J Am Oil Chem Soc (2010) 87:591–600
DOI 10.1007/s11746-009-1531-z

ORIGINAL PAPER

Liquid–Liquid Equilibrium Constant for Acetic Acid in an Epoxidized Soybean Oil–Acetic Acid–Water System

Milovan Janković · Snežana Sinadinović-Fišer · Marc Lamshoeft

Received: 27 January 2009 / Revised: 11 December 2009 / Accepted: 11 December 2009 / Published online: 27 December 2009

Abstract Dependency of the liquid–liquid equilibrium constant for acetic acid (A) in a system of epoxidized soybean oil–acetic acid–water from temperature and composition was experimentally determined. To estimate the liquid–liquid equilibrium constant for acetic acid (K_A), the interaction parameters of the Wilson, NRTL (non-random two liquid) and UNIQUAC (universal quasi chemical) models for the activity coefficient were calculated by fitting the experimental values of the equilibrium constant for acetic acid. The Marquardt method was used to fit the data. In spite of all applied simplifications, small deviations of the calculated values from those experimentally determined indicate the adequacy of all three models for the prediction of the liquid–liquid equilibrium constant for acetic acid. Comparison of the experimentally determined values of the equilibrium constant for acetic acid in the investigated system with those reported in the literature for the system with soybean oil, shows that the value of the liquid–liquid equilibrium constant for acetic aid in the system of epoxidized soybean oil–acetic acid–water is about 1.5 times higher than in the system of soybean oil–acetic acid–water for the same temperature and similar composition. For the investigated conditions, the influence of the changing of the oil phase composition on the equilibrium constant for acetic acid is more prominent than the influence of the temperature or the total acetic acid content in the system.

Keywords In-situ epoxidation · Mathematical model · Equilibrium constant for acetic acid · Liquid–liquid system · Epoxidized soybean oil–acetic acid–water

List of symbols

A	Acetic acid
a_k	Activity of component *k*
d	Measure of deviation from the certified NaOH concentration
E_A	Gram equivalent of acetic acid
ESO	Epoxidized soybean oil
FA	Fatty acid
$G_{j,k}$	NRTL model binary interaction parameter
$g^{o}_{H_2O}$	Mass fraction of water in the oil phase sample
K_A	Liquid–liquid equilibrium constant for acetic acid
k_{ESO}	Correction for ESO titration
l	Number of (CH=CH) groups in the ESO pseudo-component molecule
M_j, M_k	Molecular mass of component *j*, i.e. *k* (g/mol)
m	Number of (CHOCH) groups in the ESO pseudo-component molecule
m_k	Total mass of component *k* (g)
m_A	Total mass of acetic acid (g)
m^i	Mass of the sample of phase *i* (g)
m^i_A	Mass of acetic acid in phase *i* (g)
m^i_j, m^i_k	Mass of component *j*, i.e. *k*, respectively, in phase *i* (g)

M. Janković · S. Sinadinović-Fišer (✉)
Faculty of Technology, University of Novi Sad,
Bul. cara Lazara 1, 21000 Novi Sad, Republic of Serbia
e-mail: ssfiser@uns.ac.rs

M. Janković
e-mail: janks.janks@gmail.com

M. Lamshoeft
Institute of Environmental Research,
Dortmund University of Technology,
Otto-Hahn Str. 6, 44221 Dortmund, Germany

N	Concentration of NaOH solution (gE/L)
NE	Total number of experimental points
NG	Total number of groups in ESO pseudo-component molecule
NP	Number of model parameters
NR	Number of experiment repetitions
n	Number of (CHOH–CHCOOCH$_3$) groups in ESO pseudo-component molecule
O	Number of moles of the oil phase
OF	Objective function
p	Number of (CH$_2$) groups in the ESO pseudo-component molecule
Q_g	Area parameter of group g
q_{ESO}	Area parameter of ESO
R	Universal gas constant
R$_1$	Alkyl chain fragment of fatty acid in TG after the double bond converted to an epoxy ring
R$_2$	Residue of TG without R$_1$ after the double bond converted to an epoxy ring
R^2	Coefficient of determination
R_g	Volume parameter of group g
r_{ESO}	Volume parameter of ESO
SO	Soybean oil
s	Sample standard deviation
T	Temperature (K)
$u_{j,k}$	Adjustable binary parameter for components j and k in the mixture (J/mol)
V_j, V_k	Molar volume of the component j, i.e. k (cm^3/mol)
V^i_{NaOH}	Volume of NaOH solution consumed for titration of the sample of phase i (mL)
v_g	Number of g group species in ESO pseudo-component molecule
W	Number of moles of the water phase
x^i_{A}	Molar fraction of acetic acid in phase i
x^i_j	Molar fraction of component j in phase i

Greek letters

α	Non-randomness parameter in the NRTL model
γ^i_{A}	Activity coefficient of acetic acid in phase i
γ^i_k	Activity coefficient of component k in phase i
$\Lambda_{j,k}$	Wilson model binary interaction parameter
$\tau_{j,k}$	UNIQUAC model binary interaction parameter

Superscripts

i	Phase
o	Oil phase
w	Water phase

Subscripts

A	Acetic acid
ESO	Epoxidized soybean oil
j,k	Components of the mixture
SO	Soybean oil

Introduction

Epoxidation of unsaturated fatty acid derivatives such as vegetable oil TG is carried out on an industrial scale. Epoxides of many kinds of vegetable oils are well known commercially. They are used directly as plasticizers and stabilizers for PVC, as paint and coating components, lubricants, but also as intermediates for alcohols, glycols, alkanolamines, olefinic compounds and polymers (such as polyurethanes, polyesters and epoxy resins) production due to the high reactivity of the oxirane ring [1–3]. Today, for the production of epoxides, of all vegetable oils, soybean oil (SO) is the most frequently used. Among available technologies for the production of vegetable oil epoxides, the epoxidation with percarboxylic acids is the most widely used in industry. Percarboxylic acid can be pre-formed from carboxylic acid and hydrogen peroxide but, because of safety precautions, it is usually prepared in the reaction mixture, by an in-situ method. As it is inexpensive and less corrosive, peracetic acid is the most appropriate acid. The in-situ process involves an acid-catalyzed reaction of peracetic acid formation in the water phase, and the reaction of epoxy ring formation in the oil phase [4, 5]. The usage of heterogeneous acid catalyst such as ion exchange resin, which replaced traditional homogeneous (mainly sulphuric acid), renders cleaner products due to the reduced extent of acid-catalyzed cleavage of epoxy rings which is possible during epoxidation [4–8].

