 1000 rpm. Without stopping the stirring, six samples of about 10 mL were withdrawn from the mixture and centrifuged (20 min, 1000 rpm). The samples in centrifugation tubes were again thermostated at particular temperature for 20 min. Three samples were used to determine the content of volatile matter in the oil phase. The weighed, in grams, portions of the oil ($m^{s,o}$) and water ($m^{s,w}$) phase of other three samples were titrated to determine the mass fractions of acetic acid and hydrogen peroxide. Sampling of the phases from latter three centrifuge tubes simulated triple determination of the liquid–liquid equilibrium constant for acetic acid.

Methods

To characterize the olive oil and epoxidized olive oil, a standard gravimetric method for the moisture and volatile matter content [13], the Hanus method for the iodine number and standard HBr–acetic acid method for the epoxy oxygen content [14] were applied. All analyses were done in triplicate.

The mass fraction of hydrogen peroxide in the hydrogen peroxide aqueous solution (ω_{HP}^{aqHP}) was determined by permanganometric titration with 0.1 N $KMnO_4$.

The mass fraction of water, acetic acid and hydrogen peroxide in the oil phase ($\omega_{W,A,HP}^{o}$) of the equilibrated mixtures was determined in triplicate according to the standard gravimetric method for the moisture and volatile matter content in plant oils [13], assuming that acetic acid and hydrogen peroxide evaporate together with water.

The mass fractions of acetic acid in the oil (ω_A^o) and water (ω_A^w) phase were determined by the neutralization titration with 0.1 N NaOH, whereas the mass fractions of hydrogen peroxide in the oil (ω_{HP}^{o}) and water (ω_{HP}^{w}) phase were determined by the permanganometric titration with 0.1 N $KMnO_4$. The fractions of component *j* were calculated according to the following expressions:

$$\omega_j^o = \frac{\left(V_t^o - V_{t,cor}^o\right) N_t E_j}{1000 m^{s,o}} \tag{8}$$

$$\omega_j^w = \frac{V_t^w N_t E_j n}{1000 m^{s,w}} \tag{9}$$

where V_t^o and V_t^w (mL) are the volumes of titration solution *t* consumed for titration of the samples of the oil and water phase, respectively; N_t (gE/L) indicates the normality of titration solution *t*; E_j (g/gE) is the mass of component *j* gram equivalent, which for acetic acid is $E_A = M_A$, while for hydrogen peroxide is $E_{HP} = M_{HP}/2$; and *n* is the number of aliquots. $V_{t,cor}^o$ (mL) is the volume of titration solution *t* consumed, in the case of NaOH titration, for the neutralization of the free fatty acids and, in the case of $KMnO_4$ titration, for the oxidation of the minor components in the oil phase sample. It was calculated as follows:

$$V_{t,cor}^o = \frac{m^{s,o}\left(1-\omega_{W,A,HP}^o\right)\left(h_{OO}^t m_{OO}\left(1-\omega_W^{OO}\right) + h_{EOO}^t m_{EOO}\left(1-\omega_W^{EOO}\right)\right)}{m_{OO}\left(1-\omega_W^{OO}\right) + m_{EOO}\left(1-\omega_W^{EOO}\right)} \tag{10}$$

where h_{OO}^t and h_{EOO}^t (mL *t*/g oil) are corrections for the titration of olive oil and epoxidized olive oil, respectively, determined experimentally for both titration solutions as 0.025 mL NaOH/g OO, 0.125 mL NaOH/g EOO, 0.0199 mL $KMnO_4$/g OO and 0.0189 mL $KMnO_4$/g EOO; ω_W^{OO} and ω_W^{EOO} indicate the moisture content in the olive oil and epoxidized olive oil, respectively.

Calculation of the liquid-liquid equilibrium constant for acetic acid using the experimental data

The value of the liquid–liquid equilibrium constant for acetic acid was calculated on the basis of Eqs. (2) and (3).

For calculation of the mole fractions of acetic acid in the oil and water phase, Eq. (2), the masses of the system components were calculated using the mass balance equations and the experimental data i.e. the mass fractions of acetic acid and hydrogen peroxide in both phases and the mass fraction of water, acetic acid and hydrogen peroxide in the oil phase. The calculation proceeds as follows.

Experimentally determined mass fractions of acetic acid and hydrogen peroxide were used to calculate the masses of these components in the equilibrated phases:

$$m_{\mathrm{A}}^{\mathrm{o}} = \omega_{\mathrm{A}}^{\mathrm{o}} m^{\mathrm{o}} \tag{11}$$

$$m_{\mathrm{A}}^{\mathrm{w}} = \omega_{\mathrm{A}}^{\mathrm{w}} m^{\mathrm{w}} \tag{12}$$

$$m_{\mathrm{HP}}^{\mathrm{o}} = \omega_{\mathrm{HP}}^{\mathrm{o}} m^{\mathrm{o}} \tag{13}$$

$$m_{\mathrm{HP}}^{\mathrm{w}} = \omega_{\mathrm{HP}}^{\mathrm{w}} m^{\mathrm{w}} \tag{14}$$

where m^{o} and m^{w} (g) are the masses of the oil and water phases in equilibrium, respectively. Assuming the insolubility of oils in the water phase and knowing weighed masses of olive oil and epoxidized olive oil, as well as measured content of moisture in both oils, the masses of olive oil ($m_{\mathrm{OO}}^{\mathrm{o}}$) and epoxidized olive oil ($m_{\mathrm{EOO}}^{\mathrm{o}}$) in the oil phase are:

$$m_{\mathrm{OO}}^{\mathrm{o}} = m_{\mathrm{OO}}(1 - \omega_{\mathrm{W}}^{\mathrm{OO}}) \tag{15}$$

$$m_{\mathrm{EOO}}^{\mathrm{o}} = m_{\mathrm{EOO}}(1 - \omega_{\mathrm{W}}^{\mathrm{EOO}}) \tag{16}$$

