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Prediction of Liquid−Liquid Equilibrium for Systems of Vegetable Oils, Fatty Acids, and Ethanol

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Group interaction parameters for the UNIFAC and ASOG models were specially adjusted for predicting liquid−liquid equilibrium (LLE) for systems of vegetable oils, fatty acids, and ethanol at temperatures ranging from 20 to 45 °C. Experimental liquid−liquid equilibrium data for systems of triolein, oleic acid, and ethanol and of triolein, stearic acid, and ethanol were measured and utilized in the adjustment. The average percent deviation between experimental and calculated compositions was 0.79% and 0.52% for the UNIFAC and ASOG models, respectively. The prediction of liquid−liquid equilibrium for systems of vegetable oils, fatty acids, and ethanol was quite successful, with an average deviation of 1.31% and 1.32% for the UNIFAC and ASOG models, respectively.

Introduction

Liquid−liquid equilibrium data for systems of vegetable oils, fatty acids, and ethanol are scarce in the literature, yet such information is essential for the study of the deacidification of vegetable oils by liquid−liquid extraction. One feasible alternative which can extend the available results to other vegetable oils is the utilization of group contribution methods, UNIFAC (Fredenslund et al., 1977) and ASOG (Kojima and Tochigi, 1979).

The previously published group interaction parameters for the prediction of liquid−liquid equilibrium (Magnussen et. al., 1981) by the UNIFAC model are not satisfactory for systems containing vegetable oils (Figure 1); for example, the average percentage of deviation for experimental data of systems containing canola oil, commercial oleic acid, and ethanol at temperatures of 20 to 30 °C is 11.2% in the mass fraction (Table 10), and the ASOG model cannot be used in such predictions due to the unavailability of certain necessary group interaction parameters.

It is thus necessary to adjust new parameters for these group contribution methods when fatty systems are involved, as is the case here. The loss of convenience represented by the utilization of a single set of parameters for any class of compounds is, however, compensated by the improvements in the results predicted, as well as by the possibility of predicting liquid−liquid equilibria for systems involving a large number of vegetable oils, triglycerides, and fatty acids.

The project reported in this paper was designed to develop a prediction method for liquid−liquid equilibrium of systems of vegetable oils, fatty acids, and ethanol. It is divided into three parts: the measurement of liquid−liquid equilibria of ternary systems of triolein, oleic acid, and ethanol and of triolein, stearic acid, and ethanol; the readjustment of certain group interaction parameters of the UNIFAC and ASOG models to these data; and the prediction of the liquid−liquid equilibria of systems containing vegetable oils, fatty acids, and ethanol.

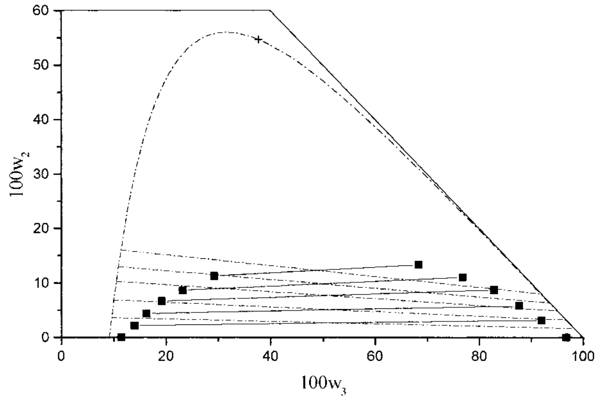

Figure 1. System of triolein (1) + oleic acid (2) + ethanol (3) at 20 °C: (■) experimental; (−·−) original UNIFAC; (+) plait point.

Materials

Triolein and oleic acid used in the experiments are from Sigma, both with a minimal purity of 99%. The stearic acid, also from Sigma, has a purity >90%, while the anhydrous ethanol was acquired from Merck, with a minimal purity of 99.8%.

Refined corn oil and commercial oleic acid from Riedel−deHaën were analyzed using the procedures previously proposed for canola oil (Batista et al., 1999). The fatty acid composition of the corn oil is presented in Table 1.

