

Prediction of the Partition Coefficient for Acetic Acid in a Two-Phase System Soybean Oil-Water

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Abstract An analytical approach for the prediction of the partition coefficient for acetic acid between soybean oil and water, dependent on temperature and composition, has been proposed. The original and three modified UNIFAC models as well as the UNIQUAC model were used to represent the liquid–liquid equilibrium data in the ternary system. To calculate the density of the water and oil phase the COSTALD method was applied. The proposed approach for the prediction of the partition coefficient for acetic acid fit the experimental data well when the UNIQUAC model was used. The results of the application of the proposed approach to the experimental data for acetic acid partition coefficient taken from the literature were also presented and discussed.

Keywords In situ epoxidation · Mathematical model · Partition coefficient for acetic acid · Two-phase system soybean oil-water

List of symbols

A	atomic mass
a	activity
C	concentration (mol/L)
JB	iodine number
K	partition coefficient
m	mass (g)
M	molecular mass
NFA	total number of FA in the oil
R	universal gas constant
T	temperature (K)

u	adjustable binary parameter
x	molar fraction
y	number of (CH ₂) groups
z	number of (CH=CH) groups

Greek letters

γ	activity coefficient
ρ	density (g/L)
τ	interaction parameter

Superscripts

i	phase
o	oil phase
w	water phase

Subscripts

A	acetic acid
J	iodine
j, k	component of the mixture
D	double bonds in oil

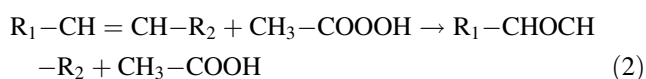
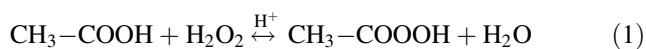
Introduction

Vegetable oils can be epoxidized, as they mainly consist of unsaturated TG. Produced epoxides are valuable as intermediates for resins, as paint and coating components, as well as the plasticizers and stabilizers for poly(vinyl chloride). Epoxidation is usually performed with organic peracid or peroxide because hydrogen peroxide is not

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soluble in oil. Peracid is prepared mostly by the in situ method, as the safest one, from an acid and hydrogen peroxide. Because it is inexpensive, peracetic acid is widely used in industry for epoxidation of, mostly, soybean oil.

The in situ process involves a heterogeneous system: in the water phase (diluted hydrogen peroxide is used) the acid-catalyzed formation of peracetic acid takes place, whereas in the oil phase the epoxidation reaction occurs, as follows:



Depending on the catalyst applied for peracid formation, the system is either two-phase (oil–water) or three-phase (oil–water–ion exchange resin). Additionally, the acid-catalyzed cleavage of oxirane groups occurs as a side reaction.

Until now published kinetic models of the reaction system for epoxidation of oils, fatty acids and their esters can be classified into two groups: approximate [1–3] and rigorous [4, 5]. In the first group of the models, in which the mixture of oil and water was considered as a single phase (pseudo-homogeneous models), the overall concentrations of components were used. In the second group the local concentrations of components in the oil and water phase were introduced into the modeling. The rigorous models contain more parameters, such as rate constants, chemical equilibrium constants, partition coefficients between phases, mass-transfer coefficients and interfacial areas. The simultaneous determination of the kinetic parameters (by fitting the experimental data) led to a very large value for the chemical equilibrium constant for peracetic acid formation [2]. Their successive determination using data of separate experiments is, on the other hand, time consuming. It would be more convenient to apply some equation for the prediction of the parameters. For this reason, in the previous paper [6], we derived an expression for temperature dependence of the chemical equilibrium constant for peracetic acid synthesis from acetic acid and hydrogen peroxide (Eq. 1) in an aqueous solution, while in the present work we proposed an analytical approach for the determination of the partition coefficient for acetic acid between the soybean oil and water dependent on temperature and composition.

Theory

The partition coefficient for acetic acid (K_A) between the oil (o) and water (w) phase is defined as follows:

$$K_A = \frac{C_A^o}{C_A^w} \quad (3)$$

where C_A^i (mol/L) is the concentration of acetic acid (A) in phase i .