The mass balance of the oil phase is defined as follows:

$$m^{\mathrm{o}} = m_{\mathrm{OO}}^{\mathrm{o}} + m_{\mathrm{EOO}}^{\mathrm{o}} + m_{\mathrm{A}}^{\mathrm{o}} + m_{\mathrm{HP}}^{\mathrm{o}} + m_{\mathrm{W}}^{\mathrm{o}} \tag{17}$$

When Eqs. (11) and (13) are substituted in (17), the mass of water in the oil phase ($m_{\mathrm{W}}^{\mathrm{o}}$) can be calculated as:

$$m_{\mathrm{W}}^{\mathrm{o}} = m^{\mathrm{o}}\left(1 - \omega_{\mathrm{HP}}^{\mathrm{o}} - \omega_{\mathrm{A}}^{\mathrm{o}}\right) - m_{\mathrm{EOO}}^{\mathrm{o}} - m_{\mathrm{OO}}^{\mathrm{o}} \tag{18}$$

The total mass of water in the system, which partitions between the oil and water phase, is the sum of weighed water and water introduced into the system with hydrogen peroxide solution, olive oil and epoxidized olive oil:

$$m_{\mathrm{W}} + m_{\mathrm{aqHP}}\left(1 - \omega_{\mathrm{HP}}^{\mathrm{aqHP}}\right) + m_{\mathrm{OO}}\omega_{\mathrm{W}}^{\mathrm{OO}} + \\ + m_{\mathrm{EOO}}\omega_{\mathrm{W}}^{\mathrm{EOO}} = m_{\mathrm{W}}^{\mathrm{o}} + m_{\mathrm{W}}^{\mathrm{w}} \tag{19}$$

where $\omega_{\mathrm{HP}}^{\mathrm{aqHP}}$ is the mass fraction of hydrogen peroxide in the hydrogen peroxide solution. Therefore, the mass of water in the water phase ($m_{\mathrm{W}}^{\mathrm{w}}$) is:

$$m_{\mathrm{W}}^{\mathrm{w}} = m_{\mathrm{W}} + m_{\mathrm{aqHP}}\left(1 - \omega_{\mathrm{HP}}^{\mathrm{aqHP}}\right) + m_{\mathrm{OO}}\omega_{\mathrm{W}}^{\mathrm{OO}} + \\ + m_{\mathrm{EOO}}\omega_{\mathrm{W}}^{\mathrm{EOO}} - m_{\mathrm{W}}^{\mathrm{o}} \tag{20}$$

The calculation of the mass of each phase in equilibrium was performed as follows. The mass of the oil phase in equilibrium can be calculated as:

$$m^{\mathrm{o}} = \frac{m_{\mathrm{OO}}^{\mathrm{o}} + m_{\mathrm{EOO}}^{\mathrm{o}}}{1 - \omega_{\mathrm{W,A,HP}}^{\mathrm{o}}} \tag{21}$$

while following expression for the mass of the water phase in equilibrium:

$$m^{\mathrm{w}} = \frac{m_{\mathrm{W}}^{\mathrm{w}}}{1 - \omega_{\mathrm{HP}}^{\mathrm{w}} - \omega_{\mathrm{A}}^{\mathrm{w}}} \tag{22}$$

can be derived when Eqs. (12) and (14) are substituted in the equation that describes the mass balance of equilibrated water phase, assuming already accepted insolubility of oils in the water phase:

$$m^{\mathrm{w}} = m_{\mathrm{A}}^{\mathrm{w}} + m_{\mathrm{W}}^{\mathrm{w}} + m_{\mathrm{HP}}^{\mathrm{w}} \tag{23}$$

In order to check the agreement of weighed and experimentally determined contents of acetic acid and hydrogen peroxide, both partitioned between the system phases, an average relative error *ARE* (%) was calculated as follows:

$$ARE = \frac{100}{NEP}\sum_{p=1}^{NEP}\left|\frac{m_{j,p}^{\mathrm{o,exp}} + m_{j,p}^{\mathrm{w,exp}} - m_{j,p}^{\mathrm{weig}}}{m_{j,p}^{\mathrm{weig}}}\right| \tag{24}$$

where *NEP* is the number of experimental points for the liquid–liquid equilibrium constant determination; $m_{j,p}^{\mathrm{o,exp}}$ and $m_{j,p}^{\mathrm{w,exp}}$ are the experimentally determined masses of component *j* in oil (o) and water (w) phase, respectively, for experimental point *p*; and $m_{j,p}^{\mathrm{weig}}$ is the weighed mass of component *j* for experimental point *p*.

RESULTS AND DISCUSSION

The olive oil was characterized with an experimentally measured iodine number (IN_{OO}) of 80.30 and the moisture content of 0.02 wt.%. For epoxidized olive oil were determined the epoxy oxygen content (*EO*) of 4.41 wt.%, the residual iodine number (IN_{EOO}) of 0.36 and the moisture content of 3.40 wt.%. Therefore, the conversion of olive oil double bonds was 99.5% and the selectivity of epoxidation was 91.9%.

