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Modeling alcohol + water + hydrocarbon mixtures with the group contribution with association equation of state GCA-EoS

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ABSTRACT

The growing interest on first- and second-generation biofuels requires the development of thermodynamic tools with predictive capacity for mixtures containing a wide variety of organo-oxygenated compounds, water and hydrocarbons. Modeling this type of mixtures is challenging due to the presence of association and solvation effects. In this work, we present a revision of the group contribution with association equation of state (GCA-EoS) parameters, with the purpose of extending and improving the predictive capacity of the model for systems containing water, alcohols and hydrocarbons.

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1. Introduction

The group contribution with association equation of state, GCA-EoS, has shown to be a versatile model for correlating and predicting the phase behavior of several mixtures, having associating as well as size-asymmetric molecules [1,2]. The GCA-EoS model takes explicit account of association effects with Wertheim's perturbation theory. In the first version of this model [1,3] water and alcohols were considered to associate via a hydroxyl group having two associating sites with the same energy and volume of association for both types of compounds. Andreatta et al. [4] revised and extended the computational methodology applied in the GCA-EoS model, following the minimization approach proposed by Michelsen and Hendriks [5] and Tan et al. [6] procedure to calculate the fraction of non-associating sites. This GCA-EoS upgrade allows dealing with mixtures having several associating groups that can self-associate or solvate with others.

The increasing interest in biofuels applications reinforces the need of appropriate phase equilibrium tools for process design and optimization in this field. These tools should be able to predict phase equilibria of highly non-ideal mixtures, having associating, polar and non-polar compounds, under a wide range of conditions. The ternary alcohol + water + hydrocarbon is a key system. For instance, methane, methanol, ethanol and butanol are fuels produced by biomass gasification, cracking or fermentation. The study

of blend properties also requires the knowledge of phase behavior of alcohols, water and hydrocarbons. Moreover, there are many other applications that involve binary and ternary mixtures of these compounds, such as the production and dehydration of alcohols and other organo-oxygenated compounds. In the petroleum industry, aqueous solutions of alcohols are widely used. Alcohols are used as fuel additives and inhibitors of hydrate formation. In general aqueous mixtures are widely found in many process streams. In this respect, this work is also a starting point for modeling solubility of hydrocarbons in aqueous solutions of alkanolamines [7,8].

In the field of fossil fuels, the most frequently used equations of state are the classical cubic equations like SRK or PR. These models do not take into account association and solvation effects, which represent an important contribution to the non-ideality of fluid mixtures containing water and/or alcohols. A well-developed approach applied in modeling association is Wertheim's perturbation theory [9,10] for fluids with highly oriented attractive forces. Wertheim's theory has been used in equations of state like the statistical associating fluid theory (SAFT) [11], the cubic plus association equation of state (CPA) [12] and the group contribution with association GCA-EoS equation [3].

Many papers have been published in the literature that model phase equilibria of binary mixtures of water + hydrocarbon, water + alcohol and hydrocarbon + alcohol. However, only few of them include the modeling of ternary mixtures using equations of states that explicitly take into account association effects. Gros et al. were the first authors to model the ternary system water + ethanol + light hydrocarbons (propane, propylene and butane) using the GCA-EoS model [1,13,14]. These authors devel-

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oped the GCA-EoS model to undertake the design of a supercritical ethanol dehydration process, and were able to represent key properties such as water/light hydrocarbon relative volatility and ethanol distribution coefficient between water and light hydrocarbons. In this work the GCA-EoS model was parameterized at the high-temperature, high-pressure range of process working conditions. Kontogeorgis et al. [15] and Voutsas et al. [16] applied the CPA equation of state to model, respectively, water + methanol + alkane (hexane and propane) and water + alcohol (methanol, ethanol and propanol) + alkane (propane, butane and hexane) mixtures. More recently, Li and Englezos [17] made a thorough review of SAFT applications to model vapor–liquid equilibrium (VLE) of systems containing alcohols, water, carbon dioxide and hydrocarbons. Finally, Folas et al. [18] evaluated the effect of the association combination rules applied in the CPA model to account for cross-association in this same type of systems. In all these papers, the ternary mixtures were studied under VLE conditions and, to our knowledge, there is no publication in which the association models were applied to represent ternary liquid–liquid equilibria (LLE).

The aim of this work is to model vapor–liquid and liquid–liquid equilibria and infinite dilution activity coefficients of mixtures containing paraffins, alcohols (C1–C8) and water, applying the GCA-EoS equation. The goal is to extend GCA-EoS model to predict phase behavior under a wide range of conditions, using a single set of model parameters. This will allow us to analyze technologies and processes for biomass treatment and biofuel production and storage. For this purpose, the model parameters are revised on the basis of an extended experimental databank.

2. Model parameterization

GCA-EoS has three contributions to the residual Helmholtz energy: free volume, attractive and association contributions. Model equations and a detailed explanation of each contribution can be found in Gros et al. [1].

Table 1 summarizes the GCA-EoS parameters that characterize each contribution to the Helmholtz energy. In this work, the self-association parameters (energy ε_{ii} and volume κ_{ii}) of the water and alcohol hydrogen-bonding groups were calculated on the basis of water and methanol monomer fractions given by spectroscopic information [19]. A first estimate for the cross-association parameters between water and alcohols was calculated applying the combining rule proposed by Elliot and Lira [20]; however, in an advanced step of the parameterization procedure, these parameters were modified in order to represent with good accuracy the

distribution of alcohol between water and hydrocarbon, under ternary liquid–liquid equilibrium conditions.

