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ORIGINAL PAPER

Partitioning of Carboxylic Acid between Oil and Water Phases. Experimental, Correlation, and Prediction

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Abstract Partition coefficients for the carboxylic acids (A) acetic and formic acids between oil and water were measured, correlated, and predicted. The experiments were conducted by equilibrating the systems, soybean oil (SO)–H_2O–A and fatty acid methyl ester (FAME)–H_2O–A, at 40 °C employing different compositions. The partition coefficients were correlated using the UNIQUAC model and, also, predicted by calculating the activity coefficients of the carboxylic acid in the two phases using a group contribution method, the UNIFAC equation. Agreement of experimental partition coefficients values with those estimated by UNIFAC are fair. Other experimental data from literature were also correlated and are discussed.

Keywords Partition coefficient for carboxylic acids · Soybean oil/FAME–water · Epoxidation systems

List of symbols

a	Activity
C	Concentration (mol/L)
K_c	Partition coefficient using molar concentration
K_w	Partition coefficient using mass fraction
K_x	Partition coefficient using molar fraction
m	Mass (g)
M	Molecular mass
N	Number of data points
NFA	Total number of FA in the oil
OF	Objective function
R	Universal gas constant
SO	Soybean oil
T	Temperature (°C or Kelvin)
u	Adjustable binary parameter (cal/mol)
w	Mass fraction
x	Molar fraction
y	Number of (CH_2) groups
z	Number of (CH=CH) groups

Greek letters

γ	Activity coefficient
ρ	Density (g/L)
ρ_m	Molar density (mol/L)
τ	Interaction parameter

Superscripts

cal	Calculated value
exp	Experimental value
i	Phase
o	Oil phase
w	Water phase

Subscripts

A	Acid
i, j, k	Component of the mixture

Introduction

Many industrial reactions are carried out in immiscible liquid–liquid reacting systems. Careful analysis of the regime(s) under which these reactions are conducted (i.e.,

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kinetic vs. diffusive control) establishes well-founded criteria for reactor design and determines whether obtaining intrinsic kinetic data under process conditions is feasible. An example of this class of reacting systems appears in vegetable oil (VO) epoxidation reactions, which are generally performed using organic peracids generated in situ [1–5]. In these in-situ processes, two liquid phases are simultaneously present in the reacting system: an aqueous phase and an oil phase. Epoxidized VOs and epoxidized fatty acid methyl esters (FAME) are extremely valuable because of the many reactions they undergo. They have been used for numerous commercial applications, e.g., as plasticizers and stabilizers in chlorine-containing resins, as additives in lubricants, as components in thermosetting plastics, in cosmetics and pharmaceutical formulations, in urethane foams, and as wood impregnates [6–13].

This work forms part of a comprehensive research program that analyzes the liquid–liquid reacting epoxidation process of VO (i.e., soybean oil, SO) and FAME, taking into account each of the transport and intrinsic kinetic steps in both phases. In particular, in this paper we determined and correlated the partition coefficient of formic and acetic acids between aqueous and oil phases. This coefficient is needed to be able to model the aforementioned two-phase system. The model used to correlate partition coefficients was UNIQUAC. The partition coefficients were also estimated by applying the activity coefficients of the carboxylic acid in the two phases using a predictive group contribution method, the UNIFAC equation.

Experimental Procedures

Materials

Edible, refined SO (Sojola brand, Aceitera General Deheza, Argentine) was used as a model VO feedstock. Its fatty acid (FA) composition was determined by gas chromatography (GLC) after derivatizing the triglycerides into fatty acid methyl esters, following the AOCS's recommended practice [14]. SO had the following composition: palmitic 9.86%, stearic 3.93%, oleic 21.10%, linoleic 57.74%, linolenic 7.05%, and arachidic 0.32% [14]. Formic acid (acs, 99.8%), glacial acetic acid (acs, 99.8%), sodium hydroxide (acs), and methanol (acs) were purchased from Fisher Scientific (Pittsburgh, PA, USA). Distilled water was used in all the experiments.