The reaction system of in-situ epoxidation of SO by peracetic acid in the presence of an ion exchange resin as catalyst is a complex three-phase system with two main and a few side reactions [5]. The rigorous mathematical model of that system, besides kinetic parameters, comprises the thermodynamic ones, as well as parameters of mass-transfer between the oil and water phase. The simultaneous determination of all parameters by fitting the experimental data for the variation of component concentrations with the reaction time is inconvenient, because it demands a lot of data; incorrect, because of mutually correlated parameters and, in the case of chemical equilibrium constant determination for the reaction of peracid formation, impossible, as this reaction is shifted to the right which is due to constant consumption of peracid in the epoxidation reaction [9]. Because of these reasons, it is more convenient to determine the parameters using data from experiments specified for particular phenomena. One of the mathematical model parameters given by Rangarajan et al. [4] is the partition coefficient for acetic acid (A) between the oil and water phase that can be calculated from the liquid–liquid phase equilibrium condition and known phase densities. In the previous paper [9] we proposed an approach for the prediction of the partition coefficient for acetic acid between soybean oil and water, dependent on temperature and composition. Since, to the best of our knowledge, no reports have yet appeared about the change of the equilibrium constant for acetic acid, and consequently its partition coefficient, during the epoxidation of soybean oil, in the present work we determined the dependency of the liquid–liquid equilibrium constant for acetic acid (K_A) in the system epoxidized soybean oil (ESO)–acetic acid–water from temperature and composition. To predict the liquid–liquid equilibrium constant for acetic acid in the investigated system, the interaction parameters of some well-known models for the activity coefficient were determined by fitting the experimental data for the equilibrium constant.

Determination of the Liquid–Liquid Equilibrium Constant

For the same reference state in both phases, the liquid–liquid equilibrium condition for the investigated system is:

$$a_k^{\mathrm{o}} = a_k^{\mathrm{w}} \tag{1}$$

i.e.,

$$\gamma_k^{\mathrm{o}} x_k^{\mathrm{o}} = \gamma_k^{\mathrm{w}} x_k^{\mathrm{w}} \tag{2}$$

where a_k is the activity of component k; γ_k indicates the activity coefficient of component k; and x_k is the molar fraction of component k. The superscripts used are for the oil (o) and water (w) phases.

The liquid–liquid equilibrium constant for acetic acid (K_A) is defined, according to Eq. 2, as:

$$K_{\mathrm{A}} = \frac{x_{\mathrm{A}}^{\mathrm{o}}}{x_{\mathrm{A}}^{\mathrm{w}}} = \frac{\gamma_{\mathrm{A}}^{\mathrm{w}}}{\gamma_{\mathrm{A}}^{\mathrm{o}}} \tag{3}$$

The molar fraction of component j in the phase i (x_j^i) can be expressed by the following equation:

$$x_j^i = \frac{m_j^i/M_j}{\sum_{k=1}^{3} m_k^i/M_k} \tag{4}$$

where m_j^i and m_k^i (g) are the masses of components j and k, respectively, in phase i; and M_j and M_k (g/mol) are molecular masses of components j and k, respectively.

The experimental value of the equilibrium constant for acetic acid (K_A) can be calculated via Eq. 3, for which the molar fractions of acetic acid are determined by Eq. 4 using the weighed masses of the oil (m^{o}) and water (m^{w}) phase samples, masses of the acetic acid in the oil ($m_{\mathrm{A}}^{\mathrm{o}}$) and water ($m_{\mathrm{A}}^{\mathrm{w}}$) phase, determined by NaOH titration and mass fraction of water in the oil phase sample ($g_{\mathrm{H_2O}}^{\mathrm{o}}$) determined by Karl-Fischer titration.

To predict the equilibrium constant for acetic acid, the model for the activity coefficient is necessary. The activity coefficient of component k in both phases is the function of composition and temperature (T):

$$\gamma_k^{\mathrm{o}} = f(x_{\mathrm{ESO}}^{\mathrm{o}}, x_{\mathrm{A}}^{\mathrm{o}}, x_{\mathrm{H_2O}}^{\mathrm{o}}, T) \tag{5}$$

$$\gamma_k^{\mathrm{w}} = f(x_{\mathrm{ESO}}^{\mathrm{w}}, x_{\mathrm{A}}^{\mathrm{w}}, x_{\mathrm{H_2O}}^{\mathrm{w}}, T) \tag{6}$$

It would be the best if some model based on the group contribution method, such as the UNIFAC (uniquac functional-group activity coefficients) [10] or ASOG (analytical solutions of groups) [11], could be applied directly for the activity coefficient calculation. However, the interaction parameters of epoxy group with other groups present in the investigated system are not given in the literature. Therefore, in this work, the Wilson [12], NRTL (non-random two liquid) [13] and UNIQUAC (universal quasi chemical) [14] models for the activity coefficients were used. The model's application demands previous determination of the interaction parameters for components of the system by fitting the experimental data for liquid–liquid equilibrium.