Water is considered to have two hydrogen-bonding groups with two associating sites each (one electronegative O and one electropositive H), which is equivalent to a 4C association model. On the other hand, association in alcohols is described with the original 2B hydroxyl group. The values of the corresponding association parameters ε and κ were adjusted to the fraction of non-bonded sites in saturated liquid water and methanol, obtained by Luck [19] from spectroscopic measurements.

The fraction of non-bonded sites in GCA-EoS depends only on the association strength (Δ) and density (ρ_k) of the associating group, given by

$$\Delta = \kappa \left[e^{(\varepsilon/T)} \left(\frac{\varepsilon}{T} \right) - 1 \right] \quad (1)$$

$$\rho_k = \frac{\nu_m}{V} \quad (2)$$

where T is temperature, V molar volume and ν_k the number of times associating group k appears in the molecule.

The advantage of fitting the association parameters to data on water and methanol is that these are pure compounds described by a single group; thus, no binary interaction parameters are involved. The following iterative procedure was used: (i) the association parameters were calculated using experimental data on the monomer fraction and on the saturated liquid density; (ii) pure compound vapor pressure was fitted to obtain the temperature dependence of the energy parameter and the corresponding liquid density at saturation calculated by the GCA-EoS equation; (iii) new association parameters were obtained using the experimental monomer fraction and the GCA-EoS calculated density. Steps (ii) and (iii) were repeated till convergence in density was achieved (only three steps were required for both compounds). The methanol association parameters were applied to all alcohols included in this study. This means that no further fitting was performed in the association term.

The free volume term is a molecular contribution in GCA-EoS and it has a single unknown parameter: the critical hard sphere diameter (d_c). Pereda et al. [21] showed the importance of this parameter in modeling liquid–liquid equilibria in general, and particularly the temperature dependence of the solubility of low-soluble compounds. For instance, the solubility of hydrocarbons in water is very sensitive to the critical diameter of water. For this reason, Pereda et al. [21] proposed to fit d_c to experimental data on liquid–liquid equilibria.

Table 1
GCA-EoS parameters.

Contribution	Parameter	Attribute		
Free-volume ^a		Hard sphere diameter	d_c	Fixed ^b
		Critical temperature	T_c	Fixed
Attractive ^c	Pure group	Reference temperature	T_i^*	Fixed
		Surface area	q_i	Fixed
		Energy ^d	$g_{ii}^*, g_{ii}', g_{ii}''$	Adjustable
	Binary	Energy interaction ^e	k_{ij}, k_{ij}'	Adjustable
		Non-randomness	α_{ij}, α_{ji}	Adjustable
Associating ^c	Pure group	Self-association energy	ε_{ii}	Fixed
		Self-association volume	κ_{ii}	Fixed
	Binary	Cross-association energy	ε_{ij}	Comb. rule/adjus ^f
		Cross-association volume	κ_{ij}	Comb. rule/adjus ^f

^a Molecular term.

^b Calculated from critical point conditions for molecular compounds.

^c Group-contribution term.

^d $g = g^*(g'(T/T^* - 1) + g'' \ln(T/T^*))$.

^e $k_{ij} = k_{ij}^*(1 + k_{ij}'T)$

^f For groups that can only cross associate, these parameters are fitted to binary data.

In the present work, d_c is calculated by solving the model equation at the vapor–liquid critical point, and making the first and second derivatives of pressure with regard to volume equal to zero. The solution of these three equations gives the values of d_c , the molecule surface energy (g) at the critical point and the critical volume. This procedure ensures that, for all compounds treated molecularly (H_2O , methanol, ethanol), the model reproduces the critical point of the pure component (T_c and P_c). This is something that most association models fail to estimate. The predictive capacity at near critical conditions is of major importance for processes using supercritical water or alcohols, like those found in the field of biomass thermal treatment. Moreover, the use of this approach gives a value of d_c that allows a good representation of liquid–liquid equilibria. In the case of compounds described by group contribution, the critical diameter is fixed so that the model reproduces a given data point of the pure compound vapor pressure curve [1].

Finally, both, pure group and binary interaction parameters of the attractive term are fitted to vapor pressure data and phase equilibrium information. Eq. (3) shows the objective function used for fitting the surface energy and binary parameters of the attractive contribution. f_i^{VAP} takes into account deviations in pure compound vapor pressure while f_i^{EQU} covers the equilibrium data

$$OF = w_1^2 \sum_{i=1}^{NVAP} f_i^{VAP} + \sum_{i=1}^{NEQUI} f_i^{EQU} \quad (3)$$

where,

$$f_i^{VAP} = \left(\frac{p_{calc}^{vap}}{p_{exp}^{vap}} - 1 \right)^2 \quad (3.1)$$

$$f_i^{EQU} = \left\{ \begin{array}{l} w_2^2 \left(\frac{y_{1,calc}}{y_{1,exp}} - 1 \right)^2 + \left(\frac{p_{calc}^{vap}}{p_{exp}^{vap}} - 1 \right)^2 \\ w_2^2 \left(\frac{y_{1,calc}}{y_{1,exp}} - 1 \right)^2 + \left(\frac{x_{1,calc}}{x_{1,exp}} - 1 \right)^2 \end{array} \right. \quad (3.2)$$