The particular concentration of acetic acid in phase i can be determined using the following equation:

$$C_A^i = \frac{m_A^i \rho^i}{M_A m^i} \quad (4)$$

where m_A^i (g) indicates the mass of acetic acid in the sample of phase i , determined experimentally by NaOH titration; m^i (g) represents the mass of the sample of phase i ; ρ^i (g/L) is the density of phase i ; and M_A is the molecular mass of acetic acid.

The mass of acetic acid in each phase can also be calculated, as was done in this work, by using the liquid–liquid phase equilibrium condition:

$$a_A^o = a_A^w \quad (5)$$

i.e.,

$$\gamma_A^o x_A^o = \gamma_A^w x_A^w \quad (6)$$

where a_A is the activity of acetic acid; γ_A indicates the activity coefficient of acetic acid; and x_A is the molar fraction of acetic acid. Immiscibility of the soybean oil and water is assumed.

The molar fraction of component j in the phase i (x_j^i) is defined by the following expression:

$$x_j^i = \frac{m_j^i M_j^{-1}}{\sum_{k=1}^3 m_k^i M_k^{-1}} \quad (7)$$

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

The experimental value of the acetic acid partition coefficient can be calculated via Eqs. 3, 4 and 7, and using the masses of the acetic acid in the water (m_A^w) and oil (m_A^o) phase, determined by titration.

To predict the partition coefficient for acetic acid, the models for the activity coefficient and for the density are necessary.

The activity coefficient for particular phase is the function of composition and temperature, as follows:

$$\gamma_A^o = f(x_A^o, x_{\text{oil}}^o, T) \quad (8)$$

$$\gamma_A^w = f(x_A^w, x_{\text{H}_2\text{O}}^w, T) \quad (9)$$

In this work, the UNIFAC (UNIQuac Functional-group Activity Coefficients) and the UNIQUAC (UNIversal QUAsi Chemical) models for calculation of the activity coefficients were used. Four versions of the UNIFAC model were applied in this work: original UNIFAC [7, 8], UNIFAC LLE (Liquid–Liquid Equilibrium) [9], and Dortmund [10–12] and Lyngby [13] modifications of the UNIFAC model. All UNIFAC models are based on the group contribution method and can be applied directly for the activity coefficient prediction, while the UNIQUAC model [14] demands previous determination of the interaction parameters for components of the system, by processing the experimental data for liquid–liquid equilibrium. The UNIQUAC binary interaction parameter ($\tau_{j,k}$) is given by the following expression [14]:

$$\tau_{j,k} = \exp\left(-\frac{\Delta u_{j,k}}{RT}\right) \quad (10)$$

where $\Delta u_{j,k}$ is adjustable binary parameter (characteristic energy) for components j and k in the mixture; and R is the universal gas constant.

The total mass of the acetic acid in the system (m_A) is the sum of the acetic acid masses in the oil and water phase:

$$m_A = m_A^o + m_A^w \quad (11)$$

Substituting the Eqs. 7–9 and 11 in 6, a nonlinear equation with one variable follows:

$$F(m_A^w) = 0 \quad (12)$$

which can be solved by the modified Newtonian method as in this work.

The COSTALD (COresponding STates Liquid Density) method [15] was used to calculate the density of the water and oil phase. To apply the method the critical temperature, critical pressure, acentric factor and characteristic volume of mixture components are necessary. For water and acetic acid the properties were taken from the literature [15, 16]. The critical temperature, acentric factor and characteristic volume of oil were determined by fitting the literature data for the oil density and density of the binary oil-alcohol mixtures [17]. The Marquardt method of the least squares sum worked well for this processing [18]. The critical pressure of oil was calculated using the Ambrose method of group contributions [16], as it could not be determined by fitting the literature data because the density of mixtures is not influenced by critical pressure of oil at temperatures and pressure quoted in the literature [17]. The critical temperatures, critical pressures and acentric factors of alcohols (methanol,

ethanol, 1-propanol, 2-propanol and 1-butanol) were taken from the literature [16], while their characteristic volumes were determined from the densities at 25 °C given in the literature [17].