For the following fatty acid composition of olive oil: 9.0% palmitic, 6.1% stearic, 77.9% oleic, 6.3% linoleic and 0.7% linolenic acid, the molecular mass of 878.3 g/mol was calculated according to equation:

$$M_{\mathrm{OO}} = 3\sum_{FA=1}^{NFA} M_{FA}x_{FA} + M_{\mathrm{G}} - 3M_{\mathrm{W}} \tag{25}$$

where *NFA* is the number of fatty acids in the olive oil triglycerides; x_{FA} is the mole fraction of particular fatty acid in the olive oil triglycerides; and M_{G} (g/mol) indicates the molecular mass of glycerol. The accepted fatty acid composition of the olive oil corresponds to the experimentally determined iodine number.

The molecular mass of epoxidized olive oil of 934.0 g/mol was calculated *via* following mole balance of olive oil's double bond (D) partial conversion to epoxy group (E) and hydroxyl acetate group (HA), assuming that hydroxyl acetate is generated as the only side product during the epoxidation of olive oil [15,16]:

$$N_{D,OO} = N_{D,EOO} + N_{E,EOO} + N_{HA,EOO} \quad (26)$$

where $N_{D,OO}$ is the number of moles of double bond per mole of olive oil; $N_{D,EOO}$, $N_{E,EOO}$ and $N_{HA,EOO}$ are the numbers of moles of residual double bond, epoxy group and hydroxyl acetate, respectively, per mole of epoxidized olive oil. By expressing $N_{D,OO}$ as a function of iodine number of olive oil, as well as $N_{D,EOO}$ and $N_{E,EOO}$ as functions of residual iodine number and epoxy oxygen content in epoxidized olive oil, respectively, the quantity of the hydroxyl acetate group can be written according to Eq. (26) as follows:

$$N_{HA,EOO} = \frac{IN_{OO}M_{OO}}{200A_I} - \frac{IN_{EOO}M_{EOO}}{200A_I} - \frac{EO\ M_{EOO}}{200A_O} \quad (27)$$

where A_I and A_O are the atomic masses of iodine and oxygen, respectively. Since the molecular mass of epoxidized olive oil can be expressed as enlarged molecular mass of olive oil due to formed epoxy group and hydroxyl acetate group, it can be calculated as:

$$M_{EOO} = M_{OO} + N_{E,EOO}A_O + N_{HA,EOO}(A_O + M_A) \quad (28)$$

After expressing $N_{E,EOO}$ as the function of *EO* and substituting Eq. (27) in Eq. (28), the equation for calculation of the molecular mass of epoxidized olive oil used in this work is established:

$$M_{EOO} = \frac{M_{OO}[1 + IN_{OO}(A_O + M_A)(200A_I)^{-1}]}{1 + EO\ M_A(100A_O)^{-1} + IN_{EOO}(A_O + M_A)(200A_I)^{-1}} \quad (29)$$

The mass fraction of hydrogen peroxide in the hydrogen peroxide aqueous solution (ω_{HP}^{aqHP}) was determined as 0.288.

Experimental values of the liquid-liquid equilibrium constant

The mass fraction of water, acetic acid and hydrogen peroxide as the volatile matter in the oil phase, as well as the mass fractions of acetic acid and hydrogen peroxide in the oil and water phase, are given in Table 1 as the average values of three experimental determinations.

Table 1. Compositions of equilibrated mixtures and experimentally determined mass fraction of water (W), acetic acid (A) and hydrogen peroxide (aqHP), $\omega_{W,A,HP}^{O}$, in the oil phase, mass fractions of acetic acid (ω_A^O) and hydrogen peroxide (ω_{HP}^O) in the oil phase, as well as mass fractions of acetic acid (ω_A^W) and hydrogen peroxide (ω_{HP}^W) in the water phase; OO: olive oil, EOO: epoxidized olive oil

Mixture	*T* K	Weighed mass[a] (m_j), g					$\omega_{W,A,HP}^{O}$	ω_A^O	ω_{HP}^O	ω_A^W	ω_{HP}^W
		OO	EOO	A	aqHP	W					
O1	308	0.00	36.78	4.65	5.03	11.86	0.0664	0.0282	0.00303	0.171	0.0671
	323	0.00	36.88	4.65	5.03	11.86	0.0777	0.0307	0.00297	0.170	0.0672
	338	0.00	36.77	4.66	5.03	11.85	0.0673	0.0300	0.00343	0.171	0.0665
O2	308	0.00	36.80	2.67	10.04	7.56	0.0872	0.0195	0.0105	0.102	0.140
	323	0.00	36.78	2.67	10.05	7.55	0.0621	0.0179	0.00763	0.102	0.139
	338	0.00	36.80	2.68	10.04	7.55	0.0588	0.0175	0.00743	0.101	0.137
O3	293	8.75	27.58	2.66	5.02	11.87	0.0319	0.0134	0.00137	0.111	0.0722
	308	8.76	27.60	2.66	5.02	11.86	0.0443	0.0135	0.00247	0.109	0.0699
	323	8.77	27.61	2.66	5.02	11.85	0.0424	0.0144	0.00240	0.109	0.0735
	338	8.75	27.58	2.66	5.04	11.87	0.3160	0.0135	0.00200	0.110	0.0721
O4	293	17.52	18.41	2.67	10.04	7.54	0.0518	0.0132	0.00433	0.114	0.140
	308	17.55	18.39	2.66	10.05	7.55	0.0510	0.0134	0.00453	0.114	0.145
	323	17.50	18.39	2.66	10.06	7.56	0.0484	0.0126	0.00410	0.111	0.142
	338	17.57	18.40	2.66	10.04	7.55	0.0307	0.0116	0.00337	0.111	0.142
O5	293	17.55	18.40	6.68	5.12	12.07	0.0360	0.0225	0.00113	0.243	0.0634
	308	17.52	18.39	6.67	5.02	11.85	0.0980	0.0409	0.00503	0.249	0.0624
	323	17.51	18.40	6.67	5.02	11.91	0.0481	0.0274	0.00173	0.248	0.0637
	338	17.50	18.43	6.66	5.02	11.86	0.0314	0.0238	0.000967	0.245	0.0616
O6	293	26.29	9.21	4.65	15.22	3.25	0.0207	0.0139	0.00230	0.180	0.191
	308	26.33	9.23	4.66	15.09	3.42	0.0243	0.0141	0.00290	0.183	0.193
	323	26.28	9.12	4.66	15.14	3.28	0.0239	0.0148	0.00277	0.178	0.193
	338	26.26	9.21	4.65	15.07	3.24	0.0325	0.0142	0.00233	0.179	0.190
O7	293	35.08	0.00	6.66	18.84	0.00	0.0206	0.0152	0.00177	0.242	0.214
	308	35.05	0.00	6.65	18.84	0.00	0.0192	0.0155	0.00177	0.243	0.218
	323	35.04	0.00	6.66	18.83	0.00	0.0197	0.0152	0.00177	0.243	0.218
	338	35.06	0.00	6.65	18.84	0.00	0.0200	0.0154	0.00177	0.243	0.212