On the basis of this fatty acid composition, it was possible to determine the probable triglyceride composition of the corn oil (Table 2) using the computational method developed by Antoniosi Filho et al. (1995). The following aspects should be considered: first, the main triglyceride is the component of greatest concentration in the set of isomers with *x* carbons and *y* double bonds. Thus, certain fatty acids which appear in Table 1 (M, Po, and A) do not appear explicitly in Table 2; for example, the triglyceride PPoS is

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Table 1. Fatty Acid Composition of Corn Oil

symbol	fatty acid		M^b (g·mol^{-1})	% molar	% mass
M	miristic	C14:0^a	228.38	0.0200	0.0164
P	palmitic	C16:0	256.43	12.8500	11.8457
Po	palmitoleic	C16:1	254.41	0.1300	0.1189
S	stearic	C18:0	284.48	2.1500	2.1988
O	oleic	C18:1	282.47	34.3200	34.8506
Li	linoleic	C18:2	280.45	49.4400	49.8454
Le	linolenic	C18:3	278.44	0.2700	0.3034
A	arachidic	C20:0	312.54	0.8200	0.8208

[a] In Cx:y, x = number of carbons, and y = number of double bonds. [b] M = molecular weight

Table 2. Probable Composition of Triglyceride of Corn Oil

group	main triglyceride	M (g·mol^{-1})	% molar	% mass
50:1^a	PPO	833.37	1.7300	1.6540
50:2	PPLi	831.35	2.5300	2.4141
52:1	PSO	861.45	0.5800	0.5717
52:2	POO	859.40	5.4600	5.3741
52:3	POLi	857.39	13.3700	13.1387
52:4	PLiLi	855.37	9.9400	9.7409
54:2	SOO	887.46	0.9500	0.9637
54:3	OOO	885.44	6.3400	6.4336
54:4	OOLi	883.43	19.4100	19.6457
54:5	OLiLi	881.41	25.9400	26.2009
54:6	LiLiLi	879.43	13.1400	13.2407
54:7	LiLiLe	877.38	0.6200	0.6219
total			100.0000	100.0000

[a] In x:y, x = number of carbons (except carbons of glycerol), and y = number of double bonds.

Table 3. Fatty Acid Composition of Riedel−deHaën Oleic Acid

fatty acid	% molar	% mass
M	1.5889	1.3025
P	4.3945	4.0450
Po	6.3728	5.8197
S	0.5951	0.6077
O	81.9848	83.1276
Li	5.0178	5.0514
Le	0.0461	0.0461

part of the group 50:1, with a main triglyceride of PPO. Moreover, groups with a total triglyceride concentration <0.5% are ignored. The average molecular weight of the corn oil was 872.6131 g·mol^{-1}.

The probable composition of fatty acids of commercial oleic acid is presented in Table 3. The molecular weight obtained for the oleic acid was equal to 278.5868 g·mol^{-1}.

Experimental Procedure

Equilibrium cells equivalent to those of Silva et al. (1997) for the determination of liquid−liquid equilibrium data were used. The cell temperature was controlled with a thermostatic bath (Cole Parmer, Model 12101-15, accurate to ±0.01 °C), and the component quantity was determined by weighing on a Sartorius analytical balance (Model A200 S, accurate to 0.0001 g). The mixture was stirred vigorously with a magnetic stirrer (FISATOM, Model 752A) for at least 15 min and left to rest for 4 h. This led to the formation of two clear and transparent phases, with a well-defined interface.

The quantity of fatty acids was determined using potentiometric titration (Modified AOCS Method Ca 5a-40, 1977) with an automatic buret (METROHM, Model Dosimat 715); the solvent was determined by evaporation in an EDG vacuum oven (Model EIV-1). Having determined the concentration of fatty acids and the solvent, the concentration of triglycerides was obtained by difference. Measurements were made in triplicate, with standard deviations of 0.035% for triolein, 0.056% for corn oil, 0.038% for fatty acids, and 0.012% for ethanol.

Table 4 shows the overall experimental composition of the mixtures and the corresponding tie lines for systems of triolein, oleic acid, and anhydrous ethanol, and Table 5 shows the overall experimental composition of the mixtures and the corresponding tie lines for the systems of triolein, stearic acid, and anhydrous ethanol. The fatty acids stearic and oleic were chosen to determine the effect of the presence of double bonds on the distribution coefficient.