Experimental Procedures

Materials

Soybean oil with an iodine value of 126.0 (Hanus) was kindly supplied by ‘‘Dijamant’’ Zrenjanin, Serbia. Its fatty acid (FA) composition was determined by GC–MS. Glacial acetic acid (>99.5%) was purchased from J.T. Baker, USA, as well as sodium metal, methanol, diethyl ether, cyclohexane and toluene (the last three chemicals were of HPLC grade), while ethyl acetate, also of HPLC grade, was purchased from Carlo Erba, Italy. Anhydrous sodium sulphate (Fluka, Chemie GmbH), heated at 460 °C for 7 h, and activated silica (Merck, Germany) were used. FAME MIX GLC-10 (Supelco, Bellefonte) was used to prepare the FAME standard solution.

Methods

FA composition of soybean oil was determined by GC–MS, using a ThermoFinnigan Trace GC unit, furnished with a PS 255 capillary column: 30 m × 0.25 mm ID × 0.25 μm film that worked temperature programmable as follows: 80 °C for 1 min, 10 °C/min to 140 °C, 4 °C/min to 184 °C, 2 °C/min to 200 °C, 10 °C/min to 250 °C that held for 5 min, with 1.5 ml/min He constant flow. L μl of the sample dissolved in toluene was injected by ThermoFinnigan AS 2000 autosampler. A PTV injector was used with splitless time lasted for 1.7 s at an initial temperature of 90 °C and heated to 280 °C. Prior to injection, the sample was transesterified to FAME with sodium methoxide [19]. The FinniganTrace mass selective (MS) detector, coupled to GC via transfer line set on 250 °C, worked with ion source temperature at 200 °C and electron impact mode of 70 eV during the full scan mode run. The response factors were obtained using standard FAME mixture solution as external standard.

The partition coefficient for acetic acid was determined for three mixtures at five temperatures. The molar ratio of the components in the investigated mixtures i.e. molar ratio of double bonds in oil:acetic acid:water was as follows: 1:0.5:5.95 for the mixture E1 (accepted from the literature [2] as the optimal one for epoxidation), 1:0.75:5.95 for the mixture E2, and 1:1:5.95 for the mixture E3. To calculate the concentration of double bonds in oil (C_D) (mol/100 g oil) the following correlation was used:

$$C_D = \frac{JB}{2A_I} \quad (13)$$

where JB represents iodine number determined according the Hanus method [20]; and A_I is the atomic mass of iodine. The mixtures were equilibrated at the temperatures of 20, 35, 50, 65 and 80 °C, under constant stirring, for 60 min. After standing at the defined temperature at least 1 h, to allow for complete separation of the phases, the weighted samples of oil and water phase were titrated by 0.1 N NaOH.

Results and Discussion

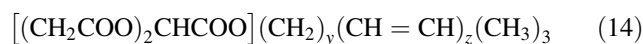
Density

Critical temperature, acentric factor and characteristic volume of soybean oil, necessary for COSTALD method application, were determined by fitting densities of soybean oil at 25 °C and its binary mixtures with methanol, ethanol, 1-propanol, 2-propanol and 1-butanol at 10, 15, 20 and

25 °C. The calculated values were: 635.0 K, 1.652 and 4.475 m³/kmol, respectively. For fitting, 317 points were taken from the literature [17]. The COSTALD model predicted the values of densities well, with average relative error (ARE) of 0.66%. The critical pressure of soybean oil, calculated by the Ambrose method of group contributions, was 499.8 kPa.

