Modeling Phase Equilibria Relevant to Biodiesel Production: A Comparison of g^E Models, Cubic EoS, EoS$-g^E$ and Association EoS

Mariana B. Oliveira,[†] Vítor Ribeiro,[†] António José Queimada,[‡] and João A. P. Coutinho[*,†]

[†]CICECO, Chemistry Department, University of Aveiro, 3810-193 Aveiro, Portugal

[‡]LSRE — Laboratory of Separation and Reaction Engineering, Faculdade de Engenharia, Universidade do Porto, Rua do Doutor Roberto Frias, 4200 - 465 Porto, Portugal

ABSTRACT: Liquid–liquid equilibrium (LLE) and vapor–liquid equilibrium (VLE) data of binary and ternary systems formed at the biodiesel production and purification industrial units were used to evaluate the performance of commonly used excess Gibbs energy (g^E) models, cubic equations of state (EoS), equations of state with EoS$-g^E$ mixing rules, and association equation of state models. The models used in this study are the UNIFAC, Soave–Redlich–Kwong (SRK) EoS, the SRK-MHV2, the Peng–Robinson (PR) EoS using the MHV2 mixing rule, the predictive Soave–Redlich–Kwong (PSRK) EoS, and the Cubic-Plus-Association (CPA) EoS. All models were used with previously established parameters, and the applicability of each model to the various systems investigated and the quality of the description of the phase equilibria are discussed. The results obtained show that the CPA EoS is the most adequate model to be used for the description of the phase equilibria of importance for the design and optimization of biodiesel production plants.

1. INTRODUCTION

For the design and optimization of industrial processes, it is essential to be able to accurately predict the phase equilibria as a function of temperature, pressure, and composition of a specific system. This allows the correct selection of suitable solvents, the most advantageous unit operations and separation sequence, and their optimal sizing and operating conditions. The use of reliable thermodynamic models is a necessary condition for an accurate description of the phase equilibria. For that purpose, various models have been proposed.

Local composition models based on the original quasi-chemical theory[1] were for a long time the most popular for phase equilibria calculations in systems of polar compounds, with the UNIFAC model[2] being the most used group contribution model in the petrochemical industry. These models have the advantage of being able to deal with apolar, polar, and associating systems in a very flexible way, but as a drawback the NRTL and the UNIQUAC models have no predictive capability toward new systems, and their applicability is restricted to low pressures and a narrow temperature range. Moreover, they cannot handle permanent gases, near or supercritical compounds, and high pressures and need significant amounts of data to regress the model parameters. These models also often perform poorly for highly polar and complex associating mixtures.

Through ongoing research work, the range of applicability of the original UNIFAC model, first proposed in 1975,[2] has been continuously extended. The accuracy and the range of applicability of the model greatly depend on the quality of its group interaction parameters. Using the original model, the UNIFAC interaction parameters were re-estimated by fitting LLE data to increase the representation of that type of phase equilibria (UNIFAC LLE).[3] By 1987, two modified UNIFAC models were proposed with several advantages over the original model, based

on the use of temperature-dependent group-interaction parameters and modifications in the combinatorial term. For the Lyngby UNIFAC,[4] a large database to fit temperature-dependent group interaction parameters was applied, simultaneously including vapor–liquid equilibrium (VLE) and H^E data. For the Dortmund UNIFAC,[5] in addition, liquid–liquid equilibrium (LLE) and γ^∞ data were considered. UNIFAC's range of applicability increased, and a better description of the temperature dependence was achieved.

Cubic equations of state are able to describe phase equilibria in a broad pressure range including near and supercritical conditions. Equations of state are indeed more complete than Gibbs free energy models as they explicitly incorporate the pressure (or density) effects, allowing the calculation of properties in a broader range of conditions.

The SRK EoS[6] along with the PR EoS,[6] with classical quadratic mixing rules, are the most popular cubic equations of state. However, they are expected to perform poorly for systems containing polar and hydrogen-bonding molecules.[6]

Aiming at getting the best of both worlds having a model that could simultaneously apply to high pressures at polar and hydrogen bonding systems, g^E models were coupled with cubic equations of state through the EoS$-g^E$ mixing rules. Huron and Vidal were the first to propose this concept[7] through the equality of the excess Gibbs energy calculated from the EoS and a g^E model. Several problems had to be overcome, the most relevant being the fact that the derivation was carried out at infinite pressure making impossible the use of g^E models based on low pressure VLE data. With g^E being a function of pressure, its value

cannot be the same at low and at infinite pressure. Consequently, g^E parameters had to be correlated to apply this model at low pressure, decreasing its predictive character.[8] It was found that it could not also safely extrapolate over temperature using temperature-independent parameters.

To overcome that disadvantage and to avoid the iterative procedure,[9] the original Huron–Vidal mixing rule was modified equating the equation of state and the g^E models at zero pressure. Michelsen et al.[10−12] established two of the most successful and popular mixing rules of that kind, the MHV1 and the MHV2 rules, a first- and a second-order approximation, respectively, making possible for EoS to use the existing g^E model parameters. The g^E model can in particular be the modified UNIFAC model. Even if the MHV1 and MHV2 rules cannot satisfy the second virial coefficient boundary condition, they can provide a good description of highly nonideal systems with strong interactions.[8] MHV2 can be used as an extrapolating tool without further modification, but the MHV1 is expected to fail at high temperatures where an "ad hoc" extrapolation is needed.[13]

A particular version of the MHV1 model forms the basis of the PSRK model[14] that is widely used in process simulators. With this model, UNIFAC results can be extended to higher temperatures and pressures. PSRK still provides, however, poor results for liquid densities and possesses all of the UNIFAC drawbacks.[15]

A vast range of possibilities can be generated through the coupling of different equations of state and g^E models, with various degrees of success. Nevertheless, when using cubic equations of state with complex g^E mixing rules, it is frequently necessary to include temperature-dependent binary interaction parameters that have to be fitted to experimental data due to the limited predictive capability of those approaches.[6]

A number of works over the last years have shown that the majority of EoS–g^E models fail to adequately represent most of the asymmetric systems, due to the large difference between the two combinatorial terms originated by the large size difference between the components.[16]

Association EoS, which explicitly describe the specific interactions between like molecules (self-association) and unlike molecules (cross-association), such as the GCA EoS,[17] SAFT,[18] APACT,[19] and the CPA EoS,[20] were the breakthrough in the modeling of polar and highly nonideal systems in large temperature and pressure ranges. Particularly, the CPA EoS has shown to be the most appropriate model of this kind to deal with complex associating systems, considering the balance between accuracy, predictivity, and simplicity.[21,22]

This work aims at providing a comparative review of how the various thermodynamic models, discussed above, perform in computing the different phase equilibria of polar binary and multicomponent systems of relevance for biodiesel production, in particular for its purification processes. Up to now, no study that compares all these models on a common basis has been reported. The available interaction parameters for the cubic EoS, g^E, and EoS–g^E models were used, and no refitting is done to keep the models predictive behavior.