Preparation of FAME

Batches of the refined soybean oil were interesterified with methanol in a 1,000 mL glass reactor furnished with a reflux condenser, at 70 °C. The oil (700 mL) was first heated to the reaction temperature, then 270 mL methanol and 8.28 g NaOH were added, under moderate mixing. The mixture was kept for 1 h, after which the agitation was stopped to allow phase separation (30 min). The heavier, glycerol rich fraction was discarded and the soybean FAME was washed with 100 mL H_3PO_4 (0.015 N) at 60 °C. After another three washes with distilled water (100 mL each) at the same temperature, the soybean FAME was dried by rotary evaporation at 10 mmHg and 60 °C for 3 h.

Determination of Partition Coefficients

For this purpose, SO or FAME were placed together with the water and the carboxylic acid (acetic or formic acid) in a three-necked 100-mL round-bottomed flask equipped with a mechanical stirrer, thermometer, and condenser. The mixtures were equilibrated to the desired temperature (40 °C) in a thermostatted bath, under constant stirring (1,000 rpm), for 4 h. The mixtures were then left to stand for 3 h until complete separation of the phases was achieved at the working temperature. The samples were then centrifuged at 10,000 rpm for 10 min. Afterwards, the phases were carefully separated and analyzed. The fatty acid composition was measured, and no differences were observed with the initial values indicating that hydrolysis reaction of the SO and FAME has not taken place during this period.

Analysis

Iodine value, acid value, and fatty acid composition of the SO and FAME were analyzed using AOCS recommended practices [14]. SO had an iodine value of 129.95 and FAME had 129.59. The mono, di, and triglycerides that resulted after the conversion of SO to FAME were determined by GLC, using a European Norm [15]. FAME contained 160 ppm H_2O (Karl–Fischer), 0.8545% monoglycerides, 0.114% diglycerides, and 0.1295% triglycerides. The FAME composition was: palmitic 9.80%, stearic 3.86%, oleic 22.03%, linoleic 56.67%, linolenic 7.11%, and arachidic 0.35% [13].The carboxylic acid content of both phases was determined by titration, NaOH for water phase and KOH for oil phase [14].

Modeling Procedures

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

$$K_c = \frac{C_A^o}{C_A^w} \qquad (1)$$

Table 1 Partition coefficients for formic acid between oil and water at 40 °C

Feed composition			Equilibrium composition		Partition coefficient, K_w			
					Exp	Calculated		
w_A	w_{H_2O}	w_{OIL}	$w_A^o \times 100$	$w_A^w \times 100$		UNIFAC	UNIQUAC -2 par.	UNIQUAC -4 par.
FAME								
0.0341	0.4864	0.4795	0.2347	6.4909	0.0362	0.0541	0.0300	0.0334
0.0518	0.4755	0.4727	0.3037	9.7162	0.0313	0.0554	0.0309	0.0332
0.0704	0.3407	0.5889	0.4961	16.8187	0.0295	0.0584	0.0330	0.0328
0.0839	0.2336	0.6825	0.7635	24.5086	0.0312	0.0625	0.0359	0.0323
0.0682	0.2345	0.6973	0.6659	17.8170	0.0374	0.0605	0.0345	0.0325
0.0428	0.3659	0.5913	0.3248	9.3727	0.0347	0.0555	0.0310	0.0332
0.0296	0.3934	0.5771	0.1533	4.6354	0.0331	0.0542	0.0301	0.0334
0.1535	0.6393	0.2072	1.5630	40.7135	0.0384	0.0599	0.0339	0.0327
0.0898	0.4515	0.4588	0.4906	16.0286	0.0306	0.0583	0.0329	0.0328
0.1282	0.4333	0.4385	0.7041	22.3730	0.0315	0.0614	0.0349	0.0325
RMSD[a]						0.0250	0.0037	0.0030
AAD[b]						0.0247	0.0034	0.0025
ARE(%)[c]						75.31	10.23	7.23
SO								
0.0547	0.4726	0.4727	0.1517	10.2301	0.0148	0.0321	0.0147	0.0151
0.1054	0.4487	0.4460	0.3362	18.7838	0.0179	0.0346	0.0159	0.0159
0.1876	0.4043	0.4081	0.5202	31.3431	0.0166	0.0390	0.0181	0.0177
0.1553	0.2153	0.6294	0.7998	40.0292	0.0200	0.0430	0.0203	0.0196
0.0563	0.7049	0.2388	0.1108	7.7087	0.0144	0.0314	0.0143	0.0148
RMSD[a]						0.0195	0.0011	0.0010
AAD[b]						0.0193	0.0008	0.0008
ARE(%)[c]						115.62	4.58	4.81