$$f_i^{EQU} = \left\{ \begin{array}{l} w_2^2 \left(\frac{y_{1,calc}}{y_{1,exp}} - 1 \right)^2 + \left(\frac{x_{1,calc}}{x_{1,exp}} - 1 \right)^2 \\ \left(\frac{x_{1,exp} \phi^{L(T,P,x)}_{exp}}{y_{1,exp} \phi^{V(T,P,x)}_{exp}} - 1 \right)^2 + w_2^2 \left(\frac{x_{2,exp} \phi^{L(T,P,x)}_{exp}}{y_{2,exp} \phi^{V(T,P,x)}_{exp}} - 1 \right)^2 \end{array} \right. \quad (3.3)$$

$$f_i^{EQU} = \left\{ \begin{array}{l} \left(\frac{x_{1,exp} \phi^{L(T,P,x)}_{exp}}{y_{1,exp} \phi^{V(T,P,x)}_{exp}} - 1 \right)^2 + w_2^2 \left(\frac{x_{2,exp} \phi^{L(T,P,x)}_{exp}}{y_{2,exp} \phi^{V(T,P,x)}_{exp}} - 1 \right)^2 \\ \left(\frac{x_{1,exp} \phi^{L(T,P,x)}_{exp}}{y_{1,exp} \phi^{V(T,P,x)}_{exp}} - 1 \right)^2 \end{array} \right. \quad (3.4)$$

$$f_i^{EQU} = \left\{ \begin{array}{l} \left(\frac{x_{1,exp} \phi^{L(T,P,x)}_{exp}}{y_{1,exp} \phi^{V(T,P,x)}_{exp}} - 1 \right)^2 \\ \left(\frac{x_{1,exp} \phi^{L(T,P,x)}_{exp}}{y_{1,exp} \phi^{V(T,P,x)}_{exp}} - 1 \right)^2 \end{array} \right. \quad (3.5)$$

w_1 and w_2 are weighting factors and f_i^{EQU} can take different forms, according to the type of equilibrium calculation that is being performed. Thus, Eq. (3.2) is used for Tx flashes, (3.3) for TP flashes, while Eqs. (3.4) and (3.5) are used when the isofugacity criterion is applied to both or one mixture component, respectively.

Tables 2 and 3 report the final attractive and association parameters, respectively. It is important to highlight that the new binary interaction parameters are closer to the ideal value of one than the original GCA-EoS parameters [1]. Due to the importance of ethanol in the biofuel field, a molecular description was used for this compound, so that its pure-component properties are well described.

The number of binary interaction parameters of this model appears to be too high. However, the benefits of a group-contribution approach should be considered. This approach is highly convenient in two situations: (i) when pure-compound properties and/or mixture phase behavior are unknown. In this case properties can be inferred by building up molecules with their functional groups, whose parameters have been determined from data on other systems; (ii) when the systems under study, such as the ones investigated in this work, are multicomponent mixtures that

Table 2

GCA-EoS pure group and binary interaction energy parameters for the attractive term.

Group	T^* (K)	q	g_{ii}^* (atm cm ⁶ mol ⁻²)	g'_{ii}	g''_{ii}
CH ₃ ^a	600.00	0.848	316,910.0	−0.9274	0.0
CH ₂ ^a	600.00	0.540	356,080.0	−0.8755	0.0
CH ₄ ^a	190.60	1.160	402,440.0	−0.2762	0.0221
C ₂ H ₆ ^a	305.32	1.696	452,560.0	−0.4630	0.0
H ₂ O	647.13	0.866	964,719.8	−1.2379	1.0084
CH ₃ OH	512.60	1.432	547,424.9	−0.6195	0.2488
CH ₃ CH ₂ OH	514.00	1.972	438,928.6	−0.6945	0.1448
CH ₂ OH	512.60	1.124	531,330.3	−0.3201	−0.0168
i	j	k_{ij}	k'_{ij}	α_{ij}	α_{ji}
H ₂ O	CH ₃	1.01	0.06	2	0
	CH ₂	1.04	0.06	2	0
	CH ₃ ^{∞b}	0.75	−0.15	0	0.5
	CH ₂ ^{∞b}	0.76	−0.15	0	2.4
	CH ₄	0.9695	−0.0261	0	0
	C ₂ H ₆	0.9247	−0.0039	0	0
	CH ₃ OH	1	0	0	0
	CH ₂ OH	1.03	0	0	0
CH ₃ OH	CH ₃	0.91	−0.05	1	3
	CH ₂	0.98	−0.05	3	6
CH ₂ OH	CH ₃	0.895	−0.09	0	0
	CH ₂	1.02	0.005	0	0
CH ₃ CH ₂ OH	CH ₃	0.92	−0.05	4	3
	CH ₂	0.99	−0.05	3	0

^a Parameters from Gros et al. [1].