Initially, a description of the experimental data used to evaluate the performance of the models chosen is presented.

Modeling results are then discussed in terms of vapor–liquid equilibria and liquid–liquid equilibria, starting each subsection with a discussion about the importance of each kind of phase equilibria for the biodiesel industrial production and purification.

It must be highlighted that the systems occurring during biodiesel production are multicomponent, but, due to the lack of information considering real systems, binary and ternary systems were here selected for model comparison.

2. RESULTS AND DISCUSSION

2.1. Vapor–Liquid Equilibria. On a biodiesel production plant, VLE takes place at the glycerol purification, alcohol recovery, and biodiesel drying units. Binary systems containing glycerol, fatty acid esters, and alcohols are present at the distillation, evaporation, and flash units of a classical biodiesel process. The correct description of the phase equilibria taking place at these units is crucial for the design and optimization of efficient purification and recovery processes.

Experimental data are available for the bubble point temperatures at atmospheric pressure of five alcohol + glycerol systems, from methanol to 1-butanol,[23] of the water + glycerol system[23] and of six fatty acid ester + alcohol (methanol or ethanol) systems, considering esters from methyl laurate to methyl oleate.[24]

Binary Systems Containing Glycerol and Alcohols. For the description of the phase equilibrium in binary systems containing glycerol and alcohols, the best non associative model found was, surprisingly, the SRK EoS, in particular for the methanol + glycerol mixture. A global average deviation (eq 1) of 1.3% in the bubble temperatures for glycerol + alcohol systems was obtained for this model.

$$\%AAD = \frac{1}{NP} \sum_{i=1}^{NP} \left| \frac{\exp_i - calc_i}{\exp_i} \right| \times 100 \qquad (1)$$

This was a somewhat unexpected result because cubic equations of state with classical mixing rules are known to be not applicable to systems with strong polar interactions. However, the near ideal behavior of these systems, in particular of the glycerol + methanol system,[25] can explain the success of the SRK EoS in the description of these systems. The other models generally overestimate the bubble temperature, the worst description being obtained with the SRK-MHV2 model, with a global average deviation of about 7.0%. Global average deviations between 3% and 6% were observed for the other models (Table 1).

When accounting for the self- and cross-association interactions, with the CPA EoS, the deviations are reduced to less than 2.0%, using a binary interaction parameter, k_{ij}, equal to zero.

Results are depicted in Figure 1 for the glycerol + 1-propanol system.

Binary System Containing Glycerol and Water. The difficulty in handling this system is here evident seeing that all the applied cubic EoS, EoS–g^E, and g^E models underestimate the bubble temperature of the mixture. None of these models can correctly consider the effects of the strong association interactions between the components.

The PR-MHV2 model is the best to describe this system followed by the SRK-MHV2 and the UNIFAC models, providing global average deviations of about 2% in the bubble points. These results are in agreement with the expected, because more complex mixing rules enable cubic equations of state to perform better for this kind of system. The SRK EoS performs considerably worse, with errors of 3.7% (Table 1).

As observed for the glycerol + alcohol systems, the CPA EoS can provide a much better description of the VLE data of the

Table 1. Modeling Results for the Bubble Temperature of Fatty Acid Ester + Methanol/Ethanol[24] and of Glycerol + Alcohol/Water Systems[23]

		ΔT_b %					
		UNIFAC	SRK	PSRK	PR-MHV2	SRK-MHV2	CPA
ester + methanol	methyl laurate + methanol	0.57	1.71	2.02	1.20	1.06	0.28
	methyl myristate + methanol	0.69	1.82	2.74	1.55	0.94	0.40
	methyl oleate + methanol	0.74	1.44	2.78	2.48	0.89	0.42
	global AAD %	0.67	1.66	2.51	1.74	0.96	0.37
ester + ethanol	methyl laurate + ethanol	0.65	1.94	1.10	0.76	0.72	0.36
	methyl myristate + ethanol	0.97	1.43	1.90	0.52	1.28	0.16
	methyl oleate + ethanol	1.47	1.03	2.74	1.14	0.91	0.35
	global AAD %	1.03	1.47	1.91	0.81	0.97	0.29
glycerol + water		2.49	3.67	2.84	1.84	2.12	0.72
glycerol + alcohol	glycerol + methanol	3.89	0.86	1.33	4.89	3.37	0.62
	glycerol + ethanol	7.33	1.47	4.03	7.60	7.66	3.52
	glycerol + propanol	3.41	1.24	1.97	4.69	5.51	1.07
	glycerol + 2-propanol	7.52	2.36	4.02	8.64	9.37	2.70
	glycerol + 1-butanol	4.83	0.76	2.98	5.91	9.03	1.03
	global AAD %	5.40	1.34	2.87	6.35	6.99	1.79
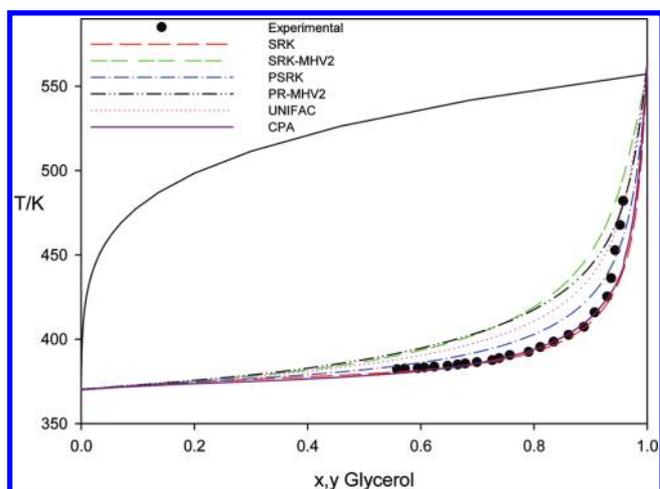
Figure 1. VLE for the glycerol + 1-propanol system, experimental[23] and model results.

extremely difficult to deal with glycerol + water system, using only a single and small binary interaction parameter,[23] providing a global average deviation of just 0.7%.