The total masses of acetic acid and hydrogen peroxide in the system were determined with an average relative error (Eq. (24)) of 2.15 and 2.12%, respectively. Since these masses were calculated *via* the mass balance equations using experimental data determined by five analytical methods, namely method for gravimetric determination of the volatile matter content in the oil phase and four titration methods for determination of acetic acid and hydrogen peroxide contents in both phases, the obtained average relative errors have to be considered as the total error of all analytical measurements.

The olive oil–epoxidized olive oil–acetic acid–hydrogen peroxide-water system was equilibrated at four temperatures for seven compositions. The temperatures, as well as mixture compositions, were varied in the range that is significant for the epoxidation of plant oils. The molar ratio of components was selected as to simulate variation of component concentrations in the epoxidation system with reaction time. However, as the oil phase of the mixtures without olive oil, namely mixtures O1 and O2 in Table 1, became solid during the equilibration at 293 K, only 26 values of the liquid-liquid equilibrium constant for acetic acid were determined. For investigated conditions, these values range from 1.52 to 2.73 and they are presented in Table 2. The defined trend of dependency of the liquid-liquid equilibrium constant for acetic acid neither from temperature nor from composition of examined mixtures of the olive oil–epoxidized olive oil–acetic acid–hydrogen peroxide-water system was observed.

Simplified calculation of the liquid-liquid equilibrium constant

A simplified approach for the calculation of the liquid–liquid equilibrium constant for acetic acid is based on the assumptions that only acetic acid is partitioned between two liquid phases of the epoxidation reaction system and that olive oil and epoxidized olive oil are insoluble in the water. This is described with the following constrains for the masses of components *j* in phase *L*:

$$m_{\mathrm{HP}}^{\mathrm{o}} = m_{\mathrm{W}}^{\mathrm{o}} = 0 \tag{30}$$

$$m_{\mathrm{OO}}^{\mathrm{w}} = m_{\mathrm{EOO}}^{\mathrm{w}} = 0 \tag{31}$$

Therefore, the activity coefficients of acetic acid in both phases are expressed as following functions:

$$\gamma_{\mathrm{A}}^{\mathrm{o}} = f\left(x_{\mathrm{OO}}^{\mathrm{o}}, x_{\mathrm{EOO}}^{\mathrm{o}}, x_{\mathrm{A}}^{\mathrm{o}}, T\right) \tag{32}$$

$$\gamma_{\mathrm{A}}^{\mathrm{w}} = f\left(x_{\mathrm{OO}}^{\mathrm{w}}, x_{\mathrm{EOO}}^{\mathrm{w}}, x_{\mathrm{A}}^{\mathrm{w}}, T\right) \tag{33}$$

As aforementioned, the mass of acetic acid in the system is partitioned between the oil and water phases:

$$m_{\mathrm{A}} = m_{\mathrm{A}}^{\mathrm{o}} + m_{\mathrm{A}}^{\mathrm{w}} \tag{34}$$

By substituting Eqs. (2), (32) and (33) in (1), a non--linear equation with one unknown variable ($m_{\mathrm{A}}^{\mathrm{w}}$) is established:

$$F\left(m_{\mathrm{A}}^{\mathrm{w}}\right) = x_{\mathrm{A}}^{\mathrm{o}}\gamma_{\mathrm{A}}^{\mathrm{o}} - x_{\mathrm{A}}^{\mathrm{w}}\gamma_{\mathrm{A}}^{\mathrm{w}} = 0 \tag{35}$$

In this work, Eq. (35) is solved by the modified Newton method.

Rigorous calculation of the liquid-liquid equilibrium constant

To check the accuracy of the simplified approach, a rigorous flash calculation of the phase equilibrium was performed. For such calculation it is assumed that all components are partitioned between the system phases. The activity coefficients of all components are expressed *via* Eqs. (4) and (5). Using the components' and total mass balance equations, after appropriate substitutions, the mole fraction of the oil phase (φ) in the investigated system has to be determined from the following non-linear equation:

$$\sum_{j=1}^{NC} \frac{z_j}{1+\varphi\left(K_j - 1\right)} = 1 \tag{36}$$

where z_j indicates the mole fraction of component *j* in the system; and K_j is the liquid–liquid equilibrium constant for component *j* in the system. The Newton method was applied to solve Eq. (36).