^b Parameters required for an accurate prediction of very low solubility of hydrocarbons in water (see text for details).

can be described with a small number of functional groups. Here, there is an important reduction in the number of binary interaction parameters required to represent the mixture. For instance, if we consider a family of 15 compounds including hydrocarbons and alcohols from C3 up to C10 and water, six sets of binary interaction parameters (i.e. a total of 24 parameters) are required by the GCA-EoS model to describe the interactions between the constituents functional groups (CH₃, CH₂, CH₂OH and H₂O). Molecular models that use a single temperature-independent binary interaction parameter will require 105 parameters to describe a 15 component mixture. In this case experimental information on all possible binaries will be needed to determine those parameters.

Table 3

GCA-EoS association parameters.

Associating group	ε (K)	κ (cm ³ mol ⁻¹)
H ₂ O self-association	2350	0.3787
OH self-association	2758.8	0.8709
H ₂ O/OH cross-association	2832.8	0.2576

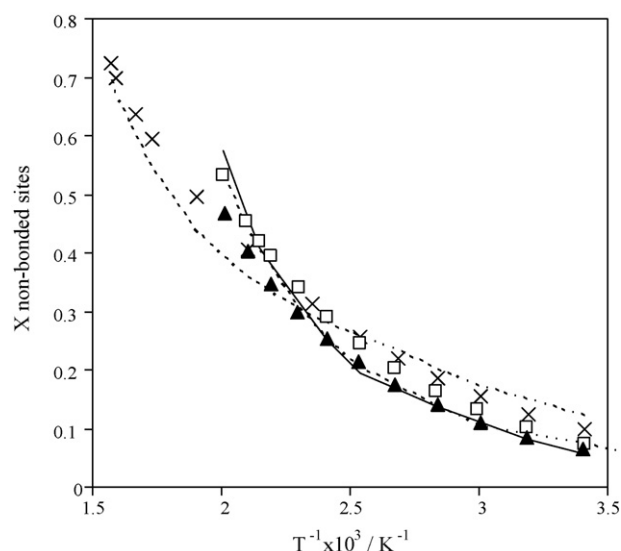


Fig. 1. Non-bonded sites in water and alcohols. Dashed lines: GCA-EoS correlation. Solid line: GCA-EoS prediction. Experimental data [19]: (x) water, (▲) methanol, (□) ethanol.

3. Results

This section reports the results obtained in the calculation of pure-component properties and phase equilibrium conditions with the GCA-EoS model. Some of the results correspond to the correlation of experimental data and show the degree of fitting achieved during parameterization, while others are pure predictions obtained with the parameters reported in Tables 2 and 3. The nature of the results (correlation or prediction) is clearly indicated in each table and figure.

Fig. 1 shows the correlation of non-bonded sites of water and methanol (average relative deviations – ARD% – equal to 8.0 and 7.1, respectively). The figure also includes the prediction of this property for ethanol (ARD% = 14.5). Fig. 2 shows the GCA-EoS correlation and prediction of vapor pressures of several alcohols.

Tables 4 and 5 summarize, respectively, the GCA-EoS correlation and prediction of phase equilibrium in binary systems. These tables report the relative errors in temperature, pressure and/or compositions, as well as the source of

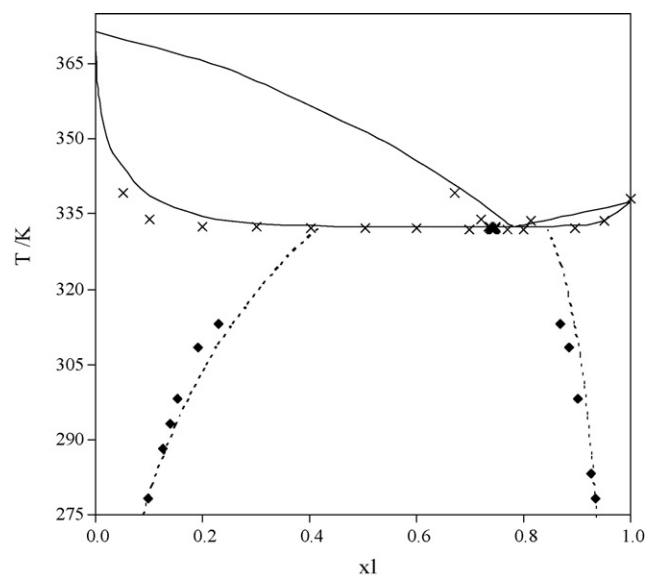


Fig. 3. Vapor–liquid and liquid–liquid equilibria in the system methanol (1) + n-heptane at 1 bar. Dashed lines: GCA-EoS correlation. Solid lines: GCA-EoS prediction. Experimental data (♦) [45], (x) [52].

experimental data, and the temperature and pressure range covered.

Fig. 3 shows GCA-EoS correlation of liquid–liquid and prediction of vapor–liquid equilibria of methanol + heptane binary mixtures. Similarly, Fig. 4 depicts the results for pentanol + water.

Fig. 5 illustrates the model predictive capacity for infinite dilution activity coefficients (γ^∞) of different ethanol + paraffin binaries. GCA-EoS gives good results at both limits of dilution and also follows the correct temperature dependence.

The extension of the model also includes light hydrocarbons (methane and ethane). Fig. 6 presents the solubility of methane in water up to high pressures. In this case the solubility of methane in water was correlated for a few isotherms and the model accurately predicts the vapor phase composition up to 50 MPa.