Binary Systems Containing Fatty Acid Esters and Methanol/Ethanol. Starting with the methanol-containing systems, the UNIFAC and the SRK-MHV2 models described quite well these phase equilibria, with global average deviations of less than 1%. Greater deviations are obtained with the PR-MHV2 model and with the SRK EoS, and even bigger ones, of 2.5%, with the PSRK EoS.

For ethanol + fatty acid ester systems, it cannot be a priori established which model is generally better, as the deviations are system dependent. For the methyl laurate system, the UNIFAC, the SRK-MHV2, and the PR-MHV2 models provide good and

similar results. For methyl myristate, the best model is the PR-MHV2 and for methyl oleate the SRK-MHV2. Global average deviations vary from 0.8% (PR-MHV2) to 1.9% (PSRK) for this kind of system (Table 1).

Using a constant cross-association binary parameter and an ester carbon number-dependent binary interaction parameter, the CPA EoS is the best model to describe the VLE of fatty acid ester + alcohol systems,[24] as seen by the resulting global average deviation lower than 0.4%.

2.2. Liquid—Liquid Equilibria. LLE can be found at several process units during the biodiesel production and purification processes, involving oils, fatty acids and esters, water, alcohols, and glycerol. LLE can be found in the multiphase reactor where the formed glycerol separates from the fatty acid esters phase and two liquid phases coexist, one rich in glycerol and the other rich in biodiesel. Another point where LLE can be found is in biodiesel washing units, where the formed fatty esters-rich current coming out from the reactor is washed in a liquid—liquid extractor in counter current with acidified water to neutralize the catalyst and to convert any soaps to free fatty acids. The raffinate current is composed of water saturated biodiesel, while the extract is a low pH aqueous solution containing the polar compounds.[26,27]

It is thus necessary to properly describe the phase equilibria of fatty acids/fatty acid esters + water and of fatty acid esters + alcohol + glycerol/water systems, to efficiently design and operate such operation units.

Experimental data are available for the water solubility in 11 pure esters (ethyl butanoate, propyl butanoate, methyl hexanoate, methyl heptanoate, methyl octanoate, ethyl decanoate, methyl dodecanoate, methyl tetradecanoate, methyl hexadecanoate, methyl octadecanoate, and methyl oleate) in the temperature range 288.15—323.15 K and at atmospheric pressure[28] and for the water solubility in six carboxylic acids (from

Table 2. Modeling Results for the Water Solubility in Fatty Acid Esters[28]

	AAD %					
	UNIFAC	SRK	PSRK	PR-MHV2	SRK-MHV2	CPA
ethyl butanoate	19.5	54.3	43.9	146	24.7	7.9
propyl butanoate	22.3	49.0	43.8	160	29.3	8.1
methyl hexanoate	25.1	42.8	44.5	168	34.3	7.7
methyl heptanoate	17.6	31.3	29.2	173	47.6	6.3
methyl octanoate	30.6	29.0	36.1	240	63.5	7.9
ethyl decanoate	31.1	28.5	12.2	546	190	6.6
methyl dodecanoate	28.3	19.5	9.1	536	185	8.0
methyl tetradecanoate	28.7	9.7	7.8	673	291	7.3
methyl hexadecanoate	15.8	31.4	11.3	613	225	8.2
methyl octadecanoate	8.3	25.2	22.7	739	322	3.9
methyl oleate	86.9	13.5	23.8	973	767	11.4
global AAD %	28.6	30.4	25.9	452	198	7.6

Figure 2. Water solubility in ethyl decanoate, experimental[28] and model results.

pentanoic to decanoic acids) at temperatures from 288.15 to 323.15 K and at atmospheric pressure.[29]

Data for multicomponent systems available in the open literature are scarce. Data were found for the ternary systems methyl oleate + glycerol + methanol at 313−373 K,[30−32] methyl myristate/methyl laurate/methyl stearate + ethanol + glycerol at 303.15 K,[33] and ethyl laurate/ethyl myristate + ethanol + water at 298.15, 313.15, and 333.15.[34]

It will be shown that opposite of what happened with the VLE modeling, a large difference is observed between the LLE results obtained from the different models. In addition, a discrepancy in the results obtained with the PR and the SRK equations is seen for this type of phase equilibria, as described below.

Description of Water Solubility in Fatty Acid Esters. For all the binary systems investigated here, the water solubility in the ester-rich phase is greatly overestimated by the PR-MHV2 model and, especially for small esters containing systems, underestimated by the SRK EoS. Particularly, the PR-MHV2 model poorly describes these equilibria as seen by its very large global average deviations (Table 2).

Different results are obtained varying with the chain length of the ester (Table 2). For the smaller esters, ethyl and propyl butanoate and methyl hexanoate, the UNIFAC and the SRK-MHV2 models are the best ones in computing the water solubility, and both models providing quite similar results, with global average deviations lower than 34%. On the contrary, for water + methyl heptanoate/methyl octanoate systems, the PSRK equation of state, along with the UNIFAC model, performs better than the SRK-MHV2.

For the heavier ester systems, the PSRK EoS performs better than the other models and performs especially well for methyl dodecanoate- and methyl tetradecanoate-containing mixtures, with global average deviations lower than 9%. However, for the methyl octadecanoate system, the UNIFAC model performs better, once again.