The Wilson binary interaction parameter ($\Lambda_{j,k}$) is given by the following expression [12]:

$$\Lambda_{j,k} = \frac{V_k}{V_j} e^{\frac{-u_{j,k}}{RT}} \tag{7}$$

where V_j and V_k (cm^3/mol) are the molar volumes of the components j and k, respectively; $u_{j,k}$ (J/mol) indicates 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 expressed as [13]:

$$G_{j,k} = e^{-\alpha \frac{u_{j,k}}{RT}} \tag{8}$$

where α indicates the non-randomness parameter which introduces the difference between the interaction energy of the central molecule with the molecules of its own kind and that with the molecules of the other kind. Typically, α is set to 0.2, 0.3, 0.4 or 0.47, depending of type of liquid mixture; a value of 0.2 is recommended for the partially miscible liquids [13].

Finally, for the UNIQUAC model, the expression for the binary interaction parameter ($\tau_{j,k}$) is given as [14]:

$$\tau_{j,k} = e^{\frac{-u_{j,k}}{RT}} \tag{9}$$

Since the masses of epoxidized soybean oil, acetic acid and water in the investigated system are known it is possible to determine the molar fraction of acetic acid in the oil ($x_{\mathrm{A}}^{\mathrm{o}}$) and water ($x_{\mathrm{A}}^{\mathrm{w}}$) phase, necessary for calculation of K_A according to the Eq. 3, by solving the system of Eqs. 2, 5 and 6 together with the following relations for the component mass balance:

$$\frac{m_k}{M_k} = O x_k^{\mathrm{o}} + W x_k^{\mathrm{w}} \tag{10}$$

and summation equations:

$$\sum_{k=1}^{3} x_k^{o} = 1 \quad \text{and} \quad \sum_{k=1}^{3} x_k^{w} = 1 \tag{11}$$

where O and W indicate the numbers of moles of the oil and water phase, respectively.

The total mass balance is defined as follows:

$$O + W = \sum_{k=1}^{3} \frac{m_k}{M_k} \tag{12}$$

If the solubility of water in epoxidized soybean oil is neglected and the immiscibility of oil and water is assumed, the following equations are defined: $m_{\mathrm{H_2O}}^{\mathrm{o}} = m_{\mathrm{ESO}}^{\mathrm{w}} = 0$ i.e. $x_{\mathrm{H_2O}}^{\mathrm{o}} = x_{\mathrm{ESO}}^{\mathrm{w}} = 0$. In that case, the calculation of K_{A} is simpler and proceeds as follows. Knowing the mass of epoxidized soybean oil and water in the system, and the total mass of partitioned acetic acid (m_{A}), which is the sum of the acetic acid masses in the oil and water phase:

$$m_{\mathrm{A}} = m_{\mathrm{A}}^{\mathrm{o}} + m_{\mathrm{A}}^{\mathrm{w}} \tag{13}$$

it is possible, by substituting Eq. 13 and Eqs. 4–6 in 2, to establish a non-linear equation with one unknown variable $m_{\mathrm{A}}^{\mathrm{w}}$:

$$x_{\mathrm{A}}^{\mathrm{o}} f\left(x_{\mathrm{A}}^{\mathrm{o}}, x_{\mathrm{ESO}}^{\mathrm{o}}, T\right) - x_{\mathrm{A}}^{\mathrm{w}} f\left(x_{\mathrm{A}}^{\mathrm{w}}, x_{\mathrm{H_2O}}^{\mathrm{w}}, T\right) = 0 \tag{14}$$

which can be solved by the modified Newtonian method as in this work. The interaction parameters of the applied model for the activity coefficient were in our work varied according to the Marquardt method [15] to minimize the particular objective function.

Experimental Procedures

Materials

Epoxidized soybean oil with an experimentally measured residual iodine number of 5.77, an epoxy oxygen content of 6.81%, an acid value of 0.26, a hydroxyl value of 8.68 and a density of 0.992 g/cm^3 at 20 °C was kindly provided by “Tarkett” Bačka Palanka, Republic of Serbia. The moisture content of ESO was measured as 0.2%. Glacial acetic acid (>99.5%) was purchased from J.T. Baker, USA and a 0.1 N NaOH solution from “Zorka Pharma” ad Šabac, Republic of Serbia.

Methods

The Hanus method for the iodine number [16], the standard HBr-acetic acid method [17] for the epoxy oxygen content, the AOCS Cd 3a-63 method for the acid value [18] and the ASTM D4274-05 procedure for the determination of the hydroxyl value [19] were used in this work. The moisture content of ESO was determined according to the gravimetric AOCS Ca 2c-25 method [20].

The liquid–liquid equilibrium constant for acetic acid in the system epoxidized soybean oil–acetic acid–water was determined for three mixtures at four temperatures (Table 1). The components of the mixture i.e. the weighed mass of epoxidized soybean oil, acetic acid and water were placed in a 3-neck 500-mL round-bottom flask equipped with a mechanical stirrer, thermometer and condenser. The mixture was equilibrated at the desired temperature in a thermostatized bath, under constant stirring (1,000 rpm), for 60 min. Then, the sample was taken and phases were separated by short centrifugation. The weighed samples of the oil and water phase were titrated by 0.1 N NaOH to determine the masses of acetic acid in particular phase. Titrations were done in triplicate.