Regarding ternary systems, part of the data available in the databank was included in the parameterization procedure, in order to assure precise prediction of alcohol partition coef-

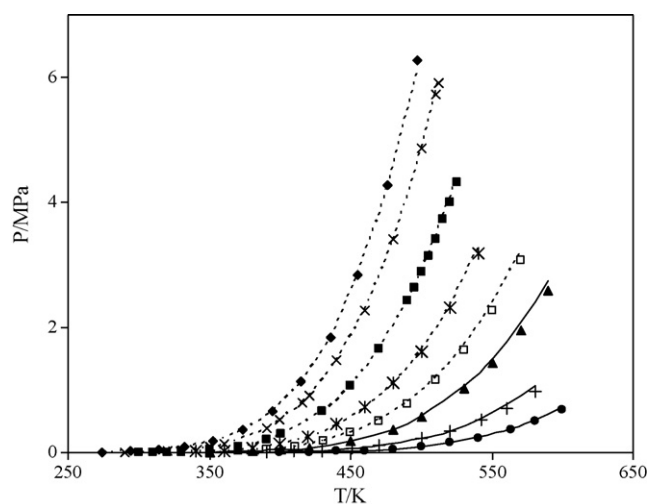


Fig. 2. Alcohol vapor pressures. Dashed lines: GCA-EoS correlation. Solid lines: GCA-EoS predictions. Experimental data DIPPR databank [22]: (♦) methanol, (x) ethanol, (■) propanol, (*) butanol, (□) pentanol, (▲) hexanol, (+) octanol, (●) decanol.

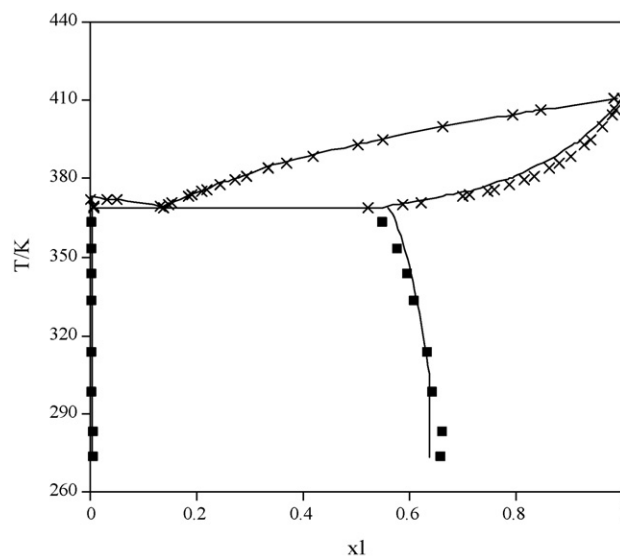


Fig. 4. Vapor–liquid and liquid–liquid equilibria in the system pentanol (1) + water (2) at 1 bar. Experimental data: (x) [42], (■) [47]. Solid lines: GCA-EoS correlation.

Table 4
GCA-EoS correlation of binary data.

Compound		T (K)	P (kPa)	$\Delta z\%$ ^a	$\Delta y_1\%$ ^b	Data points	Source
1	2						
Vapor–liquid equilibria							
Alcohols + paraffins							
Methanol	Ethane	298	1000–4400	3.4	0.6	9	[23]
Methanol	n-butane	323, 443	336–5430	3.3	1.3	18	[24]
Methanol	n-hexane	348	150–240	6.4	4.3	23	[25]
Ethanol	n-Butane	293	85–206	3.5	0.2	13	[26]
Ethanol	n-Hexane	298, 283, 263	2–26	1.9	0.78	54	[27,28]
Ethanol	n-Heptane	298, 303, 313, 343	11–96	2.3	1.2	49	[27,28]
Ethanol	n-Octane	298, 318	7–25	1.9	0.98	37	[27,29]
Propanol	n-Heptane	333	22–30	5.0	2.5	19	[30]
Butanol	n-Pentane	303	5–80	4.2	0.2	13	[31]
Butanol	n-Hexane	298	8–20	3.0	0.5	9	[32]
Butanol	n-Heptane	323	14–19	1.5	1.0	8	[33]
Pentanol	n-Hexane	298	7–20	4.2	0.2	9	[34]
Pentanol	n-Octane	373	37–54	3.2	1.6	13	[35]
Alcohols + water							
Ethanol	Water	523, 548, 573	4081–12,890	5.1	0.77	40	[36]
Ethanol	Water	326–367	33, 51, 101	3.1	1.8	49	[37,38,39]
Propanol	Water	333	21–31	6.4	5.1	13	[40]
Butanol	Water	333	12–25	5.3	3.4	12	[40]
Water	Butanol	366–385	101	4.5	1.2	15	[41]
Water	Pentanol	369–411	101	5.8	0.5	23	[42]
Paraffins + water							
Methane	Water	300–377	2000–25,000	4.7	–	16	[43]
Ethane	Water	278, 293, 343	400–4800	2.8	–	12	[44]
Liquid–liquid equilibria							
Alcohols (A) + paraffins (HC)							
				AAD (ARD%) ^c			
				A in HC	HC in A		
Methanol	n-Heptane	278–313	101	0.006 (4.8)	0.03 (28)	7	[45]
Methanol	n-Hexane	260–307	101	0.08 (35)	0.08 (44)	10	[46]
Alcohol (A) + water (WC)							
				A in W	W in A		
Butanol	Water	273–387	101	0.003 (12)	5×10^{-2} (7)	11	[47]
Pentanol	Water	273–433	101	0.002 (29)	4×10^{-2} (7)	11	[47]
Hexanol	Water	273–443	101	5×10^{-4} (29)	2×10^{-2} (5)	9	[47]
Heptanol	Water	288–323	101	1.4×10^{-4} (50)	2×10^{-2} (7)	4	[47]
Octanol	Water	293–333	101	9×10^{-5} (65)	2.4×10^{-2} (10)	4	[47]