The characteristic difficulty of the SRK MHV2 and PR-MHV2 models, with the existing Lyngby modified UNIFAC parameter table, to describe asymmetric systems[16] is here shown through deviations severely increasing while increasing the chain length of the ester (Table 2).
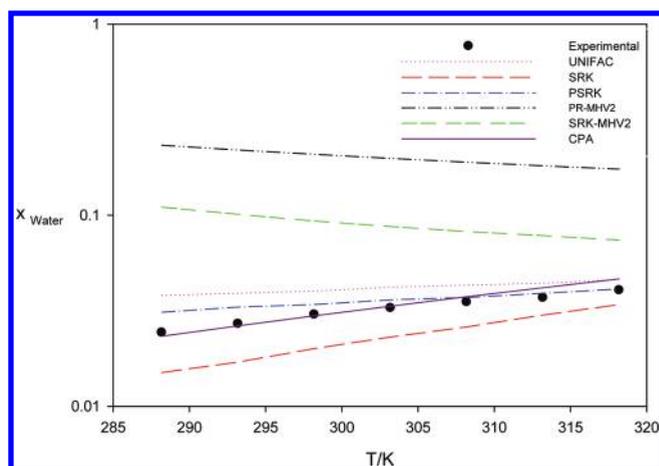
The very good original UNIFAC model results for the small ester systems are expected remembering this model's good ability to deal with associating mixtures at moderate temperature and pressure conditions, such as the phase equilibria of small esters and water-containing systems investigated here. These results show that the original UNIFAC parameters estimated from VLE data can be extrapolated to predict LLE in the considered temperature range.

The SRK EoS underestimates the water solubility and shows to be unable to take into account the solvation between the polar small ester compounds and water.

Surprisingly, the PR and the SRK equations of state do not provide similar results using the same mixing rule, and the PR EoS performs considerably worse for small esters-containing systems.

With a solvation scheme that only involves a constant cross-association binary parameter and an ester carbon number-dependent binary interaction parameter, the CPA EoS performs better than any of the other models to describe the water solubility in fatty acid esters,[28] with a global average deviation of only 7.6%.

Results for the water solubility in ethyl decanoate are shown as an example in Figure 2.

Description of the Mutual Solubilities of Water + Fatty Acid Systems. Systems with carboxylic acids usually have strongly non ideal behavior, therefore being significantly more difficult to model than ester mixtures. Actually, the deviations obtained for these mixtures are significantly higher than the deviations obtained for water + fatty ester systems.

The MHV2 models and the SRK EoS poorly describe the mutual solubilities of these systems. The PR-MHV2 and the SRK-MHV2 models overestimate the solubilities with global average deviations of, for instance, up to 190% for the water solubility, and the SRK EoS, not able to take into account the association interactions, strongly underestimates the mutual solubilities.

The best model is the PSRK EoS followed by the UNIFAC model, as expected due to the good capability of these models to handle systems with strong interactions such as the ones between water and acids.

The complexity in describing these highly polar systems is demonstrated by the overall large average deviations provided by the above referred models for the mutual solubilities of water + fatty acid systems (Table 3).

The advantage of being able to theoretically describe the interactions happening in water + carboxylic acids systems through the CPA EoS is here explicitly shown, seeing that with this association equation of state the deviations are reduced to

Table 3. Modeling Results for the Mutual Solubilities of Water + Acid Systems[29]

	UNIFAC		SRK		PSRK		PR-MHV2		SRK-MHV2		CPA	
	water in acid-rich phase	acid in water-rich phase	water in acid-rich phase	acid in water-rich phase	water in acid-rich phase	acid in water-rich phase	water in acid-rich phase	acid in water-rich phase	water in acid-rich phase	acid in water-rich phase	water in acid-rich phase	acid in water-rich phase
pentanoic acid	8.2	73.0	84.7	168	4.6	53.3	49.0	79.5	19.7	56.8	54.0	51.8
hexanoic acid	26.4	120	76.2	150	26.8	78.5	107	83.9	57.1	77.5	13.0	18.8
heptanoic acid	58.1	282	69.7	100	50.8	414	180	1842	106	677	22.0	2.8
octanoic acid	102	422	63.0	100	79.6	584	317	3271	187	939	25.1	34.7
nonanoic acid	65.9	383	64.8	100	52.1	547	217	4107	124	1029	11.1	8.1
decanoic acid	64.6	220	61.6	100	39.0	366	271	3371	150	375	9.9	9.7
global AAD %	54.2	250	70.0	120	42.2	340	190	2126	107	526	22.5	21.0

Table 4. Modeling Results for the Ternary System Methyl Oleate + Methanol + Glycerol[30−32]

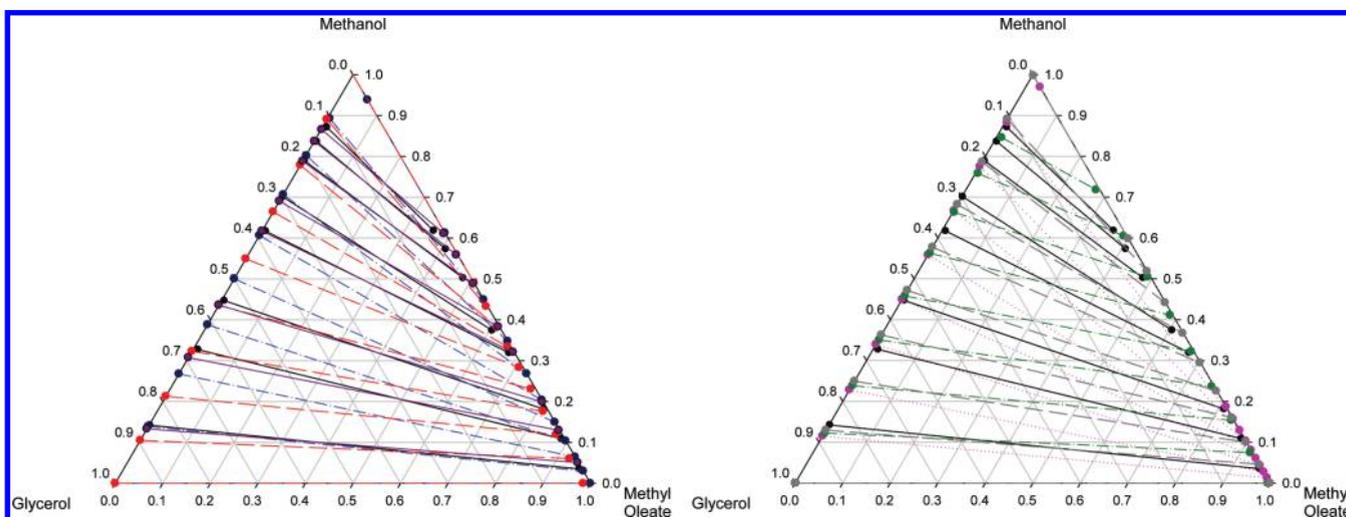|		Δx %					
	T/K	UNIFAC	SRK	PSRK	PR-MHV2	SRK-MHV2	CPA
	313	9.7	5.7	11.6	10.2	4.0	1.6
	333	5.3	6.4	28.4	7.9	3.0	2.7
global Δx %		7.5	6.0	20.0	9.0	3.5	2.2

Figure 3. LLE for the methyl oleate + methanol + glycerol system at 333 K. Experimental,[30−32] "●" and solid lines. Model results, color "●" and lines (blue and dashed−dotted line, UNIFAC; red and dashed line, SRK; pink and dotted line, PSRK; green and dashed−dotted line, PR-MHV2; gray and dashed line, SRK-MHV2; dark pink and solid line, CPA EoS).