The masses of acetic acid in the oil ($m_{\mathrm{A}}^{\mathrm{o}}$) and water ($m_{\mathrm{A}}^{\mathrm{w}}$) phase, in grams, were calculated as:

$$m_{\mathrm{A}}^{\mathrm{o}} = \frac{NdE_{\mathrm{A}}\left(V_{\mathrm{NaOH}}^{\mathrm{o}} - m^{\mathrm{o}} k_{\mathrm{ESO}}\right)}{1,000 - NdE_{\mathrm{A}} k_{\mathrm{ESO}}} \tag{15}$$

$$m_{\mathrm{A}}^{\mathrm{w}} = \frac{NV_{\mathrm{NaOH}}^{\mathrm{w}} dE_{\mathrm{A}}}{1,000} \tag{16}$$

where N (gE/L) is concentration of NaOH; $V_{\mathrm{NaOH}}^{\mathrm{w}}$ and $V_{\mathrm{NaOH}}^{\mathrm{o}}$ (mL) indicate the volumes of NaOH solution used for titration of the samples of the water and oil phase, respectively; d is the measure of deviation from the certified NaOH concentration; E_{A} is the gram equivalent of acetic acid; m^{o} (g) is the weighed mass of the oil phase sample; and k_{ESO} is the correction for the titration of ESO in the absence of acetic acid, determined as 0.047 mL NaOH/g ESO. The NaOH titration of ESO in the absence of acetic acid was performed in quadruplicate to verify if there were any minor components within the ESO that could skew the titration. To check the accuracy of the titration approach for the determination of the masses of acetic acid in the oil and water phase, the control experiments were done. Some ESO samples “spiked” with a known concentration of acetic acid, and some samples of known acetic acid–water composition, were titrated using NaOH. Karl-Fischer titration was used to determine the presence of water in the oil phase samples. Titration was performed with a coulometric Aquameter KFM 1000 S instrument (BAUR, Austria).

The mass measurement of ESO was done by APCI-FT-MS analysis. The APCI-MS spectra were obtained with an LTQ-Orbitrap Spectrometer (Thermo Scientific, USA). The spectrometer was operated in the positive mode

Table 1 Experimentally determined equilibrium molar fractions of acetic acid in the system epoxidized soybean oil–acetic acid–water

Temp (°C)	Mixture[a]	Mass fraction of water in oil phase sample[b]	Molar fraction of A in oil and water phase[c]		Standard deviation of molar fraction of A in phases[d]		Total mass of A (g)	
							Weighed	Determined
		$g^{o}_{H_2O}$	x^{o}_{A}	x^{w}_{A}	$s_{x^{o}_{A}}$	$s_{x^{w}_{A}}$	m_A	m^{exp}_{A}
35	M1	0.0358	0.1455	0.0623	0.0031	0.0006	21.97	21.42
	M2	0.0288	0.2146	0.0908	–	–	32.88	32.08
	M3	0.0218	0.3044	0.1199	0.0018	0.0008	44.03	44.47
50	M1	0.0304	0.1595	0.0629	0.0007	0.0002	21.97	21.79
	M2	0.0252	0.2348	0.0921	0.0030	0.0008	32.88	32.93
	M3	0.0199	0.3130	0.1189	0.0024	0.0013	44.03	44.20
65	M1	0.0252	0.1695	0.0614	–	–	21.97	21.32
	M2	0.0216	0.2350	0.0931	0.0035	0.0018	32.88	32.84
	M3	0.0181	0.3216	0.1173	0.0018	0.0003	44.03	43.69
80	M1	0.0197	0.2030	0.0579	0.0022	0.0008	21.97	20.91
	M2	0.0179	0.2537	0.0894	0.0044	0.0001	32.88	31.88
	M3	0.0162	0.3423	0.1101	0.0034	0.0008	44.03	41.81
RMSD[e]								0.856
AAD[f]								0.625
ARE[g] (%)								2.00

[a] M1, M2 and M3 mixtures of epoxidized soybean oil, acetic acid and water were of the following composition given in grams: 150.23, 21.97 and 80.02; 150.06, 32.88 and 80.10; and 150.52, 44.03 and 80.40, respectively

[b] Determined by Karl-Fischer titration

[c] Average value of three measurements, calculated as: $x^{o}_{A} = \frac{1}{NR}\sum_{j=1}^{NR} x^{o}_{A,j}$ and $x^{w}_{A} = \frac{1}{NR}\sum_{j=1}^{NR} x^{w}_{A,j}$ where is

$x^{o}_{A,j} = \frac{\frac{m^{o}_{A,j}}{M_A}}{\frac{m^{o}_{A,j}}{M_A} + \frac{m^{o}_{j}\left(1-g^{o}_{H_2O}\right)-m^{o}_{A,j}}{M_{ESO}} + \frac{m^{o}_{j}g^{o}_{H_2O}}{M_{H_2O}}}$ and $x^{w}_{A,j} = \frac{\frac{m^{w}_{A,j}}{M_A}}{\frac{m^{w}_{A,j}}{M_A} + \frac{m^{w}_{j}-m^{w}_{A,j}}{M_{H_2O}}}$ and where $m^{o}_{A,j}$ and $m^{w}_{A,j}$ were calculated by Eqs. 15 and 16. NR is number of experiment repetitions, which was three for all experimental points, except for points M2 at 35 °C and M1 at 65 °C when NR was one

[d] Sample standard deviation $s_{x^{i}_{A}} = \sqrt{\frac{1}{NR-1}\sum_{j=1}^{NR}\left(x^{i}_{A,j} - x^{i}_{A}\right)^2}$ where is $x^{i}_{A} = \frac{1}{NR}\sum_{j=1}^{NR} x^{i}_{A,j}$

[e] Root mean square deviation, RMSD $= \sqrt{\frac{1}{NE}\sum_{i=1}^{NE}\left(m_{A,i} - m^{exp}_{A,i}\right)^2}$

[f] Average absolute deviation, AAD $= \frac{1}{NE}\sum_{i=1}^{NE}\left|m_{A,i} - m^{exp}_{A,i}\right|$

[g] Average relative error (%), ARE $= \frac{100}{NE}\sum_{i=1}^{NE}\left|\frac{m_{A,i}-m^{exp}_{A,i}}{m_{A,i}}\right|$

(1 spectrum s^{-1}; mass range 200–2,000) with a nominal mass resolving power of 60,000 at *m*/*z* 400 (with a scan rate of 1 Hz) with automatic gain control to provide high-accuracy mass measurements within 2 ppm deviation using an internal standard Bis(2-ethylhexyl)phthalate of *m*/*z* = 391.284286. The spectrometer was equipped with a Surveyor HPLC system (Thermo Scientific, USA) consisting of LC-Pump, UV detector ($\lambda = 254$ nm) and autosampler (injection volume 10 µL). Nitrogen was employed as both the sheath (40 arbitrary units) and auxiliary (4 arbitrary units) gas. The compounds were detected after direct injections into a flow (500 µL min^{-1}) of methanol (+0.1% formic acid).