Modeling of activity coefficients for acetic acid

Due to lack of the interaction parameters for epoxy group with other groups present in the investigated system, none of the models based on the group contribution method for direct calculation of the activity coefficient, such as the UNIFAC (uniquac functional-group activity coefficients) and ASOG (analytical solution of groups) models, were applied in this work. Consequently, the UNIQUAC and NRTL models for the activity coefficient were used to correlate the liquid-liquid equilibrium constant for acetic acid with temperature and composition.

The UNIQUAC structural parameters r_j and q_j, which are the van der Waals volume and area of the molecule of component *j* relative to those of a standard segment, respectively, were calculated using the UNIFAC LLE (liquid–liquid equilibrium) group contribution data [17]:

$$r_j = \sum_{g=1}^{NG} \nu_{g,j} R_g \tag{37}$$

Table 2. Comparison of experimentally determined values of the liquid–liquid equilibrium constant for acetic acid (K_A) in the system olive oil–epoxidized olive oil–acetic acid–hydrogen peroxide–water and those calculated by simplified and rigorous approach when the UNIQUAC and NRTL models for the activity coefficient were applied

T / K	Mixture	Experimental	Calculated		
			Simplified		Rigorous
			UNIQUAC	NRTL	NRTL
293	O1	–	–	–	–
	O2	–	–	–	–
	O3	2.637	2.247	2.259	2.311
	O4	1.657	1.706	1.729	1.726
	O5	1.908	1.907	1.853	1.791
	O6	2.031	1.768	1.859	1.808
	O7	1.561	1.669	1.714	1.685
308	O1	2.212	2.267	2.195	2.108
	O2	1.936	1.982	2.132	2.034
	O3	2.115	2.324	2.365	2.322
	O4	1.725	1.816	1.772	1.819
	O5	1.542	1.866	1.862	1.867
	O6	1.836	1.819	1.828	1.837
	O7	1.672	1.599	1.629	1.649
323	O1	2.115	2.308	2.249	2.242
	O2	2.353	2.154	2.213	2.275
	O3	2.346	2.456	2.512	2.534
	O4	1.706	1.964	1.872	1.904
	O5	1.871	1.865	1.900	1.941
	O6	2.034	1.844	1.813	1.848
	O7	1.609	1.584	1.590	1.602
338	O1	2.376	2.383	2.322	2.342
	O2	2.438	2.369	2.334	2.444
	O3	2.731	2.640	2.689	2.629
	O4	2.213	2.147	2.008	1.983
	O5	2.323	1.895	1.956	1.998
	O6	1.515	1.905	1.842	1.855
	O7	1.626	1.596	1.571	1.552
Objective function, S			0.9485	0.8566	0.7951
Root mean square deviation, $RMSD = \sqrt{\sum_{i=1}^{NE}(K_{A,i}^{calc} - K_{A,i}^{exp})^2}$			0.1910	0.1815	0.1749
Average relative deviation, $ARE\ (\%) = \frac{100}{NE}\sum_{i=1}^{NE}\left\lvert\frac{K_{A,i}^{calc} - K_{A,i}^{exp}}{K_{A,i}^{exp}}\right\rvert$			7.23	7.30	7.24
Average absolute deviation, $AAD = \frac{1}{NE}\sum_{i=1}^{NE}\left\lvert K_{A,i}^{calc} - K_{A,i}^{exp}\right\rvert$			0.1418	0.1438	0.1414

$$q_j = \sum_{g=1}^{NG} \nu_{g,j} Q_g \tag{38}$$

where NG is the total number of group species in the system; $\nu_{g,j}$ is the number of groups of type g in the molecule of component j; and R_g and Q_g are the parameters related to the volume and area of group g, respectively. In order to calculate the structural parameters from the literature data, the molecule of hydrogen peroxide was presented with two hydroxyl groups, whereas the olive oil and epoxidized olive oil, each considered as one pseudo-component, were presented with the following molecular structures, respectively:

$(CH_2COO)_3CH(CH_2)_b(CH{=}CH)_c(CH_3)_3$,
$[(CH_2COO)_3(CH)_d(CH_2)_b(CH{=}CH)_f$ and
$(FCH_2O)_l(OH)_y(CH_3COO)_y(CH_3)_3$.

Since the structural parameters for epoxy group are not available in the literature, an ether group of cyclic ethers, FCH_2O, was included into the pseudo-component molecule of epoxidized olive oil instead. The coefficients in the pseudo-component molecules *b*, *c*, *d*, *f*, *l* and *y* were accepted as 40.904, 2.778, 3.9559, 0.0134, 2.5733 and 0.1913, respectively, on the basis of the iodine numbers, epoxy oxygen content and fatty acid composition of the olive oil and epoxidized olive oil. Although the number of groups in a molecule is usually defined with an integer within UNIFAC model, the decimal numbers have been successfully used for coefficients in the pseudo-component molecules of plant oils when the liquid-liquid equilibrium of the systems similar to the system investigated in this work was studied [7,9]. The calculated values of r_{OO} and q_{OO} parameters are 38.867 and 31.529, respectively, whereas the values of r_{EOO} and q_{EOO} parameters are 40.0194 and 33.1965, respectively.

Binary interaction parameters of both NRTL and UNIQUAC activity coefficient models were determined by minimization of the following objective function *S*:

$$S = \sum_{i=1}^{NE} \left(K_{A,i}^{calc} - K_{A,i}^{exp} \right)^2 \tag{39}$$

where *NE* is the number of experiments; and $K_{A,i}^{calc}$ and $K_{A,i}^{exp}$ are calculated and experimentally determined values, respectively, of the liquid–liquid equilibrium constant for acetic acid for the experiment *i*. The Marquardt method was applied to minimize the objective function [18]. Therefore, the fitting of interaction parameters was based on the algorithm with two loops. The outer loop is the minimization of the objective function, and inner loop is either the simplified or the rigorous calculation of the liquid–liquid equilibrium constant for acetic acid. The determined interaction parameters for simplified and rigorous calculations are given in Tables 3–5.