23%, with a single, small, and acid chain length-dependent binary interaction parameter.[29]

Again, the VLE group interaction parameters of the original UNIFAC model can be extrapolated to LLE data description. A refitting of the SRK/PR-MHV2 models group interaction parameters seems necessary for water + carboxylic acid systems.

Modeling of the Methyl Oleate + Methanol + Glycerol System. Within the selected cubic EoS, EoS−g^E, and g^E models, the best one to compute the LLE of this system for all the selected temperatures is the SRK-MHV2, providing global average deviations, according to eq 2, of 3.5% (Table 4).

$$\Delta x\% = 100\sqrt{\frac{\sum_n^N \sum_i^C [(x_{i,n}^{\text{phase1, exp}} - x_{i,n}^{\text{phase1, calc}})^2 + (x_{i,n}^{\text{phase2, exp}} - x_{i,n}^{\text{phase2, calc}})^2]}{2NC}}$$
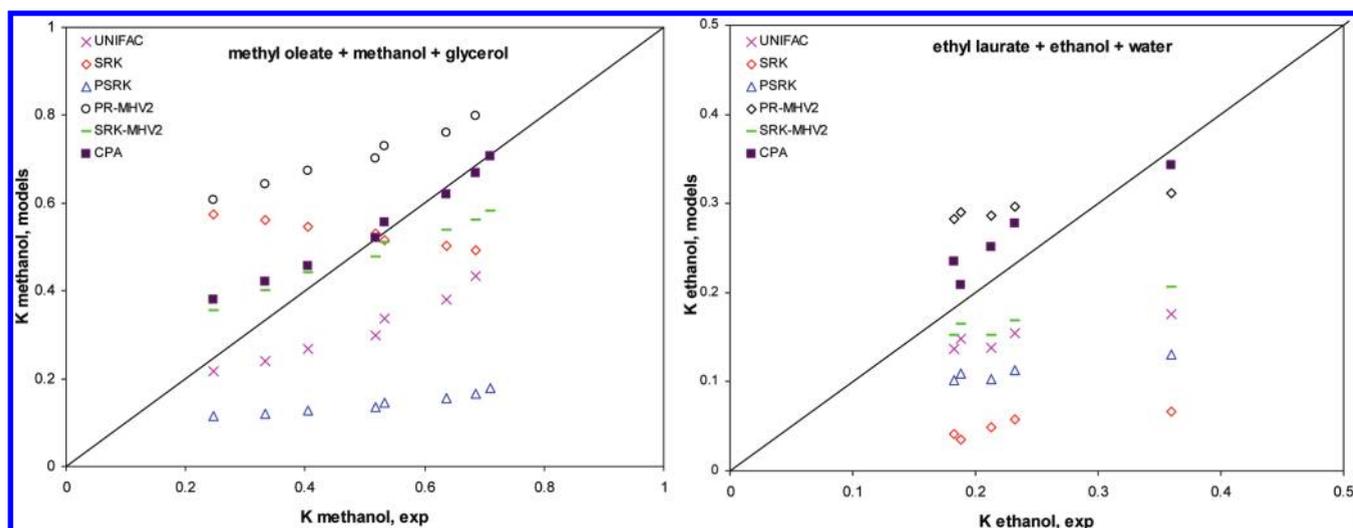
(2)

Figure 4. Alcohol distribution coefficients from the different models versus the experimental distribution coefficients for the methyl oleate + methanol + glycerol and ethyl laurate + ethanol + water systems at 333.15 K.
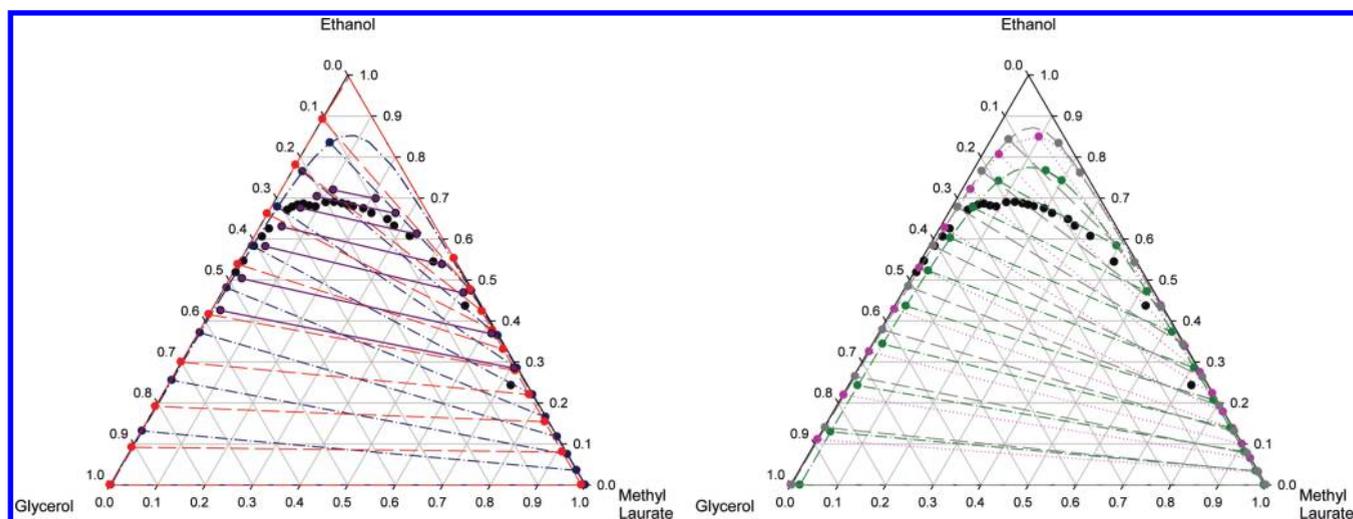

Figure 5. LLE for the methyl laurate + ethanol + glycerol system at 303.15 K. Experimental,[33] "●". Model results, color "●" and lines (blue and dashed−dotted line, UNIFAC; red and dashed line, SRK; pink and dotted line, PSRK; green and dashed−dotted line, PR-MHV2; gray and dashed line, SRK-MHV2; dark pink and solid line, CPA EoS).

where N is the total number of tie lines and C is the total number of components.