[a] Root mean square deviation, RMSD $= \sqrt{\sum_{i=1}^{N}\left(y_i^{exp} - y_i^{cal}\right)^2/N}$; $y = K_w$

[b] Average absolute deviation, AAD $= \frac{1}{N}\sum_{i=1}^{N}\left|y_i^{exp} - y_i^{cal}\right|$

[c] Average relative error (%), ARE $= \frac{100}{N}\sum_{i=1}^{N}\left|\frac{y_i^{exp} - y_i^{cal}}{y_i^{exp}}\right|$

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

The particular concentration of acid in phase i can be determined by the equation:

$$C_A^i = \frac{m_A^i \rho^i}{M_A m^i} = x_A^i \rho_m^i \tag{2}$$

where m_A^i, mentioned in the list of symbols, indicates the mass of acid in the sample of phase i, determined experimentally by NaOH/KOH titrations; m^i indicates the mass of the sample of phase i; ρ^i (g/L) is the density of phase i; M_A is the molecular mass of acid; x_A^i is the molar fraction of acid in phase i; and ρ_m^i is the molar density of phase i. Combining Eqs. 1 and 2:

$$K_c = \frac{\frac{m_A^o}{M_A}\frac{\rho^o}{m^o}}{\frac{m_A^w}{M_A}\frac{\rho^w}{m^w}} = \frac{w_A^o \rho^o}{w_A^w \rho^w} = K_w \frac{\rho^o}{\rho^w} = \frac{x_A^o \rho_m^o}{x_A^w \rho_m^w} = K_x \frac{\rho_m^o}{\rho_m^w} \tag{3}$$

where w_j^i is the mass fraction of component j in phase i; K_w is the partition coefficient as a quotient of mass fraction, and K_x is the partition coefficient as quotient of molar fraction. If immiscibility between oil and water is assumed:

$$a_A^o = \gamma_A^o x_A^o = \gamma_A^w x_A^w = a_A^w \tag{4}$$

where a_A is the activity of the acid; γ_A indicates the activity coefficient of the acid; and x_A is the molar fraction of the acid. Eq. 4 could be combined with Eq. 3 giving:

$$K_c = K_x \frac{\rho_m^o}{\rho_m^w} = \frac{x_A^o \rho_m^o}{x_A^w \rho_m^w} = \frac{\gamma_A^w \rho_m^o}{\gamma_A^o \rho_m^w} \tag{5}$$

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

$$x_j^i = \frac{m_j^i M_j^{-1}}{\sum_{k=1}^{3} m_k^i M_k^{-1}} \tag{6}$$

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.

Table 2 Partition coefficients for acetic acid between oil and water at 40 °C

Feed composition			Equilibrium composition		Partition coefficient, K_w			
					Exp	Calculated		
w_A	w_{H_2O}	w_{OIL}	$w_A^o \times 100$	$w_A^w \times 100$		UNIFAC	UNIQUAC-2 par	UNIQUAC-4 par
FAME								
0.0453	0.4774	0.4772	0.5884	8.1795	0.0719	0.1064	0.0704	0.0711
0.0705	0.4624	0.4671	0.9550	12.5631	0.0760	0.1060	0.0723	0.0725
0.1346	0.4334	0.4320	1.6925	22.8881	0.0740	0.1054	0.0773	0.0770
0.2098	0.3922	0.3980	3.0769	39.0088	0.0789	0.1053	0.0850	0.0846
0.0707	0.6960	0.2334	0.6692	9.3924	0.0713	0.1063	0.0708	0.0713
RMSD[a]						0.0316	0.0015	0.0016
AAD[b]						0.0315	0.0012	0.0012
ARE(%)[c]						42.52	1.67	1.64
SO								
0.2076	0.0945	0.6980	1.2971	28.9786	0.0448	0.0624	0.0489	0.0488
0.2510	0.2503	0.4988	2.4585	47.9959	0.0512	0.0595	0.0415	0.0426
0.3806	0.3832	0.2362	2.5406	68.3759	0.0372	0.0595	0.0416	0.0428
0.0446	0.4818	0.4736	0.2875	8.1515	0.0353	0.0637	0.0381	0.0371
0.0743	0.4627	0.4630	0.5193	13.2669	0.0391	0.0628	0.0382	0.0375
0.1314	0.4345	0.4342	0.8609	22.2165	0.0388	0.0614	0.0386	0.0383
0.2397	0.3812	0.3791	1.5306	36.5292	0.0419	0.0597	0.0397	0.0404
0.1877	0.2044	0.6079	2.2437	44.6376	0.0503	0.0594	0.0409	0.0420
0.0727	0.6954	0.2319	0.3327	9.2847	0.0358	0.0635	0.0381	0.0372
RMSD[a]						0.0209	0.0051	0.0047
AAD[b]						0.0197	0.0040	0.0037
ARE(%)[c]						50.33	9.03	8.35