The experimental data for the system of corn oil, commercial oleic acid, and anhydrous ethanol at 25 °C are presented in Table 6. All concentrations are expressed as percentage of mass.

Modeling

Following the procedure developed by Stragevitch and d'Avila (1997), adjustments of group interaction parameters of the UNIFAC and ASOG models were made by minimization of the maximum likelihood objective function.

The groups most characteristic of fatty systems in alcoholic solutions were selected. For the UNIFAC model, the following groups were selected—CH_2COO, CH═CH, COOH, and OH—and only the interaction parameters with these groups were readjusted. The parameters involving interaction with other groups present in the system were taken from Magnussen et al. (1981). Table 7 presents the new group interaction parameters for the UNIFAC model.

Table 4. Liquid−Liquid Equilibrium Data for the Ternary System of Triolein (1) + Oleic Acid (2) + Anhydrous Ethanol (3)^a

	overall composition			alcohol phase			oil phase		
T (°C)	$100w_3$	$100w_2$	$100w_1$	$100w_3$	$100w_2$	$100w_1$	$100w_3$	$100w_2$	$100w_1$
20	53.42		46.58	96.75		3.25	11.41		88.59
	54.51	2.80	42.69	91.96	3.15	4.89	13.97	2.15	83.88
	54.28	5.24	40.48	87.70	5.82	6.48	16.28	4.35	79.37
	52.03	7.68	40.29	82.86	8.72	8.42	19.24	6.69	74.07
	49.73	10.13	40.14	76.81	11.03	12.16	23.16	8.64	68.20
	49.31	12.68	38.01	68.39	13.34	18.27	29.25	11.22	59.53
30	55.80		44.20	95.72		4.28	13.97		86.03
	54.98	2.83	42.19	90.40	3.19	6.41	17.10	2.26	80.64
	53.73	2.83	43.44	90.02	3.30	6.68	16.86	2.37	80.77
	54.99	5.28	39.73	85.42	5.75	8.83	20.09	4.47	75.44
	52.88	5.80	41.32	83.76	6.68	9.56	20.53	5.10	74.37
	52.10	7.67	40.23	79.50	8.46	12.04	24.04	6.81	69.15
	50.08	8.20	41.72	78.17	9.04	12.79	26.09	7.27	66.64
	49.80	10.21	39.99	71.52	10.71	17.77	30.27	8.95	60.78

[a] w_i = mass fraction of component i.

Table 5. Liquid-Liquid Equilibrium Data for the Ternary System of Triolein (1) + Stearic Acid (4) + Anhydrous Ethanol (3)

	overall composition			alcohol phase			oil phase		
T (°C)	$100w_3$	$100w_4$	$100w_1$	$100w_3$	$100w_4$	$100w_1$	$100w_3$	$100w_4$	$100w_1$
30	54.11	2.48	43.41	90.95	2.40	6.65	16.89	1.99	81.12
	48.53	6.12	45.35	83.96	6.34	9.69	22.79	5.52	71.69
45	50.44	9.14	40.42	76.88	8.72	14.40	34.40	8.62	56.98

Table 6. Liquid−Liquid Equilibrium Data for the Ternary System of Corn Oil (5) + Commercial Oleic Acid (6) + Anhydrous Ethanol (3)

	overall composition			alcohol phase			oil phase		
T (°C)	$100w_3$	$100w_6$	$100w_5$	$100w_3$	$100w_6$	$100w_5$	$100w_3$	$100w_6$	$100w_5$
25	52.08		47.92	94.20		5.80	14.27		85.73
	51.20	2.40	46.40	89.85	2.62	7.53	16.78	1.88	81.34
	50.04	4.90	45.06	84.89	5.46	9.65	18.44	4.28	77.28
	50.31	7.91	41.78	76.27	8.75	14.98	25.56	6.94	67.50
	49.43	10.03	40.54	67.63	10.82	21.55	32.68	9.19	58.13

Table 7. New UNIFAC Group Interaction Parameters

m	n	a_{mn}	a_{nm}
CH=CH	CH_2COO	−149.180	−2692.200
CH=CH	COOH	−851.340	194.320
CH=CH	OH	1172.400	−2457.900
CH_2COO	COOH	17.081	−167.6700
CH_2COO	OH	511.190	247.520
COOH	OH	−424.310	70.196