Comparison of Predicted Values of the Partition Coefficient for Acetic Acid with Experimental Data

To model the liquid–liquid phase equilibrium of the system soybean oil:acetic acid:water by UNIFAC and UNIQUAC models, the soybean oil has to be defined as a pseudo-component. In this work it was represented as pseudo-triglyceride with the following molecular structure [21]:



The values of y and z that indicates the numbers of (CH₂) and (CH=CH) groups in oil, respectively, were calculated from FA composition of soybean oil as follows:

Table 1 Comparison of the acetic acid partition coefficient values determined experimentally and calculated by UNIFAC/UNIQUAC model

Temp. (°C)	Mixture ^a	Partition coefficient for acetic acid					
		Exp.	Calculated				
			UNIFAC	UNIFAC LLE	UNIFAC Dortmund	UNIFAC Lyngby	UNIQUAC
20	E1	0.0389	0.0315	0.121	0.0440	0.0471	0.0402
	E2	0.0424	0.0301	0.117	0.0374	0.0456	0.0414
	E3	0.0408	0.0292	0.115	0.0336	0.0448	0.0426
35	E1	0.0409	0.0362	0.129	0.0377	0.0483	0.0414
	E2	0.0482	0.0346	0.126	0.0319	0.0464	0.0423
	E3	0.0424	0.0337	0.124	0.0286	0.0453	0.0433
50	E1	0.0400	0.0409	0.137	0.0336	0.0489	0.0424
	E2	0.0451	0.0393	0.134	0.0284	0.0468	0.0432
	E3	0.0433	0.0382	0.133	0.0254	0.0455	0.0440
65	E1	0.0427	0.0457	0.144	0.0307	0.0489	0.0434
	E2	0.0466	0.0440	0.141	0.0259	0.0466	0.0439
	E3	0.0403	0.0429	0.140	0.0233	0.0453	0.0446
80	E1	0.0452	0.0505	0.150	0.0286	0.0483	0.0442
	E2	0.0423	0.0488	0.148	0.0241	0.0459	0.0446
	E3	0.0477	0.0476	0.147	0.0217	0.0445	0.0451
RMSD ^b			0.00719	0.0910	0.0149	0.00479	0.00246
AAD ^c			0.00601	0.0904	0.0135	0.00409	0.00199
ARE (%) ^d			14.01	210.4	30.64	9.82	4.56

^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

^bRoot mean square deviation, $\text{RMSD} = \sqrt{\sum_{i=1}^N (y_i^{\text{exp}} - y_i^{\text{calc}})^2 / N}$

^cAverage absolute deviation, $\text{AAD} = \frac{1}{N} \sum_{i=1}^N |y_i^{\text{exp}} - y_i^{\text{calc}}|$

^d Average relative error (%), $\text{ARE} = \frac{100}{N} \sum_{i=1}^N \left| \frac{y_i^{\text{exp}} - y_i^{\text{calc}}}{y_i^{\text{exp}}} \right|$

$$y = \sum_{j=1}^{NFA} x_j y_j = 37.80 \quad (15)$$

$$z = \sum_{j=1}^{NFA} x_j z_j = 4.35 \quad (16)$$

where x_j is the molar fraction of the FA j ; y_j is the number of (CH₂) groups in the FA j ; z_j is the number of (CH=CH) groups in the FA j ; and NFA is the total number of FA in soybean oil determined by GC-MS. The FA composition of soybean oil is as follows (mole fraction): palmitic 0.0848, stearic 0.0868, oleic 0.2557, linoleic 0.5248, and linolenic acid 0.0479.

For the UNIFAC method application the following groups of the system components had been taken into consideration: CH₃, CH₂, CH, CH=CH, CH₂COO, COOH and H₂O. The interaction parameters of the components in the UNIQUAC model were determined by fitting the experimental values of the partition coefficient for acetic acid given in Table 1. The Marquardt method was used to fit the data. The interaction parameters for soybean oil–water and vice versa were not determined, as their immiscibility was assumed, whereas the other values were as follows (kJ/kmol): –647.0 for soybean oil–acetic acid; 7,550 for acetic acid–soybean oil; –1,769 for acetic acid–water; and 1,909 for water–acetic acid. A comparison of the values of the acetic acid partition coefficient, experimentally determined and calculated by UNIFAC versions as well as the UNIQUAC model, is shown in Table 1. Of

all the UNIFAC models applied, the Lyngby modification predicted the partition coefficient the best. The UNIFAC LLE modification was non-applicable for the prediction of the partition coefficient, even though it is recommended for modeling the liquid–liquid equilibrium. The lowest ARE of 4.56% was achieved when the UNIQUAC model was used to predict the acetic acid partition coefficient.