The UNIFAC model and the SRK EoS are also able to provide results in good agreement with the experimental data. The PR-MHV2 model underestimates the alcohol solubility in the ester-rich phase, and the PSRK EoS provides a wrong slope for the tie lines. Modeling results obtained at 333 K are depicted in Figure 3, and the methanol distribution coefficient from the different models is plotted versus the experimental coefficient in Figure 4.

As seen in Table 4, the CPA EoS is the most successful model to describe this system at all temperatures, providing deviations of only 2%.

Modeling of the Methyl Laurate/Myristate/Stearate + Ethanol + Glycerol Systems. Because no tie-line data were available for these systems, average deviations cannot be computed as before. However, some results at 303.15 K are presented, as example, in Figure 5, and the following conclusions can be drawn.

Contrary to what is observed for the methyl oleate + methanol + glycerol system, the best model to compute the solubility curve is the PR-MHV2. The other models provide a very large immiscibility region, particularly the SRK EoS. In general, the methyl laurate-containing system is the system better represented by all thermodynamic models.

However, with the same binary interaction and cross-association interaction parameters used to compute the methyl oleate + methanol + glycerol system, the CPA EoS provides a very good prediction of the solubility curves of these systems.[35]

Modeling of the Ethyl Laurate/Myristate + Ethanol + Water Systems. The SRK EoS completely fails to describe these systems at all the considered temperatures. The other models, the PSRK EoS, the SRK-MHV2, the PR-MHV2, and the UNIFAC models, perform very similarly, providing results in good agreement with the experimental data, with global average deviations inferior to 10% (eq 2). Nevertheless, the PSRK EoS performs slightly worse than the other models. Results are presented, as example, in Figures 4 and 6, with global average deviations in Tables 5 and 6.
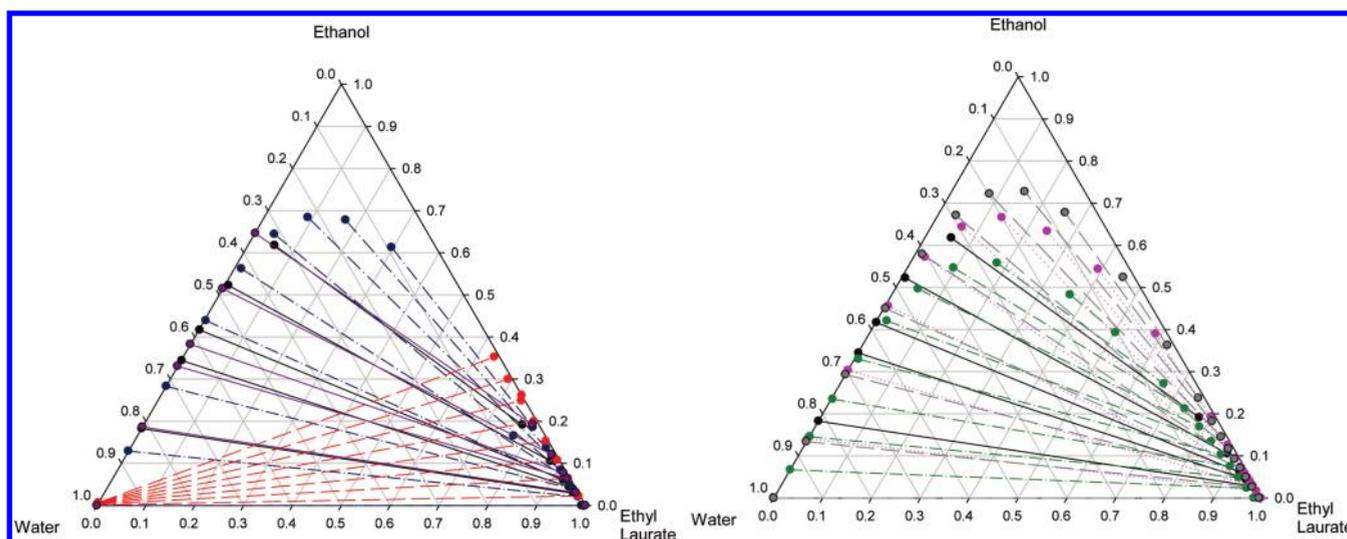
Figure 6. LLE for the ethyl laurate + ethanol + water system at 313.15 K. Experimental,[34] "●" and solid lines. Model results, color "●" and lines (blue and dashed−dotted line, UNIFAC; red and dashed line, SRK; pink and dotted line, PSRK; green and dashed−dotted line, PR-MHV2; gray and dashed line, SRK-MHV2; dark pink and solid line, CPA EoS).

Table 5. Modeling Results for the Ternary System Ethyl Laurate + Ethanol + Water[34]

		Δx %				
	T/K	UNIFAC	PSRK	PR-MHV2	SRK-MHV2	CPA
	298.15	7.9	10.7	10.5	4.9	1.3
	313.15	5.5	7.5	7.8	2.2	2.6
	333.15	3.7	10.0	5.6	7.8	3.3
global Δx %		5.7	9.4	8.0	5.0	2.4

Table 6. Modeling Results for the Ternary System Ethyl Myristate + Ethanol + Water[34]

		Δx %				
	T/K	UNIFAC	PSRK	PR-MHV2	SRK-MHV2	CPA
	298.15	5.4	23.5	16.0	9.1	0.4
	313.15	6.7	23.4	4.4	4.4	1.8
	333.15	16.5	18.2	3.1	1.4	7.9
global Δx %		9.5	21.7	7.8	5.0	3.4

It is also shown that the CPA EoS can provide a very good description of the liquid−liquid equilibria of the selected multicomponent systems in the considered temperature range, using transferable (from binary data) and temperature-independent binary parameters, with global average deviations smaller than 3%. In contrast with what succeeds with the other thermodynamic models, transferable and temperature-independent binary interaction parameters were used with the CPA EoS to successfully predict the LLE of the ternary systems, with the lowest deviations with respect to the experimental data.