Results and Discussion

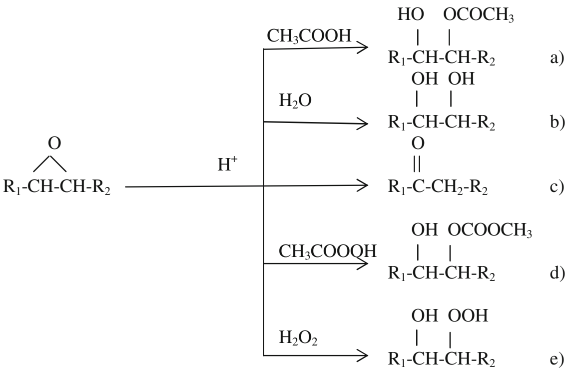
Experimentally Derived Values of Molar Fractions

The molar fractions of acetic acid in the oil (x^{o}_{A}) and water (x^{w}_{A}) phase determined by NaOH and Karl-Fischer titrations of phase samples and calculated by Eqs. 15, 16 and 4, as well as a comparison of the weighed total mass of acetic acid (m_A) and the total mass of acetic acid (m^{exp}_{A}) calculated on the basis of titrations, are given in Table 1. The molar fractions of acetic acid in the water phase (x^{w}_{A}) increased, with an increasing total acetic acid content in the system, but mainly decreased with raising of the temperature. In the oil phase the molar fractions of acetic acid (x_A^o) increased, while the mass fractions of water ($g_{H_2O}^o$) decreased, with an increase of total acetic acid concentration in the system and temperature too. It would be intuitive that the presence of more polar acetic acid in the oil-rich phase would increase partitioning of less polar water to this phase; however, under the conditions of this investigation, it displaces the water. The solubility of water in epoxidized soybean oil determined by Karl-Fischer titration was 5.75% mass, and in the presence of acetic acid the water content in the oil phase was in the range of 1.62–3.58% mass.

The determination of the total mass of acetic acid by titrations was performed with an average relative error (ARE) of 2%. This value is in the range of the ARE values of 2.17% and 0.89% achieved in quadruplicate control experiments for determination of the masses of acetic acid in the oil and water, respectively.

Estimation of Molecular Mass for Epoxidized Soybean Oil

In Eq. 4 the necessary but unknown molecular mass of ESO was estimated using the values of the epoxy oxygen content, the iodine number of ESO, and the hydroxyl value, all three experimentally measured, as well as the adjusted average fatty acid (FA) composition of SO. Since the ESO was purchased and SO was not available for experimental analysis, the average FA composition of SO taken from the literature [21] was adjusted so that the calculated values of iodine number, epoxy oxygen content and hydroxyl value of ESO corresponded to the measured values. The adjusted average FA composition of SO was accepted as follows: 12.34% palmitic, 5.0% stearic, 25.0% oleic, 51.66% linoleic, and 6.0% linolenic acids. As the experimentally measured hydroxyl value indicated the presence of hydroxyl groups in ESO, it was assumed that some side reactions such as epoxy ring cleavage occurred during the production of ESO. A range of possible side reactions during in-situ epoxidation is as follows [5, 8]:



(17)

where R_1 is alkyl chain fragment of fatty acid in TG after double bond converted to epoxy ring and R_2 is residue of TG without R_1 after double bond converted to epoxy ring.

According the reported data in the literature [6, 7, 22–24] the most likely side reaction that takes place during the epoxidation is the reaction of the epoxy ring with acetic acid (17a) that leads to the formation of some hydroxyl acetate as by-product. Consequently, if the epoxidation does not occur completely (when the residual iodine number of ESO is not zero) and only when this side reaction of epoxy ring cleavage with acetic acid proceeds, may the partially epoxidized soybean oil with some hydroxyl acetate by-products be presented as one pseudo-component of the following molecular structure:

$$[(CH_2COO)_2CHCOO](CH_2)_p(CH{=}CH)_l(CHOCH)_m$$
$$(CHOH{-}CHCOOCH_3)_n(CH_3)_3$$

The values of p, l, m and n that indicate the numbers of (CH_2), ($CH{=}CH$), ($CHOCH$) and ($CHOH{-}CHCOOCH_3$) groups in the ESO pseudo-component molecule, respectively, were calculated from the FA composition of soybean oil and the iodine number, the hydroxyl value, and the epoxy oxygen content of the epoxidized soybean oil, as follows: 38.5, 0.22, 4.03 and 0.14, respectively. The molecular mass of ESO was estimated as 947.6 g/mol. On the basis of the average mass of ions present in APCI-MS spectrum of ESO, the calculated average molecular mass of ESO was 958.2 g/mol. However, for the calculations, the value of 947.6 g/mol was accepted since the applied approach for its determination comprises data that are also used for calculation of the UNIQUAC volume (r_{ESO}) and area (q_{ESO}) parameters. Finally, according to Eq. 3 the liquid–liquid equilibrium constant for acetic acid was calculated and the values are given in Table 2 as experimental.