[a] Root mean square deviation, RMSD $= \sqrt{\sum_{i=1}^{N} (y_i^{\exp} - y_i^{\text{cal}})^2 / N}$; $y = K_w$

[b] Average absolute deviation, AAD $= \frac{1}{N} \sum_{i=1}^{N} \left| y_i^{\exp} - y_i^{\text{cal}} \right|$

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

The activity coefficient of the acid in the phase i is a function of composition and temperature:

$$\gamma_A^i = f(x_A^i, x_{H_2O}^i, x_{OIL}^i, T). \tag{7}$$

Activity coefficients were calculated using the UNIFAC [16] and the UNIQUAC [17] models. UNIFAC is based on a group contribution method and UNIQUAC requires two binary parameters for each component of the system. The UNIQUAC binary interaction parameter (τ_{ij}) is given by the expression [17]:

$$\tau_{ij} = \exp(-\frac{u_{ij}}{RT}) \tag{8}$$

where u_{ij} is an adjustable binary parameter for components i and j in the mixture; and R is the universal gas constant.

The masses of each component in both phases (m_j^i) are obtained doing liquid–liquid separation calculation [18, 19]. Given the feed mixture, composition m_j^i are calculated using activity coefficient models solving the mass balances and liquid–liquid equilibrium conditions.

The phase molar densities (ρ_m^i) are calculated assuming ideal mixture and using the Rackett equation [19] for water, formic acid, and acetic acid. SO and FAME are treated as pseudo components with ρ [kg/m^3] = 1,106.9 − 0.64T [K] for SO [20] and ρ [kg/m^3] = 879.71 − 1.24T [°C] for FAME [21].

Results and Discussion

Tables 1 and 2 present the experimental partition coefficients of formic and acetic acid, respectively. The tables show feed mixture composition and acid mass fraction in the oil and in the water phases. Each table displays experimental partition coefficient with FAME and SO.

To model the liquid–liquid phase equilibrium of the SO–acid–water system by use of the UNIFAC and UNIQUAC models, the SO has to be defined as a pseudo-component. In this work, it was represented as pseudo-triglyceride with the molecular structure [22], RCOO-CH_2CH(-OOCR′) CH_2-OOCR″ or for UNIFAC group counting:

$$[(CH_2COO)(CHCOO)(CH_2COO)]\\ (CH_2)_y(CH=CH)_z(CH_3)_3 \tag{9}$$

where $(CH_3)_3$ are the three terminal methyl group of R, R′, and R″. The values of y and z that indicate the numbers of (CH_2) and (CH=CH) groups in oil, respectively, were calculated from the fatty acid (FA) composition of SO as follows:

$$y = \sum_{j=1}^{\mathrm{NFA}} x_j y_j = 38 \tag{10}$$

$$z = \sum_{j=1}^{\mathrm{NFA}} x_j z_j = 5 \tag{11}$$

where x_j is the molar fraction of the FA j; y_j is the number of (CH_2) 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 SO. The FA composition of SO is given above. To model the liquid–liquid phase equilibrium of the FAME–acid–water system by use of the UNIFAC and UNIQUAC models, the FAME was represented by a pseudo-fatty acid methyl ester with the molecular structure [22], $RCOOCH_3$ or for UNIFAC group counting:

$$(CH_3)(CH=CH)_z(CH_2)_y(CH_2COO)(CH_3) \tag{12}$$

where $y = 11$ and $z = 2$ obtained using Eqs. 10 and 11 with the FA composition of FAME given above.

For application of the UNIFAC method, the following groups of system components were taken into consideration: CH_3, CH_2, CH, CH=CH, CH_2COO, COOH, and H_2O. The interaction parameters of the components in the UNIQUAC model were determined by fitting the experimental values of the partition coefficient for the acids given in Tables 1 and 2.