Table 3. Interaction parameters $u_{j,k}$ (J/mol) of the UNIQUAC model for activity coefficient applied within the simplified calculation of K_A

Component	Olive oil	Epoxidized olive oil	Acetic acid	Hydrogen peroxide	Water
Olive oil	0	–1170.159	6072.516	–	–
Epoxidized olive oil	–2670.553	0	–504.9471	–	–
Acetic acid	–2399.01	5145.97	0	–8082.141	–4950.184
Hydrogen peroxide	–	–	3865.073	0	–8162.745
Water	–	–	15163.77	1847.888	0

Table 4. Interaction parameters $u_{j,k}$ (J/mol) of the NRTL model for activity coefficient applied within the simplified calculation of K_A

Component	Olive oil	Epoxidized olive oil	Acetic acid	Hydrogen peroxide	Water
Olive oil	0	23.00308	–6792.634	–	–
Epoxidized olive oil	5154.96	0	–2190.579	–	–
Acetic acid	1638.673	–5827.824	0	–18728.77	–11964.42
Hydrogen peroxide	–	–	35188.14	0	–22226.66
Water	–	–	24023.41	19073.41	0

Table 5. Interaction parameters $u_{j,k}$ (J/mol) of the NRTL model for activity coefficient applied within the rigorous calculation of K_A

Component	Olive oil	Epoxidized olive oil	Acetic acid	Hydrogen peroxide	Water
Olive oil	0	10764.7	239.1269	–9235.735	–88.59006
Epoxidized olive oil	–6781.327	0	1949.265	34458.26	–472.6696
Acetic acid	–1795.675	–1056.141	0	4409.27	9341.472
Hydrogen peroxide	16563.09	123.3846	1710.127	0	–3772.03
Water	17447.25	36863.31	–1869.315	7440.163	0

Comparison of activity coefficient models and types of calculation

The values of the liquid-liquid equilibrium constant for acetic acid calculated using determined interaction parameters of UNIQUAC and NRTL models for the activity coefficient are presented in Table 2 for both types of calculations.

The simplified approach for calculation of the liquid-liquid equilibrium constant for acetic acid shows good agreement with experimental data since the relative

mean square deviations (*RMSD*) for both UNIQUAC and NRTL activity coefficient models are low, namely 0.1910 and 0.1815, respectively. The rigorous calculation was performed applying only NRTL model for activity coefficient as it showed slightly better correlation in the case of simplified calculation. Although the number of adjustable parameters is higher for rigorous than for simplified calculation, 20 compared to 12, the predicted values of the equilibrium constant are similar, *i.e*., the *RMSD* for rigorous calculation is 3.64% lower than for simplified. This implies that the application of proposed simplified calculation of the liquid-liquid equilibrium constant for acetic acid is acceptable.

As previously mentioned, the applicability of different activity coefficient models for describing the liquid-liquid equilibrium in the systems relevant for epoxidation of plant oils was reported in the literature. Thus, for the system soybean oil-acetic acid-water, the original and three modified UNIFAC models, as well as the UNIQUAC model, were used to correlate the liquid-liquid equilibrium data by assuming the immiscibility of soybean oil and water. For such system, the UNIQUAC model was significantly more accurate than other models [7,8]. The UNIQUAC model was also more adequate than modified UNIFAC model for describing the equilibrium of the system soybean oil-formic acid-water [8]. To estimate the liquid-liquid equilibrium constant for acetic acid in the epoxidized soybean oil-acetic acid-water system, the Wilson, NRTL and UNIQUAC models were used to correlate the experimental data. In spite of all simplifications, the conclusion was that all three models are adequate to predict the equilibrium constant for acetic acid. However, according to the analysis of ARE, the most successful prediction of the liquid–liquid equilibrium constant for acetic acid in the investigated system was obtained with UNIQUAC model when partial miscibility of epoxidized soybean oil and water was assumed [9]. Under the conditions applied in the present investigation, the adequacy of both NRTL and UNIQUAC models for prediction of the liquid-liquid equilibrium constant for acetic acid in the olive oil-epoxidized olive oil-acetic acid-hydrogen peroxide–water system is confirmed, although the computationally less demanding NRTL model slightly better correlates the experimental equilibrium data.

CONCLUSION

The liquid–liquid equilibrium constant for acetic acid in the system olive oil–epoxidized olive oil–acetic acid–hydrogen peroxide–water was experimentally determined and successfully estimated under conditions of temperature and component ratios significant for the process of plant oil epoxidation with peracetic acid generated *in situ*. The experimentally determined values of the constant are better correlated when NRTL than when UNIQUAC model for the activity coefficient was applied, under the accepted simplifications regarding the partitioning and solubility of particular components in the system phases. When the NRTL model was used within the rigorous flash calculation of the equilibrium, slightly better fitting was achieved than with simplified calculation. Since the values of the liquid-liquid equilibrium constant for acetic acid predicted by simplified and by rigorous calculation are comparable, the usage of proposed simplified approach can be recommended when establishing the mathematical model that describes the reaction system for epoxidation of plant oils.

Acknowledgment

This work is part of Project No. III45022 supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia.