The inconsistency of the results from the other models reveals that the existing binary parameters cannot be safely extrapolated from binary systems to ternary data and are not transferable between ternary systems constituted by a fatty acid ester, an alcohol, and glycerol or water. Only the CPA EoS displays a

Table 7. Summary of the Best Models To Be Applied for the Different Systems Selected

	system	best model
VLE	fatty acid ester + methanol/ethanol	UNIFAC
		SRK-MHV2
		CPA
	glycerol + alcohol	SRK
		CPA
	glycerol + water	PR-MHV2
		SRK-MHV2
		CPA
LLE	fatty acid esters + water	UNIFAC
		SRK-MHV2
		CPA
	fatty acids + water	PSRK
		UNIFAC
		CPA
	methyl oleate + methanol + glycerol	UNIFAC
		SRK
		CPA
	methyl laurate + ethanol + water	SRK-MHV2
		PR-MHV2
		UNIFAC
		CPA

reliability that allows its application to all types of phase equilibria and mixtures studied, consistently presenting the best description of the phase equilibria studied.

Table 7 resumes the discussion made above, presenting the best 2−3 models to describe each kind of system.

3. CONCLUSIONS

VLE and LLE data for binary and multicomponent systems composed of fatty acid esters, fatty acids, alcohols, water, and glycerol were used to evaluate the performance of a cubic EoS, g^{E}, EoS−g^{E}, and an association EoS models.

The SRK EoS, as expected, cannot handle the VLE of the polar systems considered, excepting glycerol + alcohol mixtures for which the SRK EoS provides the best results, being related to the near ideal behavior of this system.

With the currently available interaction parameters, the PR-MHV2 and the SRK-MHV2 models can correctly describe the VLE of glycerol and water-containing systems and the VLE of fatty acid ester + methanol/ethanol mixtures. The original UNIFAC and the SRK-MHV2 models are adequate for computing the LLE of water + small fatty acid ester systems and the PSRK EoS and the UNIFAC models to describe water + acid and water + heavier fatty acid ester systems. The SRK EoS provides good results for the LLE of water + heavy fatty acid ester/fatty acid systems than the more complicated models PR-MHV2 and SRK-MHV2, which are unable to deal with asymmetric systems.

Considering ternary systems constituted by a fatty acid ester, an alcohol, and glycerol, the SRK-MHV2 and the PR-MHV2 models are able to calculate tie-lines results in good agreement with the experimental data. When water is involved instead of glycerol, the SRK EoS is not able to describe the LLE data, and the other models provide similar satisfactory results.

Nevertheless, this work conclusively shows that the CPA EoS, through its association term that explicitly takes into consideration the association interactions, is the most adequate, consistent, and reliable model to describe the phase equilibria in the biodiesel production related binary and multicomponent systems. Its predictive character, flexibility, simplicity, and accuracy are self-evident from the results reported in this work.

■ APPENDIX A

A considerable volume of research and review works show in detail the cubic EoS, associative EoS, EoS$-g^E$, and g^E models used in this work. For that reason, that information is only shortly reviewed here.

The Soave−Redlich−Kwong (SRK) equation can be summarized as follows:[6]

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b)} \tag{3}$$

$$a_i = 0.42747 \frac{R^2 T_{c,i}^2}{P_{c,i}} \alpha(T_{R,i}, \omega_i) \tag{4}$$

$$\alpha(T_{R,i}, \omega_i) = [1 + m_i(1 - T_{R,i}^{0.5})]^2 \tag{5}$$

$$b_i = 0.08664 \frac{RT_{c,i}}{P_{c,i}} \tag{6}$$

$$m_i = 0.480 + 1.574\omega_i - 0.176\omega_i \tag{7}$$

The Peng and Robinson (PR) equation is described as:[6]

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)} \tag{8}$$

$$a_i = 0.45724 \frac{R^2 T_{c,i}^2}{P_{c,i}} \alpha(T_{R,i}, \omega_i) \tag{9}$$

$$\alpha(T_{R,i}, \omega_i) = [1 + m_i(1 - T_{R,i}^{0.5})]^2 \tag{10}$$

$$b_i = 0.07780 \frac{RT_{c,i}}{P_{c,i}} \tag{11}$$

$$m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \tag{12}$$

where a_i and b_i are the pure compound parameters, obtained from the pure component critical data, T_c and P_c, and the acentric factor, ω.

When dealing with mixtures, the energy and covolume parameters of the physical term are calculated employing the conventional van der Waals one-fluid mixing rules, with one binary interaction parameter, k_{ij}, for the energy parameter.

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{13}$$

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \tag{14}$$

$$b = \sum_i x_i b_i \tag{15}$$

The SRK and the PR EoS can also be used with the modified Huron−Vidal first- and second-order mixing rules at zero pressure reference state, developed by Dahl and Michelsen,[12] respectively, MHV1 and MHV2. The mixture parameters can be written as:

$$q_1\left(\alpha - \sum_i x_i \alpha_i\right) + q_2\left(\alpha^2 - \sum_i x_i \alpha_i^2\right)$$
$$= \frac{g_0^E}{RT} + \sum_i x_i \ln\left(\frac{b}{b_i}\right) \tag{16}$$

$$\alpha = \frac{a}{bRT} \tag{17}$$

$$\alpha_i = \frac{a_i}{b_i RT} \tag{18}$$

$$b = \sum_i x_i b_i \tag{19}$$

for the SRK EoS form, $q_1 = -0.593$ and $q_2 = 0$ for the MHV1, and $q_1 = -0.478$ and $q_2 = -0.0047$ for the MHV2. For the PR EoS form, $q_1 = -0.53$ and $q_2 = 0$ for the MHV1 and $q_1 = -0.4347$ and $q_2 = -0.003654$ for the MHV2. g_0^E is the excess Gibbs free energy at zero pressure.