The following objective function was used:

$$\mathrm{OF} = \sum_{i=1}^{N} \left[\left(K_w^{\exp} - K_w^{\mathrm{cal}} \right) / K_w^{\exp} \right]_i^2 \tag{13}$$

where $K_w^{\exp}$ and K_w^{cal} are experimental and calculated partition coefficients (using mass fraction) and N the number of data points. The program SIMULIS [19] was used for all calculations. Interaction parameters for water–SO and water–FAME were set at 1×10^4 given the assumption of immiscibility. Two cases were considered. In the first, interaction parameters for acid–SO and acid–FAME were determined while interaction parameters for acid–water were obtained from UNIFAC; binary system activity coefficients calculated using UNIFAC were fitted with UNIQUAC. In the second case, all four interaction parameters were determined by fitting the experimental partition coefficient, $K_w^{\exp}$. Table 3 reports interaction parameters. The experimental values of the partition coefficient for the carboxylic acids and the calculated K_w with UNIFAC and the two cases of UNIQUAC are presented in Tables 1 and 2. As expected, the lowest errors are obtained when all four binary parameters of UNIQUAC are fitted to the data, but differences are not large and acid–water binary parameters could be obtained from UNIFAC parameters given in the literature [16]. Errors using UNIFAC are larger than those achieved by application of UNIFAC correlation.

Table 3 UNIQUAC binary parameters (u_{ij}) for the ternary systems

	Formic acid	Water	FAME
Formic acid	–	-171.51^{a} 392.66^{c}	$3{,}385.55^{b}$ $3{,}387.93^{c}$
Water	-179.03^{a} -112.03^{c}	–	10,000
FAME	28.05^{b} 512.28^{c}	10,000	–
	Formic acid	**Water**	**SO**
Formic acid	–	-171.51^{a} 371.42^{c}	$3{,}868.36^{b}$ -20.81^{c}
Water	-179.03^{a} -753.51^{c}	–	10,000
SO	280.54^{b} 801.44^{c}	10,000	–
	Acetic acid	**Water**	**FAME**
Acetic acid	–	61.45^{a} 811.71^{c}	-321.91^{b} 71.48^{c}
Water	34.62^{a} -635.49^{c}	–	10,000
FAME	$1{,}002.43^{b}$ 232.10^{c}	10,000	–
	Acetic acid	**Water**	**SO**
Acetic acid	–	61.45^{a} -344.80^{c}	-352.42^{b} $1{,}065.52^{c}$
Water	34.62^{a} 362.10^{c}	–	10,000
SO	$1{,}197.09^{b}$ 34.62^{c}	10,000	–

$\tau_{ij} = \exp\left(-\frac{u_{ij}}{RT}\right), u_{ij}(\mathrm{cal/mol})$

[a] From UNIFAC at $T = 40$ °C

[b] UNIQUAC-2 par

[c] UNIQUAC-4 par

Table 4 Comparison of experimental and calculated acetic acid partition coefficients between soybean oil and water