Thermodynamic Modeling of Activity Coefficients for Acetic Acid

To model the liquid–liquid phase equilibrium of the system epoxidized soybean oil–acetic acid–water by the UNIQUAC model for activity coefficient, the volume (r_{ESO}) and area (q_{ESO}) parameters of ESO, which are the van der Waals volume and area of the molecule relative to those of a standard segment, had to be determined [14]. These parameters were calculated by the UNIFAC method of group contributions as the function of volume (R_g) and area (Q_g) parameters of groups (g) present in the assumed ESO pseudo-component molecule:

Table 2 Comparison of experimentally determined values of the liquid–liquid equilibrium constant for acetic acid in the system epoxidized soybean oil–acetic acid–water and those calculated by the Wilson, NRTL and UNIQUAC Models

Temp. (°C)	Mixture[a]	Liquid–liquid equilibrium constant for acetic acid						
		Experimental		Calculated, $K_{\mathrm{A}}^{\mathrm{calc}}$				
		$K_{\mathrm{A}}^{\mathrm{exp}}$	$s_{K_{\mathrm{A}}}$[b]	Wilson	NRTL[c]		UNIQUAC[c]	
					4 par.	6 par.	4 par.	6 par.
35	M1	2.34	0.035	2.33	2.42	2.33	2.15	2.21
	M2	2.36	–	2.35	2.42	2.34	2.35	2.38
	M3	2.54	0.027	2.38	2.42	2.50	2.50	2.51
50	M1	2.53	0.017	2.59	2.62	2.61	2.54	2.52
	M2	2.55	0.053	2.58	2.61	2.61	2.57	2.58
	M3	2.63	0.048	2.58	2.61	2.61	2.62	2.61
65	M1	2.76	–	2.86	2.81	2.86	2.94	2.93
	M2	2.52	0.011	2.81	2.80	2.83	2.79	2.79
	M3	2.74	0.023	2.77	2.79	2.80	2.74	2.72
80	M1	3.50	0.012	3.13	3.00	3.08	3.34	3.38
	M2	2.84	0.046	3.04	2.98	3.02	3.00	3.00
	M3	3.11	0.050	2.96	2.97	2.97	2.85	2.82
Objective function (OF)[d]				0.328	0.411	0.347	0.261	0.241
RMSD[e]				0.216	0.242	0.263	0.193	0.220
R^2[f]				0.725	0.656	0.709	0.781	0.798
AAD[g]				0.122	0.132	0.119	0.109	0.106
ARE (%)[h]				4.26	4.64	4.11	3.95	3.81

[a] M1, M2 and M3 mixture compositions are defined in Table 1

[b] Sample standard deviation, $s_{K_{\mathrm{A},i}} = \sqrt{\frac{1}{\mathrm{NR}-1}\sum_{j=1}^{\mathrm{NR}}\left(K_{\mathrm{A},i,j}^{\mathrm{exp}} - K_{\mathrm{A},i}^{\mathrm{exp}}\right)^2}$, $K_{\mathrm{A},i}^{\mathrm{exp}} = \frac{1}{\mathrm{NR}}\sum_{j=1}^{\mathrm{NR}} K_{\mathrm{A},i,j}^{\mathrm{exp}}$

[c] Results are given for the case of immiscibility of the oil and water, when the number of binary adjustable model parameters is four (4 par.), and for the case of partial miscibility of oil and water, when that number is six (6 par.)

[d] Calculated using Eq. 20

[e] Root mean square deviation, $\mathrm{RMSD} = \sqrt{\frac{1}{\mathrm{NE}-\mathrm{NP}-1}\sum_{i=1}^{\mathrm{NE}}\left(K_{\mathrm{A},i}^{\mathrm{calc}} - K_{\mathrm{A},i}^{\mathrm{exp}}\right)^2}$

[f] Coefficient of determination, $R^2 = 1 - \frac{\sum_{i=1}^{\mathrm{NE}}\left(K_{\mathrm{A},i}^{\mathrm{calc}} - K_{\mathrm{A},i}^{\mathrm{exp}}\right)^2}{\sum_{i=1}^{\mathrm{NE}}\left(K_{\mathrm{A},i}^{\mathrm{exp}} - \overline{K_{\mathrm{A}}}\right)^2}$, $\overline{K_{\mathrm{A}}} = \frac{1}{\mathrm{NE}}\sum_{i=1}^{\mathrm{NE}} K_{\mathrm{A},i}^{\mathrm{exp}}$

[g] Average absolute deviation, $\mathrm{AAD} = \frac{1}{\mathrm{NE}}\sum_{i=1}^{\mathrm{NE}}\left|K_{\mathrm{A},i}^{\mathrm{exp}} - K_{\mathrm{A},i}^{\mathrm{calc}}\right|$

[h] Average relative error (%), $\mathrm{ARE} = \frac{100}{\mathrm{NE}}\sum_{i=1}^{\mathrm{NE}}\left|\frac{K_{\mathrm{A},i}^{\mathrm{exp}} - K_{\mathrm{A},i}^{\mathrm{calc}}}{K_{\mathrm{A},i}^{\mathrm{exp}}}\right|$

$$r_{\mathrm{ESO}} = \sum_{g=1}^{\mathrm{NG}} v_g R_g \qquad (18)$$

$$q_{\mathrm{ESO}} = \sum_{g=1}^{\mathrm{NG}} v_g Q_g \qquad (19)$$

where NG is the total number of group species in the ESO molecule; and v_g is the number of groups of type g in the ESO molecule. The values of R_g and Q_g parameters for all group species, except for the epoxy group, were taken from the literature [25]. The R and Q values for the epoxy group were accepted as 1.5 and 1.2, respectively, as their changing in the range of 1–2 insignificantly influenced the results of the fitting. The calculated values of r_{ESO} and q_{ESO} parameters were 40.28 and 32.78, respectively.