Table 8. New ASOG Group Interaction Parameters

k	l	$m_{k,l}$	$m_{l,k}$	$n_{k,l}$	$n_{l,k}$
C=C	COOH	0.23690	13.15200	435.010	−3000.000
C=C	COO	−0.84113	6.12620	710.960	−1584.800
C=C	OH	1.19260	−4.42290	−146.170	−1881.600
COOH	COO	−2.33200	1.68420	868.940	109.390
COOH	OH	−4.64600	−1.188190	2643.400	459.170
COO	OH	2.10340	0.06637	−859.160	−654.970

For the ASOG model, the following groups were selected—COO, C=C, COOH, and OH. The other parameters were taken from Tochigi et al. (1990). Table 8 presents the new group interaction parameters.

The experimental data were compared to those calculated by liquid−liquid flash using the adjusted parameters.

Figures 2 and 3 present the experimental and calculated tie lines and the calculated heterogeneous area for the system of triolein, oleic acid, and ethanol. Table 9 shows the average percent deviation in phase composition for this system.

Figure 4 presents the distribution of oleic acid and stearic acid at 30 °C. At this temperature, pure stearic acid is in a solid state, and the tie line with the overall composition of the mixture containing 6.12% (w/w) stearic acid is close to the limit of solubility (Bailey, 1950). Thus, the tie line with the overall composition of the mixture containing 9.14% (w/w) stearic acid (Table 5) was measured at 45 °C to avoid the formation of crystals of this acid.

It can be seen in Figure 4 that the solubility of fatty acids in ethanol increases with an increase in unsaturation. In general, solubility decreases with an increase in molecular weight and increases with the number of double bonds (Bailey, 1950).

Prediction of Liquid−Liquid Equilibrium for Multicomponent Systems

The adjusted parameters of the UNIFAC and ASOG models were tested in the prediction of liquid−liquid equilibria in systems of vegetable oils, fatty acids, and ethanol available in the literature. Experimental data for the following systems were used to validate the model: canola oil, commercial oleic acid, and ethanol (Batista et al., 1999); corn oil, commercial oleic acid, and ethanol (from the present paper); and Spanish olive oil, oleic acid, and ethanol (Rius and Martinez Moreno, 1947).

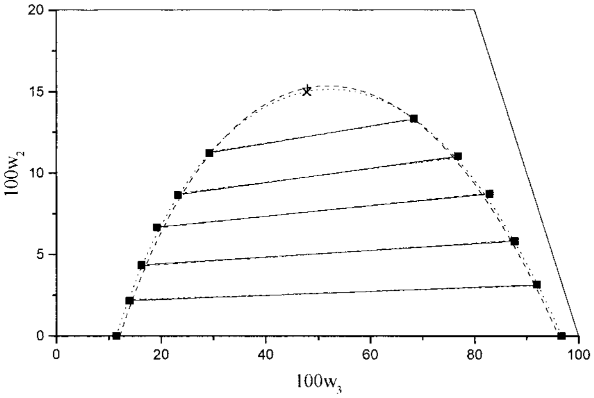

Figure 2. System of triolein (1) + oleic acid (2) + ethanol (3) at 20 °C: (■) experimental; (− - −) UNIFAC; (···) ASOG; (+) plait point UNIFAC; (×) plait point ASOG.

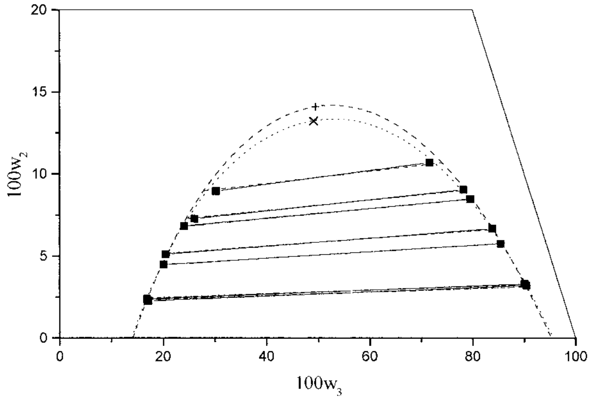

Figure 3. System of triolein (1) + oleic acid (2) + ethanol (3) at 30 °C: (■) experimental; (− - −) UNIFAC; (···) ASOG; (+) plait point UNIFAC; (×) plait point ASOG.