Temperature (°C)	Feed composition			Partition coefficient, K_c				Reference Exp K_c
				Exp	Calculated			
	w_A	w_{H_2O}	w_{SO}		UNIFAC	UNIQUAC-2 par	UNIQUAC-4 par	
Literature								
20	0.0871	0.3199	0.5929	0.0389	0.0678	0.0317	0.0318	[23]
	0.1263	0.3040	0.5697	0.0424	0.0670	0.0319	0.0326	[23]
	0.1606	0.2920	0.5474	0.0408	0.0665	0.0322	0.0333	[23]
35	0.0871	0.3199	0.5929	0.0409	0.0587	0.0342	0.0340	[23]
	0.1263	0.3040	0.5697	0.0482	0.0576	0.0345	0.0347	[23]
	0.1606	0.2920	0.5474	0.0424	0.0569	0.0348	0.0354	[23]
40	0.2413	0.2532	0.5054	0.0980	0.0538	0.0372	0.0382	[1]
	0.0713	0.2058	0.7229	0.0671	0.0559	0.0352	0.0350	[1]
	0.3852	0.3843	0.2305	0.0750	0.0538	0.0376	0.0386	[1]
50	0.0871	0.3199	0.5929	0.0400	0.0524	0.0368	0.0362	[23]
	0.1263	0.3040	0.5697	0.0451	0.0513	0.0371	0.0368	[23]
	0.1606	0.2920	0.5474	0.0433	0.0505	0.0375	0.0375	[23]
60	0.2441	0.2618	0.4941	0.0280	0.0466	0.0408	0.0408	[1]
	0.0710	0.2021	0.7269	0.0360	0.0487	0.0387	0.0379	[1]
	0.3838	0.3862	0.2300	0.0230	0.0466	0.0413	0.0413	[1]
65	0.0871	0.3199	0.5929	0.0427	0.0479	0.0395	0.0383	[23]
	0.1263	0.3040	0.5697	0.0466	0.0467	0.0398	0.0389	[23]
	0.1606	0.2920	0.5474	0.0403	0.0460	0.0402	0.0395	[23]
80	0.0871	0.3199	0.5929	0.0452	0.0444	0.0422	0.0405	[23]
	0.1263	0.3040	0.5697	0.0423	0.0433	0.0426	0.0410	[23]
	0.1606	0.2920	0.5474	0.0477	0.0426	0.0430	0.0416	[23]
RMSD[a]					0.0143	0.0067	0.0089	[23]
AAD[b]					0.0110	0.0060	0.0063	[23]
ARE(%)[c]					26.40	13.71	14.47	[23]
RMSD[a]					0.0245	0.0332	0.0327	[1]
AAD[b]					0.0219	0.0273	0.0269	[1]
ARE(%)[c]					49.08	48.77	47.96	[1]
This work								
40	0.2076	0.0945	0.6980	0.0407	0.0561	0.0440	0.0438	
	0.2510	0.2503	0.4988	0.0463	0.0538	0.0374	0.0385	
	0.3806	0.3832	0.2362	0.0333	0.0538	0.0375	0.0386	
	0.0446	0.4818	0.4736	0.0323	0.0583	0.0348	0.0340	
	0.0743	0.4627	0.4630	0.0358	0.0575	0.0349	0.0343	
	0.1314	0.4345	0.4342	0.0353	0.0560	0.0351	0.0349	
	0.2397	0.3812	0.3791	0.0381	0.0542	0.0360	0.0366	
	0.1877	0.2044	0.6079	0.0456	0.0538	0.0370	0.0379	
	0.0727	0.6954	0.2319	0.0328	0.0581	0.0349	0.0340	
RMSD[a]					0.0191	0.0047	0.0043	
AAD[b]					0.0180	0.0036	0.0033	
ARE(%)[c]					50.50	9.04	8.37	

[a] Root mean square deviation, RMSD $= \sqrt{\sum_{i=1}^{N} (y_i^{\mathrm{exp}} - y_i^{\mathrm{cal}})^2 / N}$; $y = K_c$

[b] Average absolute deviation, AAD $= \frac{1}{N} \sum_{i=1}^{N} \left| y_i^{\mathrm{exp}} - y_i^{\mathrm{cal}} \right|$

[c] Average relative error (%), ARE $= \frac{100}{N} \sum_{i=1}^{N} \left| \frac{y_i^{\mathrm{exp}} - y_i^{\mathrm{cal}}}{y_i^{\mathrm{exp}}} \right|$

An additional calculation was performed, using the binary parameters of Table 3. In Table 4, calculated partition coefficients, K_c^{cal}, are compared with experimentally determined partition coefficients taken from Refs. [1] and [23]. To obtain K_c from K_w with Eq. 3, SO density was calculated as ρ [kg/m^3] = 1,106.9 − 0.64T [K], [20]. As shown, the deviation for Rangarajan et al. [1] are much larger than for Sinadinović-Fišer and Janković [23]. These results seem to indicate that our experiments are consistent with those of Ref. [23].

The work described in this manuscript is extremely important, because it facilitates better understanding of the epoxidation system. This work forms part of a comprehensive research program that analyzes this liquid–liquid reacting system. The partition coefficient, as mentioned in the Introduction, is an important property that must be known to enable modeling of this two-phase system. This property will help in the design of the epoxidation reaction with the objective of obtaining high yields of epoxide. As we can observe, UNIQUAC can be employed to calculate the partition coefficient of carboxylic acids in a two-phase system, and this method will be useful on an industrial scale when modeling the epoxidation system to predict the yields of epoxide.

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