The interaction parameters of the Wilson, NRTL and UNIQUAC models were determined by fitting the experimental values of the liquid–liquid equilibrium constant for acetic acid given in Table 2. The Marquardt method was

Table 3 Interaction parameters $u_{j,k}$ of the Wilson, NTRL and UNIQUAC models for activity coefficient

Component	Interaction parameter $u_{j,k}$ (J/mol)		
	Water	Acetic acid	Epoxidized soybean oil
	Wilson model		
Water	0	38,090	–
Acetic acid	−577.5	0	8,160
Epoxidized soybean oil	–	−3,880	0
	NRTL model (4 parameters)[a]		
Water	0	−730.9	–
Acetic acid	30,410	0	−40.46
Epoxidized soybean oil	–	−120.8	0
	UNIQUAC model (4 parameters)[a]		
Water	0	10,370	–
Acetic acid	−4,121	0	23,650
Epoxidized soybean oil	–	−2,933	0
	NRTL model (6 parameters)[b]		
Water	0	−1,489	45,290
Acetic acid	29,030	0	3,491
Epoxidized soybean oil	3,270	−5,325	0
	UNIQUAC model (6 parameters)[b]		
Water	0	16,280	9,146
Acetic acid	−4,307	0	7,113
Epoxidized soybean oil	2,430	−3,028	0

[a] Values calculated when the immiscibility of oil and water is assumed

[b] Values calculated when the partial miscibility of oil and water is assumed

applied to fit the data. The following objective function (OF) was minimized:

$$\mathrm{OF} = \sum_{i=1}^{\mathrm{NE}} \left(K_{\mathrm{A},i}^{\mathrm{calc}} - K_{\mathrm{A},i}^{\mathrm{exp}} \right)^2 \tag{20}$$

where NE is total number of experimental points. The values of the liquid–liquid equilibrium constant for acetic acid calculated by applied models for activity coefficient are shown in Table 2, while the interaction parameter values are given in Table 3. For the NRTL model, only results for the value of 0.2 for non-randomness parameter α in Eq. 8 are presented since of all for fitting used parameter values, namely 0.2, 0.3, 0.4 and 0.47, 0.2 gave the best agreement of the calculated and experimentally determined equilibrium constants. In Table 2 are presented results of $K_{\mathrm{A}}^{\mathrm{calc}}$ for the Wilson, NRTL (4 parameter) and UNIQUAC (4 parameter) models when the solubility of water in epoxidized soybean oil is neglected i.e. the immiscibility of oil and water is assumed, together with the results for the NRTL (6 parameters) and UNIQUAC (6 parameters) models when the partial miscibility of ESO and water is accepted. The Wilson model cannot be applied in the case of partially miscible liquids as it does not predict the separation of phases. The number of binary adjustable model parameters is 6 in the case of partial miscibility because of the presence of binary epoxidized soybean oil – water.

Despite all assumptions and simplifications, the data presented in Table 2, with an average relative error (ARE) of 3.8–4.6%, indicate the adequateness of all three models used in this work for prediction of the liquid–liquid equilibrium constant for acetic acid in the system epoxidized soybean oil–acetic acid–water under the investigated temperatures and compositions.

Comparison of the Partitioning of Acetic Acid between Water and Soybean Oil versus Epoxidized Soybean Oil

To determine the influence of changing of the oil phase composition during the epoxidation on the equilibrium constant for acetic acid, the comparison of the results presented in this work with those reported in the literature for the system soybean oil–acetic acid–water should be done. Comparison was possible since the experimental conditions used for the system with epoxidized soybean oil are analogous to those used for the system with soybean oil, namely temperatures are the same and mass compositions of the mixtures M1, M2 and M3 are similar to E1, E2 and E3, respectively. The values of the liquid–liquid equilibrium constant for acetic acid in the system with soybean oil, calculated on the basis of experimentally determined partition coefficient data given in Table 1 in the reference [9], are shown in Table 4. Comparison of these values with

Table 4 Experimentally determined values of the liquid–liquid equilibrium constant for acetic acid in the system soybean oil–acetic acid–water

Temp. (°C)	Mixture[a]	Liquid–liquid equilibrium constant for acetic acid K_A^b
35	E1	1.76
	E2	1.81
	E3	1.49
50	E1	1.73
	E2	1.71
	E3	1.51
65	E1	1.87
	E2	1.76
	E3	1.42
80	E1	1.93
	E2	1.64
	E3	1.66

[a] E1, E2 and E3 mixtures of soybean oil, acetic acid and water were of the following composition given in grams: 150.00, 22.04 and 80.94; 150.39, 33.33 and 80.25; and 150.00, 44.00 and 80.00, respectively

[b] Calculated on the basis of experimental data used in the reference [9] for determination of the acetic acid partition coefficient

those given in Table 2 shows that the value of the liquid–liquid equilibrium constant for acetic aid in the system epoxidized soybean oil–acetic acid–water is about 1.5 times higher than in the system with soybean oil, what would be expected since the presence of epoxy and hydroxyl groups within the epoxidized soybean oil would increase its polarity relative to soybean oil, which should increase the partitioning of a polar solute such as acetic acid to the oil-rich phase. For the investigation conditions, it can also be concluded for both systems, that the influence of changing of oil phase composition on the equilibrium constant for acetic acid is more prominent than the influence of acetic acid total content in the system or temperature. However, the trends for the equilibrium constant for acetic acid vs total acetic acid mass fraction in the system and vs temperature are not consistent between the systems with soybean oil or with epoxidized soybean oil. With an increase in the total acetic acid content in the system with soybean oil, the equilibrium constant for acetic acid decreased, while the influence of temperature cannot be generally defined. On the other hand, with an increasing of total acetic acid content in the system with epoxidized soybean oil, the equilibrium constant for acetic acid increased for temperatures of 35 and 50 °C, while a minimum was observed at 65 and 80 °C. With an increase in temperature, the equilibrium constant for acetic acid increased for all mixtures M1, M2 and M3. These changes of trends are a consequence of the decreasing quantity of water dissolved in epoxidized soybean oil with an increase of both total content of acetic acid in the system and temperature.