^a $\Delta z\%$ correspond to average relative deviation (ARD) in pressure for isothermal data, in liquid phase composition for isobaric data and in solubility for liquid–liquid equilibria (LLE).

^b $\Delta y\%$ correspond to ARD in vapor phase composition or in solubility for LLE.

^c AAD, average absolute deviation; ARD%, percent average relative deviation.

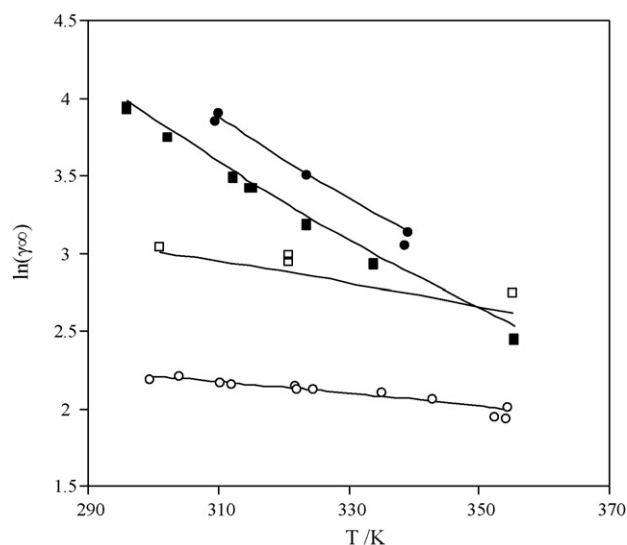


Fig. 5. Ethanol + n-alkane infinite dilution activity coefficients. Experimental data [72]: (●) γ^∞ ethanol in pentane, (■) γ^∞ ethanol in nonane, (□) γ^∞ n-pentane in ethanol and (○) γ^∞ n-nonane in ethanol. Solid lines: GCA-EoS predictions.

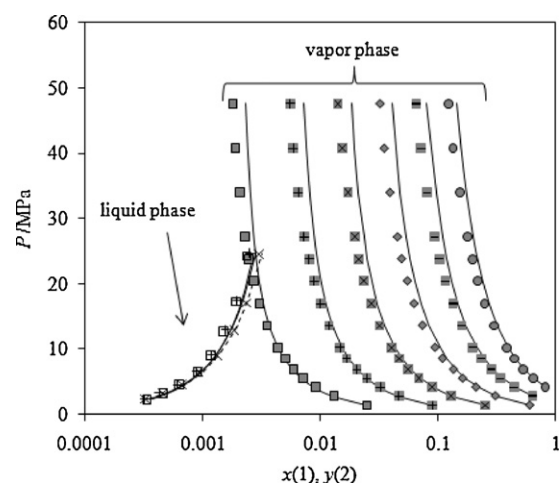


Fig. 6. Vapor–liquid equilibria for the system methane (1) + water (2). Experimental data: empty symbols [43]; methane in liquid phase; full symbols: water in vapor phase [70]. Temperatures: (□) 344 K; (+) 377 K; (×) 410 K; (◇) 444 K; (–) 477 K; 511 K. Dashed lines: GCA-EoS correlation. Solid lines: GCA-EoS predictions.

Table 5
GCA-EoS prediction of binary data.