List of symbols

A	Acetic acid
A_I,A_O	Atomic mass of iodine i.e. oxygen, respectively
aqHP	Hydrogen peroxide aqueous solution
b	Number of (CH_2) groups present in OO and EOO pseudo-component molecules
c	Number of (CH=CH) groups present in OO pseudo-component molecule
D	Double bond
d	Number of (CH) groups present in EOO pseudo-component molecule
E	Epoxy group
E_j	Mass of component j gram equivalent (g/gE)
EO	Epoxy oxygen content (wt%)
EOO	Epoxidized olive oil
f	Number of (CH=CH) groups present in EOO pseudo-component molecule
$G_{j,k}$	NRTL binary interaction parameter for components j and k in the mixture
h^t_{OO} , h^t_{EOO}	Correction for titration of OO and EOO, respectively, with titration solution t (mL t/g oil)
HA	Hydroxyl acetate group
HP	Hydrogen peroxide
IN_j	Iodine number of component j
K_j	Liquid–liquid equilibrium constant for component j
$K^{calc}_{A,i}$, $K^{exp}_{A,i}$	Calculated, *i.e*., experimentally determined value of K_A, respectively, for experiment i
l	Number of (FCH_2O) groups present in EOO pseudo-component molecule
M_j , M_k	Molecular mass of component j, *i.e*., k, respectively (g/mol)
m_j	Weighed mass of component j (g)
m^o,m^w	Mass of the oil, *i.e*. ,water phase, respectively, in equilibrium (g)

m_j^L, m_k^L Mass of component *j* i.e. *k*, respectively, in phase *L* (g)
$m^{s,L}$ Mass of the sample of phase *L* (g)
$m_{j,p}^{L,\mathrm{exp}}$ Experimentally determined mass of component *j* in phase *L* for experimental point *p* (g)
$m_{j,p}^{\mathrm{weig}}$ Weighed mass of component *j* for experimental point *p* (g)
n Number of aliquots
N_t Normality of titration solution *t* (gE/L)
$N_{\mathrm{D,OO}}$ Number of moles of double bond per mole of olive oil
$N_{\mathrm{D,EOO}}$, $N_{\mathrm{E,EOO}}$, $N_{\mathrm{HA,EOO}}$ Number of moles of residual double bond, epoxy group *i.e.*, hydroxyl acetate, respectively, per mole of epoxidized olive oil
NC Number of components in the system
NE Number of experiments
NEP Number of experimental points
NFA Number of fatty acids in the olive oil triglycerides
NG Total number of group species in the system
OO Olive oil
Q_g Area parameter of group *g*
q_j Area parameter of molecule of component *j*
R Universal gas constant
R_g Volume parameter of group *g*
r_j Volume parameter of molecule of component *j*
S Objective function
T Temperature (K)
$u_{j,k}$ Adjustable binary parameter for components *j* and *k* in the mixture (J/mol)
V_t^L Volume of titration solution *t* consumed for titration of the sample of phase *L* (mL)
$V_{t,\mathrm{cor}}^{\mathrm{o}}$ Correction volume of titration solution *t* consumed for titration of the oil phase sample (mL)
W Water
x_{FA} Mole fraction of fatty acid FA in the olive oil triglycerides
x_j^L Mole fraction of component *j* in phase *L*
y Number of (OH) groups, as well as number of (CH_3COO) groups present in EOO pseudo-component molecule
z_j Mole fraction of component *j* in the system

Greek letters

α Non-randomness parameter in the NRTL model
γ_j^L Activity coefficient of component *j* in phase *L*
$\nu_{g,j}$ Number of groups of type *g* in the molecule of component *j*
$\tau_{j,k}$ UNIQUAC binary interaction parameter for components *j* and *k* in the mixture
φ Mole fraction of the oil phase
ω_j^L Mass fraction of component *j* in phase *L*
$\omega_{\mathrm{HP}}^{\mathrm{aqHP}}$ Mass fraction of hydrogen peroxide in the hydrogen peroxide solution
$\omega_{\mathrm{W}}^{\mathrm{OO}}$, $\omega_{\mathrm{W}}^{\mathrm{EOO}}$ Moisture content in OO, *i.e.*, EOO, respectively
$\omega_{\mathrm{W,A,HP}}^{\mathrm{o}}$ Mass fraction of water, acetic acid and hydrogen peroxide in the oil phase

Superscripts

L Phase
o Oil phase
w Water phase

Subscripts

A Acetic acid
aqHP Hydrogen peroxide aqueous solution
D Double bond
E Epoxy group
EOO Epoxidized olive oil
G Glycerol
HA Hydroxyl acetate group
HP Hydrogen peroxide
OO Olive oil
W Water

REFERENCES

[1] S.G. Tan, W.S. Chow, Biobased epoxidized vegetable oils and its greener epoxy blends: A review, Polym.-Plast. Technol. Eng. **49** (2010) 1581–1590.

[2] S-C. Chua, X. Xu, Z. Guo, Emerging sustainable technology for epoxidation directed toward plant oil-based plasticizers, Process Biochem. **47** (2012) 1439–1451.

[3] B. Rangarajan, A. Havey, E.A. Grulke, P.D. Culnan, Kinetic parameters of a two-phase model for *in situ* epoxidation of soybean oil, J. Am. Oil Chem. Soc. **72** (1995) 1161–1169.

[4] R.L. Musante, R.J. Grau, M.A. Baltanás, Kinetics of liquid-phase reactions catalyzed by acidic resins: the formation of peracetic acid for vegetable oil epoxidation, Appl. Catal., A **197** (2000) 165–173.

[5] E. Santacesaria, R. Tesser, M. Di Serio, R. Turco, V. Russo, D. Verde, A biphasic model describing soybean oil epoxidation with H_2O_2 in a fed-batch reactor, Chem. Eng. J. **173** (2011) 198–209.