For the olive oil system, the probable triglyceride composition proposed by Constante (1988) was used. The average molecular weight calculated for olive oil was 877.2282 g·mol^{-1}.

Liquid−liquid flash for the calculation of phase compositions was executed on the basis of the overall experimental composition of the mixtures. The compositions of oils and commercial oleic acid were used to expand the ternary overall composition of the mixture to the multicomponent.

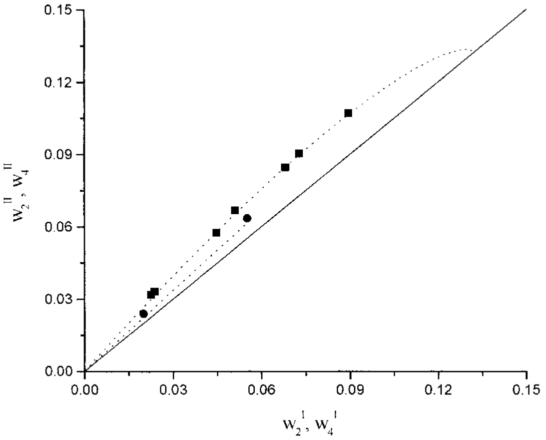

Figure 4. Distribution of the fatty acids in the ternary systems at 30 °C: (■) oleic acid (2); (●) stearic acid (4); (···) ASOG.

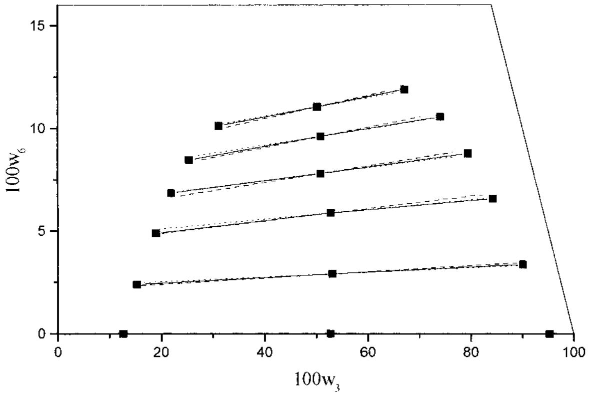

Figure 5. Prediction of liquid–liquid equilibrium for the system of canola oil (7) + commercial oleic acid (6) + ethanol (3) at 20 °C (■) experimental; (– - –) UNIFAC; (···) ASOG.

Table 9. Average Percent Deviation in Phase Composition

	Δ*w* (%)		
system	original UNIFAC	UNIFAC	ASOG
triolein/oleic acid/ethanol, 20 °C	9.00	0.70	0.35
triolein/oleic acid/ethanol, 30 °C	9.26	0.87	0.55
triolein/stearic acid/ethanol, 30 °C	7.38	0.68	0.52
triolein/stearic acid/ethanol, 45 °C	15.95	1.10	1.00
global	9.52	0.79	0.52

Table 10. Average Percent Deviations for the Systems Studied

	Δ*w* (%)		
system	original UNIFAC	UNIFAC	ASOG
canola oil/commercial oleic acid/ethanol, 20 °C	11.38	1.87	1.34
canola oil/commercial oleic acid/ethanol, 30 °C	11.00	0.79	1.54
corn oil/commercial oleic acid/ethanol, 25 °C	11.99	0.69	0.68
olive oil/commercial oleic acid/ethanol, 25 °C	5.56	1.58	1.31
global	10.16	1.31	1.32

After the multicomponent flash, the mass fractions of triglycerides for each of the phases were grouped and compared to the experimental composition of the phases in vegetable oils. The same procedure was utilized for the fatty acids. The mass fractions of the different fatty acids were grouped and compared to the composition observed.