Compound		T (K)	P (kPa)	$\Delta z\%$ ^a	$\Delta y_1\%$ ^b	Data points	Source
1	2						
Vapor–liquid equilibria							
Alcohols + paraffins							
Methanol	n-Butane	364, 373, 403	370–3090	3.8	2.3	50	[24,48]
Methanol	n-Pentane	303–335	100	4.8	4.4	22	[49]
Methanol	n-Pentane	373	451–846	6.5	5.3	10	[50]
Methanol	n-Hexane	293, 298, 308, 318, 323, 333	13–150	3.5	2.5	142	[25,27,46,51]
Methanol	n-Heptane	298	19.5–22.2	4.0	1.0	15	[27]
Methanol	n-Heptane	331–340	101	5.1	2.5	11	[52]
Methanol	n-Octane	336–345	101	4.9	4.3	11	[52]
n-Hexane	Ethanol	333, 343, 353	91–212	2.8	2.6	56	[53][54]
Ethanol	n-Octane	338, 348	16–95	4.0	1.4	37	[29]
Propanol	n-Pentane	468, 483, 498, 513	1680–4729	2.0	0.9	45	[55]
Propanol	n-Hexane	318	41–48	3.4	0.73	5	[56]
Butanol	n-Hexane	342–381	101	0.2	0.67	18	[57]
Pentanol	n-Pentane	303	3–79	8.7	0.6	13	[58]
Pentanol	n-Heptane	373	57–104	1.8	1.3	10	[35]
Hexanol	n-Hexane	344–421	101	0.37	3.5	15	[59]
Hexanol	n-Heptane	372–427	101	0.95	5.7	14	[59]
Alcohols + alcohols							
Propanol	Butanol	373–388	101	0.15	0.18	7	[60]
Butanol	Pentanol	314–328	3	0.26	4.9	9	[61]
Hexanol	Octanol	365–375	7	0.24	1.2	4	[62]
Octanol	Decanol	441–459	40	0.37	3.4	7	[63]
Alcohols + water							
Methanol	Water	298, 308, 338, 373, 423	4–1355	4.3	2.0	62	[64,65,66]
Methanol	Water	368–424	304, 507	4.2	3.2	52	[67]
Ethanol	Water	423, 473, 598, 623	557–19,000	4.5	0.8	45	[36]
Ethanol	Water	296–355	7, 13	4.0	1.7	25	[38,68]
Water + paraffins							
Water	Methane	310–377	203–2533	8.7	–	24	[43]
Water	Methane	603	1925–9930	53	–	5	[69]
Water	Methane	311–511	132–7397	–	14	123	[70]
Water	Ethane	274–323	41–496	4.0	–	34	[44]
Water	Ethane	298–373	233–365	–	2.1	17	[71]
Water	Ethane	311–511	132–6890	–	29	130	[69]
Infinite dilution activity coefficient γ^∞							
Alcohols(A) + paraffins(HC)							
				A in HC	HC in A		
Ethanol	n-Pentane	310–340, 300–354	101	1.1	1.0	17	[72]
Ethanol	n-Hexane	283–353	101	1.7	1.1	8	[72,73]
Ethanol	n-Heptane	314–366, 322–354	101	2.1	1.3	9	[72]
Ethanol	n-Octane	288–353	101	0.9	1.8	7	[72,73]
Ethanol	n-Nonane	296–355	101	1.9	2.7	17	[72]
Ethanol	n-Decane	306–357	101	1.5	–	4	[72]
Liquid–liquid equilibria							
Alcohols(A) + paraffins (HC)							
				AAD (ARD%) ^c			
				A in HC	HC in A		
Methanol	n-Octane	298–333	101	0.022 (11)	0.046 (45)	8	[74]
Water (W) + paraffins (HC)							
				HC in W	W in HC		
Water	n-Propane	288–370	567–4398	6×10^{-4} (240)	5×10^{-3} (170)	24	[75,76]
Water	n-Butane	298–353	531–1059	1.6×10^{-4} (267)	2.4×10^{-2} (235)	23	[76,77]
Water	n-Pentane	273–343	101–508	2.5×10^{-5} (226)	5×10^{-4} (196)	10	[76,78]
Water	n-Hexane	273–423	101–1255	1.6×10^{-5} (220)	1.7×10^{-2} (191)	13	[76,79,80]
Water	n-Octane	311–539	10–7410	5×10^{-5} (104)	6×10^{-2} (185)	6	[81]

^a $\Delta z\%$ correspond to average relative deviation (ARD) in pressure for isothermal data, in liquid phase composition for isobaric data and in solubility for liquid–liquid equilibria (LLE).

^b $\Delta y\%$ correspond to ARD in vapor phase composition or in solubility for LLE.

^c AAD, average absolute deviation; ARD%, percent average relative deviation.

ficient between water and hydrocarbon. This property is of utmost importance when designing separation processes. The data fitted were liquid–liquid equilibria of ethanol + hexane + water [81,82] and butanol + heptane + water [83] (shown in Fig. 7). The same set of association and interaction parameters are used for all alcohols in the GCA-EoS group-contribution model, which

allows excellent predictions of data on other ternary systems. Fig. 8 presents GCA-EoS predictions of methanol partition coefficients in the ternary methanol + hexane + water [85]. The model accurately reproduces the experimental data. Also a good prediction of the binodal curve is obtained (not shown in the figure).

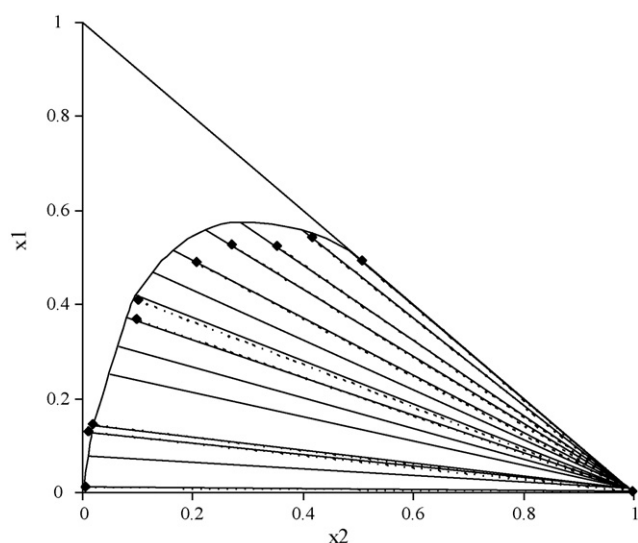


Fig. 7. Ternary system butanol (1)+water (2)+n-heptane (3) at 298.2 K and atmospheric pressure. Experimental data: [84] (dots and dashed tie lines). Solid lines: GCA-EoS correlation.