Comparison of Predicted Values of the Partition Coefficient for Acetic Acid with Literature Data

The approach proposed in this work for the prediction of the partition coefficient values for acetic acid using the UNIFAC/UNIQUAC model to determine the activity coefficient and the COSTALD method to calculate the density was applied to the literature data [5]. Comparison of the experimentally determined (in the literature [5]) and the predicted values of the partition coefficient for acetic acid by this approach is presented in Table 2. Calculated values deviate from the experimental ones. All of the model applied, except the Dortmund modification of the UNIFAC model, predicted a slight increase in the partition coefficient for acetic acid with temperature, while a considerable decrease in the coefficient with temperature is apparent from the literature data. For example, for the mixtures of very similar compositions, L1 and L2, the experimental value of partition coefficient decreased 3.5 times with a temperature increase of 20 °C. To explain the disagreement between the literature and the predicted values of partition coefficients for acetic acid, additional

Table 2 Comparison of experimentally determined values of the acetic acid partition coefficient [5] and those calculated by the UNIFAC, UNIQUAC and RECALCULATED UNIQUAC models

Temp. (°C)	Mixture ^a	Partition coefficient for acetic acid						
		Exp. [5]	Calculated					
			UNIFAC	UNIFAC LLE	UNIFAC Dortmund	UNIFAC Lyngby	UNIQUAC	RECALCULATED UNIQUAC ^b
40	L1	0.0980	0.0334	0.126	0.0232	0.0444	0.0467	0.0696
60	L2	0.0280	0.0395	0.137	0.0205	0.0444	0.0467	0.0448
40	L3	0.0671	0.0367	0.130	0.0338	0.0482	0.0420	0.0677
60	L4	0.0360	0.0430	1.140	0.0292	0.0484	0.0432	0.0245
40	L5	0.0750	0.0334	0.126	0.0230	0.0444	0.0471	0.0698
60	L6	0.0230	0.0394	0.138	0.0201	0.0445	0.0474	0.0470
RMSD ^c			0.0348	0.0846	0.0398	0.0290	0.0290	0.0174
AAD ^c			0.0286	0.0780	0.0296	0.0255	0.0258	0.0144
ARE (%) ^c			49.7	227.2	42.3	51.5	53.3	38.8

^a Composition of the mixtures of soybean oil, acetic acid and water, reported in the literature [5], given in grams are as follows: 100.0, 47.7439 and 50.1 for L1; 50.0, 24.7 and 26.5 for L2; 100.1, 9.8755 and 28.5 for L3; 101.4, 9.9067 and 28.2 for L4; 24.0, 40.0969 and 40.0 for L5; and 24.0, 40.0553 and 40.3 for L6

^b Interaction parameters of the UNIQUAC model were determined by fitting the literature data [5]

^c RMSD, AAD and ARE are defined in Table 1

testing was done. The interaction parameters for a RECALCULATED UNIQUAC model were determined by fitting the literature data [5]. The Marquardt method was applied and the values obtained were as follows (kJ/kmol): 10,669 for soybean oil-acetic acid; -5,278 for acetic acid-soybean oil; 2,975 for acetic acid-water; and -11,086 for water-acetic acid. These parameters were used to recalculate the partition coefficient which was again compared with the experimental one [5], what is shown in Table 2. In this case, the same trend of decreasing the partition coefficient for acetic acid with increasing the temperature is achieved. High deviation of the RECALCULATED UNIQUAC-calculated values of partition coefficient for acetic acid from those experimentally determined, however, indicates that data from the literature cannot be reasonably well predicted, even by the model with adjustable parameters, which worked well in our case.

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