As the epoxidation is usually carried out at a constant temperature and with an approximately constant content of acetic acid in the system, the change of the equilibrium constant for acetic acid can only be the consequence of the changing of the oil phase composition during the reaction. Investigation of the variation of the equilibrium constant i.e. the partition coefficient for acetic acid between the oil and water phase during in-situ epoxidation is important for the correct determination of the kinetic parameter values in modeling the reaction system. Any further development of the mathematical model of the reaction system for epoxidation of vegetable oils must take these facts into consideration.

Conclusion

Under conditions of temperature and component ratios relevant for in-situ epoxidation of soybean oil, the liquid–liquid equilibrium constant for acetic acid in the system epoxidized soybean oil–acetic acid–water can be successfully predicted by applying the Wilson, NRTL and UNIQUAC models used most frequently for modeling the activity coefficients for acetic acid, despite of all the necessary simplifications.

Due to the presence of epoxy and hydroxyl groups within epoxidized soybean oil, the water is soluble to a significant extent in this oil, unlike in soybean oil. Under the conditions in this investigation, the more polar acetic acid displaces the less polar water from the oil phase. As a consequence, the equilibrium constant for acetic acid in the system epoxidized soybean oil–acetic acid–water is only about 1.5 times higher that in the system with soybean oil.

Modeling of the variation of the equilibrium constant for acetic acid with changing of the oil phase composition during epoxidation would make it possible to determine the intrinsic kinetic parameters of the reaction system for in-situ epoxidation of soybean oil.

Acknowledgments This work is part of Project No. 142045 supported by the Ministry of Science and Technology Development of the Republic of Serbia.

References

1. Meier MAR, Metzger JO, Schubert US (2007) Plant oil renewable resources as green alternatives in polymer science. Chem Soc Rev 36:1788–1802
2. Biswas A, Sharma BK, Willett JL, Erhan SZ, Cheng HN (2008) Soybean oil as a renewable feedstock for nitrogen-containing derivatives. Energy Environ Sci 1:639–644
3. Güner FS, Yagci Y, Erciyes AT (2006) Polymers from triglyceride oils. Prog Polym Sci 31:633–670

4. Rangarajan B, Havey A, Grulke EA, Culnan PD (1995) Kinetic parameters of a two-phase model for in situ epoxidation of soybean oil. J Am Oil Chem Soc 72:1161–1169
5. Sinadinović-Fišer S, Janković M, Petrović ZS (2001) Kinetics of in situ epoxidation of soybean oil in bulk catalyzed by ion exchange resin. J Am Oil Chem Soc 78:725–731
6. Zaher FA, El-Malah MH, El-Hefnawy MM (1989) Kinetics of oxirane cleavage in epoxidized soybean oil. J Am Oil Chem Soc 66:698–700
7. Gan LH, Goh SH, Ooi KS (1992) Kinetic studies of epoxidation and oxirane cleavage of palm olein methyl esters. J Am Oil Chem Soc 69:347–351
8. Petrović ZS, Zlatanić A, Lava CC, Sinadinović-Fišer S (2002) Epoxidation of soybean oil in toluene with peroxoacetic and peroxoformic acids. Kinetics and side reactions. Eur J Lipid Sci Technol 104:293–299
9. Sinadinović-Fišer S, Janković M (2007) Prediction of the partition coefficient for acetic acid in a two-phase system soybean oil–water. J Am Oil Chem Soc 84:669–674
10. Fredenslund A, Jones RL, Prausnitz JM (1975) Group-contribution estimation of activity coefficients in nonideal liquid mixtures. AIChE J 21:1086–1099
11. Kojima K, Tochigi K (1979) Prediction of vapor–liquid equilibria by the ASOG method. Elsevier, Englewood Cliffs
12. Wilson GM (1964) Vapor–liquid equilibrium XI: a new expression for the free energy of mixing. J Am Oil Chem Soc 86:127–130
13. Renon H, Prausnitz JM (1968) Local compositions in the thermodynamic excess functions for liquid mixtures. AIChE J 14:135–144
14. Abrams DS, Prausnitz JM (1975) Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems. AIChE J 21:116–127
15. Marquardt DW (1963) An algorithm for least-squares estimation of nonlinear parameters. J Soc Ind Appl Math 11:431–441
16. Determination of Iodine Value (1987) The Hanus method. In: Standard methods for the analysis of oils, fats and derivatives, 7th edn. Blackwell Scientific Publications, London
17. Determination of epoxy-group oxygen (1987) In: Standard methods for the analysis of oils, fats and derivatives, 7th edn. Blackwell Scientific Publications, London
18. American Oil Chemists' Society Official Methods (1987) Acid value. AOCS Cd 3a-63, Champaign, pp 1–3
19. American Society for Testing Materials (2005) Polyurethane raw materials: determination of hydroxyl numbers for polyols, ASTM (D4274-05), ASTM, West Coushohocken, pp 1–9
20. American Oil Chemists' Society Official Methods (1987) Moisture and volatile matter, AOCS Ca 2c-25, Champaign, p 1
21. Swern D (1979) Bailey's industrial oils and fats products, 4th edn. Wiley, New York
22. Campanella A, Baltanás MA (2005) Degradation of the oxirane ring of epoxidized vegetable oil in liquid–liquid systems: I. Hydrolysis and attack by H_2O_2. Lat Am Appl Res 35:205–210
23. Campanella A, Baltanás MA (2005) Degradation of the oxirane ring of epoxidized vegetable oil in liquid–liquid systems: II. Reactivity with solvated acetic acid and peracetic acids. Lat Am Appl Res 35:211–216
24. Campanella A, Baltanás MA (2006) Degradation of the oxirane ring of epoxidized vegetable oils in liquid–liquid heterogeneous reaction systems. Chem Eng J 118:141–152
25. Magnussen T, Rasmussen P, Fredenslund A (1981) UNIFAC parameter table for prediction of liquid–liquid equilibria. Ind Eng Chem Process Des Dev 20:331–339