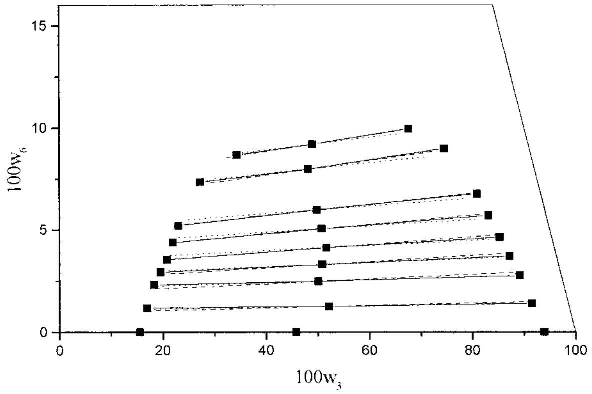

Figure 6. Prediction of liquid–liquid equilibrium for the system of canola oil (7) + commercial oleic acid (6) + ethanol (3) at 30 °C (■) experimental; (– - –) UNIFAC; (···) ASOG.

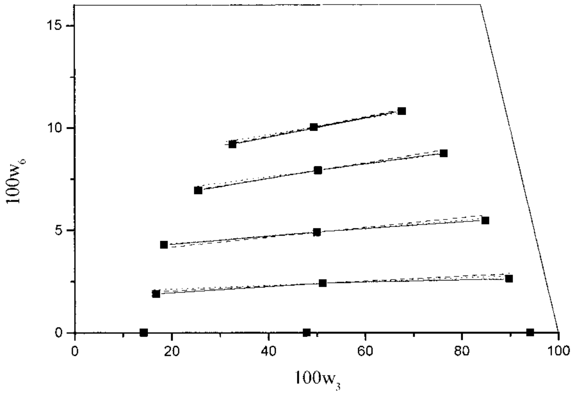

Figure 7. Prediction of liquid–liquid equilibrium for the system of corn oil (5) + commercial oleic acid (6) + ethanol (3) at 25 °C: (■) experimental; (– - –) UNIFAC; (···) ASOG.

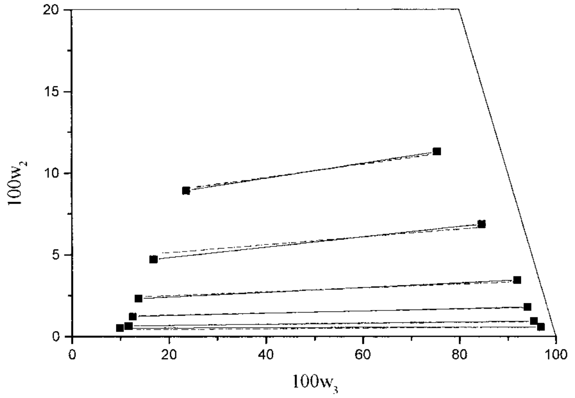

Figure 8. Prediction of liquid–liquid equilibrium for the system of olive oil (8) + oleic acid (2) + ethanol (3) at 25 °C (■) experimental; (– - –) UNIFAC; (···) ASOG.

Table 10 presents the average deviation for the systems studied.

Figures 5–8 show the experimental tie lines predicted for the systems of vegetable oil, fatty acids, and ethanol.

In addition to these multicomponent systems, the prediction was extended to systems with other solvents, such as those of canola oil, commercial oleic acid, and methanol and of canola oil, commercial oleic acid, ethanol, and water (Batista et al., 1999). The mean percent deviations are presented in Table 11.

The prediction for the system of ethanol and water as a solvent overestimated the concentration of canola oil and fatty acids in the oil phase, while simultaneously overestimating the amount of ethanol and water in the alcoholic

Table 11. Average Percent Deviations for Systems with Other Solvents

system	Δ*w* (%)		
	original UNIFAC	UNIFAC	ASOG
canola oil/commercial oleic acid/methanol, 20 °C	8.05	3.07	4.66
canola oil/commercial oleic acid/methanol, 30 °C	3.89	1.86	4.42
canola oil/commercial oleic acid/ethanol/water, 30 °C	5.71	2.33	2.98

phase, resulting in somewhat greater values for the average percent deviation.

Conclusion

The parameters for the UNIFAC and ASOG group contribution models presented here make predictions of liquid−liquid equilibrium possible for systems of vegetable oils, fatty acids, and ethanol between the temperatures 20 °C and 45 °C. The improvements in the results predicted, as well as the possibility of predicting liquid−liquid equilibrium for systems involving a large number of vegetable oils, triglycerides, and fatty acids, will support a study of the deacidification of vegetable oils with better accuracy.

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