[6] E. Santacesaria, A. Renken, V. Russo, R. Turco, R. Tesser, M. Di Serio, Biphasic model describing soybean oil epoxidation with H_2O_2 in a continuous reactors, Ind. Eng. Chem. Res. **51** (2012) 8760–8767.

[7] S. Sinadinović-Fišer, M. Janković, Prediction of the partition coefficient for acetic acid in a two-phase system soybean oil-water, J. Am. Oil Chem. Soc. **84** (2007) 669–674.

[8] A. Campanella, B.A. Mandagarán, E.A. Campanella, Partitioning of a carboxylic acid between oil and water phases. Experimental, correlation, and prediction, J. Am. Oil Chem. Soc. **86** (2009) 513–519.

[9] M. Janković, S. Sinadinović-Fišer, M. Lamshoeft, Liquid-liquid equilibrium constant for acetic acid in an epox-

idized soybean oil-acetic acid-water system, J. Am. Oil Chem. Soc. **87** (2010) 591–600.

[10] D.S. Abrams, J.M. Prausnitz, Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems, AIChE J. **21** (1975) 116–128.

[11] H. Renon, J.M. Prausnitz, Local composition in thermodynamic excess functions for liquid mixtures, AIChE J. **14** (1968) 135–144.

[12] S. Sinadinović-Fišer, M. Janković, Z. Petrović, Kinetics of *in situ* epoxidation of soybean oil in bulk catalyzed by ion exchange resin, J. Am. Oil Chem. Soc. **78** (2001) 725–731.

[13] Method Ca 2c-25 in Official Methods and Recommended Practices, 3rd ed., American Oil Chemists' Society, Champaign, IL, 1987.

[14] Standard Methods for the Analysis of Oils, Fats and Derivatives, Blackwell Scientific Publications, London, 1987.

[15] A. Campanella, M.A. Baltanás, Degradation of the oxirane ring of epoxidized vegetable oil with solvated acetic acid using cation-exchange resin, Eur. J. Lipid Sci. Technol. **106** (2004) 524–530.

[16] A. Campanella. M.A. Baltanás, Degradation of the oxirane ring of epoxidized vegetable oil in a liquid-liquid-solid heterogeneous reaction system, Chem. Eng. Process **46** (2007) 210–221.

[17] T. Magnussen, P. Rasmussen, A. Fredenslund, UNIFAC parameter table for prediction of liquid-liquid equilibria, Ing. Eng. Chem. Process Des. Dev. **20** (1981) 331–339.

[18] D.W. Marquardt, An algorithm for least-squares estimation of nonlinear parameters, J. Soc. Ind. Appl. Math. **11** (1963) 431–441.

IZVOD

KONSTANTA RAVNOTEŽE TEČNO–TEČNO SIRĆETNE KISELINE U SISTEMU MASLINOVO ULJE–EPOKSIDOVANO MASLINOVO ULJE–SIRĆETNA KISELINA–VODONIK-PEROKSID–VODA

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Epoksidovanje biljnih ulja se industrijski izvodi perorganskom kiselinom formiranom *in situ* iz odgovarajuće organske kiseline i vodonik peroksida u prisustvu kiselog katalizatora. Kada se kao homogeni katalizator primenjuje neka mineralna kiselina, reakcioni sistem epoksidovanja ulja je dvofazni (ulje–voda), dok pri primeni heterogenog katalizatora, kakva je kisela jonoizmenjivačka smola, pomenuti sistem je trofazni (ulje–voda–katalizator). Pri postavljanju pouzdanog matematičkog modela koji opisuje ovaj višefazni reakcioni sistem, a za potrebe optimizovanja procesa epoksidovanja biljnih ulja, neophodno je uzeti u obzir raspodelu sirćetne kiseline između uljne i vodene faze. U ovom radu je konstanta fazne ravnoteže tečno-tečno sirćetne kiseline u kvinarnom sistemu maslinovo ulje–epoksidovano maslinovo ulje–sirćetna kiselina–vodonik peroksid–voda određena eksperimentalno za temperature u opsegu 293–338 K i za različite odnose komponenata. Odnos komponenata u ispitivanim smešama je odabran tako da odgovara uslovima izvođenja epoksidovanja, ali i da simulira promenu odnosa komponenata u sistemu usled odigravanja reakcija. Za uslove ispitivanja, eksperimentalno određene vrednosti konstante ravnoteže se kreću u opsegu 1,52–2,73. U cilju izračunavanja konstante ravnoteže sirćetne kiseline, eksperimentalne vrednosti konstante su korelisane UNIQUAC (universal quasi-chemical) i NRTL (non-random two liquid) modelima za koeficijent aktivnosti. Binarni interakcioni parametri ovih modela su određeni primenom metode Marquardt-a za fitovanje eksperimentalnih podataka. Pri uprošćenom proračunu, u kom je usvojeno da se maslinovo ulje i epoksidovano maslinovo ulje ne rastvaraju u vodi, kao i da se voda i vodonik peroksid ne rastvaraju u maslinovom i epoksidovanom maslinovom ulju, standardno odstupanje je 0,1910 za UNIQUAC i 0,1815 za NRTL model. Pri rigoroznom flash proračunu, u kojem je pretpostavljeno prisustvo svih komponenata u obe faze, standardno odstupanje za jedino primenjeni NRTL model je 0,1749. Kako je ovo odstupanje manje za samo 3,64% od standardnog odstupanja postignutog pri uprošćenom proračunu, kada se primenjuje isti model za koeficijent aktivnosti, upotreba uprošćenog proračuna je prihvatljiva za modelovanje reakcionog sistema epoksidovanja biljnih ulja.

Ključne reči: Ravnoteža tečno–tečno • Sirćetna kiselina • Biljno ulje • Epoksidovanje