The simplest first-order approximation is used in the PSRK model:[14]

$$\alpha = \frac{1}{A_1}\left(\frac{g_0^E}{RT} + \sum_{i=1}^n x_i \ln\left(\frac{b}{b_i}\right)\right) + \sum_{i=1}^n x_i \alpha_i \tag{20}$$

with $A_1 = -0.64663$.

The excess Gibbs energy is subsequently replaced by the term calculated from an activity coefficient model, the Lyngby modified UNIFAC model for MHV2, and the original UNIFAC model for the PSRK.

The original UNIFAC is expressed as a sum of a combinatorial and a residual part:[2]

$$\ln \gamma_i = \ln \gamma_i^{comb} + \ln \gamma_i^{res} \tag{21}$$

The combinatorial expression is the following:

$$\ln \gamma_i^{comb} = \ln \frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i} - 5q_i\left(\ln \frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i}\right) \tag{22}$$

$$\phi_i = \frac{x_i r_i}{\sum_j x_j r_j}$$

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j}$$

where q_i is the pure-component area parameter and r_i is the pure-component volume parameter.

The residual part is given by:

$$\ln \gamma_i^{\text{res}} = \sum_k v_k^{(i)}(\ln \tau_k - \ln \tau_k^{(i)}) \tag{23}$$

$$\ln \tau_k = Q_k \left[1 - \ln(\sum_m \theta_m \psi_{mk}) - \sum_m \frac{\theta_m \psi_{km}}{\sum_n \theta_n \psi_{nm}} \right] \tag{24}$$

where we have the group area fraction θ_m and the group interaction parameter Ψ_{nm}.

Two interaction parameters are needed per pair of functional groups, Ψ_{nm} and Ψ_{mn}. For the Lyngby modified UNIFAC, a temperature dependency is considered for the group interaction parameters. These are also the interaction parameters necessary for EoS/g^E models.

The Aspen Plus 7 software containing the SRK EoS, the PSRK EoS, the SRK-MHV2, the PR-MHV2, and the UNIFAC models was used for model evaluation. The corresponding values for the interaction parameters are available from the Aspen Plus 7 databank.

The Cubic-Plus-Association (CPA) EoS is formed by the combination of the Soave−Redlich−Kwong (SRK) EoS for describing the physical interactions with the association contribution proposed by Wertheim. The CPA EoS is expressed in terms of the compressibility factor as:[20,36]

$$Z = Z^{\text{phys.}} + Z^{\text{assoc.}} = \frac{1}{1 - b\rho} - \frac{a\rho}{RT(1 + b\rho)}$$
$$- \frac{1}{2}\left(1 + \rho \frac{\partial \ln g}{\partial \rho}\right) \sum_i x_i \sum_{A_i} (1 - X_{Ai}) \tag{25}$$

A Soave-type temperature dependency of the pure component energy parameter, a, is used:

$$a(T) = a_0[1 + c_1(1 - \sqrt{T_r})]^2 \tag{26}$$

and b is the covolume parameter, ρ is the molar density, g is a simplified radial distribution function,[37] X_{Ai} is the mole fraction of component i not bonded at site A, and finally x_i is the mole fraction of component i.

X_{Ai} is calculated through the association strength, Δ^{AiBj}, between two sites belonging to two different molecules and is calculated by solving the following set of equations:

$$X_{Ai} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} X_{Bj} \Delta^{A_i B_j}} \tag{27}$$

where

$$\Delta^{A_i B_j} = g(\rho)\left[\exp\left(\frac{\varepsilon^{A_i B_j}}{RT}\right) - 1\right] b_{ij}\beta^{A_i B_j} \tag{28}$$

The following simplified hard-sphere radial distribution function is used:[37]

$$g(\rho) = \frac{1}{1 - 1.9\eta} \tag{29}$$

$$\eta = \frac{1}{4}b\rho \tag{30}$$

The conventional van der Waals one-fluid mixing rules, with one adjustable parameter, k_{ij}, for the energy parameter are applied for the physical part, and the Elliot rule is the most commonly used combining rule for the association energy and volume parameters of the association term.

For the special case of a nonassociating compound that can cross-associate with an associating compound, we used a solvation scheme involving combining rules for the cross-association energy and leaving the cross-association volume, β_{ij}, as an adjustable parameter along with the k_{ij}.

For the CPA EoS, FORTRAN routines previously written were used to compute the phase equilibria.

The previously proposed[23,24,28,29,35] linear correlations for the binary interaction parameters (k_{ij}'s) with the ester/acid carbon number and constant values for the cross-association volumes (β_{ij}) were here applied.

■ AUTHOR INFORMATION

Corresponding Author
*Tel.: +351 234401507. Fax: +351 234370084. E-mail: jcoutinho@ua.pt.

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■ NOMENCLATURE

List of Abbreviations
APACT=associated perturbed anisotopic chain theory
CPA=Cubic-Plus-Association
EoS=equation of state
GC=group contribution
g^E=excess molar Gibbs energy
LLE=liquid−liquid equilibria
MHV1=first-order modified Huron−Vidal mixing rules
MHV2=second-order modified Huron−Vidal mixing rules
NRTL=nonrandom two liquid
PR=Peng−Robinson
PSRK=predictive Soave−Redlich−Kwong
SAFT=statistical associating fluid theory
SRK=Soave−Redlich−Kwong
UNIFAC=universal functional activity coefficient model
UNIQUAC=universal quasichemical model
VLE=vapor−liquid equilibria

List of Symbols

a=energy parameter in the physical term
a_0, c_1=parameters for calculating a
A_i=site A in molecule i
b=covolume
C=total number of components
g=radial distribution function
k_{ij}=binary interaction parameters
N=total number of tie lines
P=vapor pressure
q_i=UNIFAC pure-component area parameter
R=gas constant
T=temperature
x=mole fraction
X_A=fraction of molecule not bonded at site A
Z=compressibility factor
z=UNIFAC coordination number

Greek Symbols

β=association volume
γ=activity coefficient
Δ=association strength
ε=association energy
η=reduced fluid density
θ_i=UNIFAC surface area fraction of component i
ρ=mole density
ϕ_i=UNIFAC segment fraction of component i
Ψ_{nm}=UNIFAC group interaction parameter
ω=acentric factor

Subscripts

i,j=pure component indexes
liq.=liquid
r=reduced

Superscripts

assoc.=association
phys.=physical

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