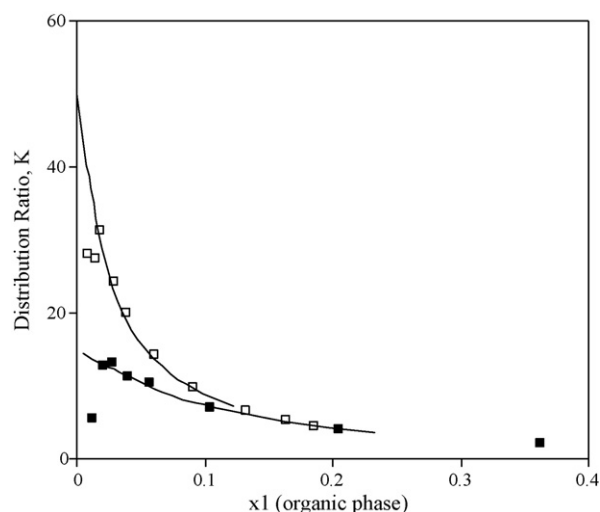


Fig. 8. Methanol partition coefficient in the ternary system methanol (1)+n-hexane (2)+water (3) at (□) 288.15 K and (■) 318 K and atmospheric pressure. Solid lines: GCA-EoS prediction. Experimental data: [85].

The revised set of parameters reported in this work gives low average *relative* deviations for most of the data available (see Tables 4 and 5), except for the binaries water + hydrocarbon (HC), which have extremely low mutual solubility. In this case the average *absolute* deviations are 1.60×10^{-4} for HC solubility

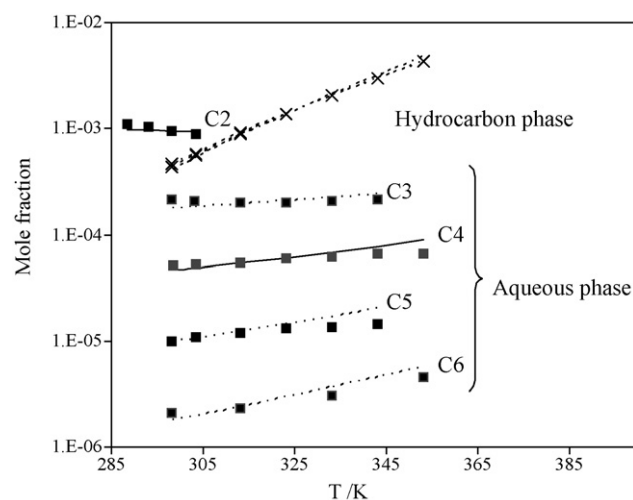


Fig. 9. Water-hydrocarbon mutual solubility. Dashed lines: GCA-EoS correlation. Solid lines: GCA-EoS predictions. Experimental data: (■) hydrocarbon solubility in water phase [76] and (×) water solubility in hydrocarbon phase [86].

in water, 1.16×10^{-2} for water solubility in HC and 1.30×10^{-2} for water composition in the vapor phase. These deviations are reasonably low when the model is used for the exploration of fluid phase conditions. Better results (i.e. low *relative* deviations) should not be expected with group-contribution models, since the environment of paraffin groups when an alcohol is dissolved in water is completely different to that of an alkane dissolved in water.

In previous versions of the group-contribution equation, binary interaction parameters for paraffin groups contained in water-insoluble compounds infinitely diluted in water, are different from the regular paraffin group. Following this approach, the binary interaction parameters reported in Table 2 as H_2O/CH_3^∞ and H_2O/CH_2^∞ should be used in any application of the model that requires highly accurate predictions of the mutual solubility water/hydrocarbon. Table 6 reports the average *relative* deviations for water + hydrocarbon binaries, when this set of parameters is used. Fig. 9 summarizes the degree of fitting achieved in the correlation of water/hydrocarbon mutual solubility from ethane up to hexane. The model correctly reproduces the temperature dependence of the mutual solubility. Butane was left out of the parameterization procedure in order to check the model predictive capacity.

Fig. 10 shows the good accuracy achieved in the prediction of vapor–liquid–liquid equilibria (VLLE) of butane + water system. To our knowledge, there is no other equation of state able to correlate VLLE data of water + hydrocarbons with the accuracy that GCA-EoS does. It is also important to highlight that the use of the H_2O/CH_3^∞ and H_2O/CH_2^∞ parameters is also valid if a low concentration of

Table 6
GCA-EoS modeling of LLVE for water + hydrocarbon (HC) systems.

Compound	N	T (K)	P (kPa)	ARD% _{w-phase} HC in W	ARD% _{HC-phase} W in HC	ARD% _{vapor} W in vapor	Source
Correlation							
Propane	24	288–370	567–4398	17.40	25.8	13.5	[75,76]
n-Pentane	10	273–343	101–508	14.26	2.60	–	[76,78]
n-Hexane	13	273–423	101–1255	31.00	26.0	–	[76,79,80]
n-Octane	6	311–539	10–7410	40	18	–	[81]
Prediction							
n-Butane	23	298–424	414–4300	12.50	50	9.4	[77,76]

ARD%: percent average relative deviation.

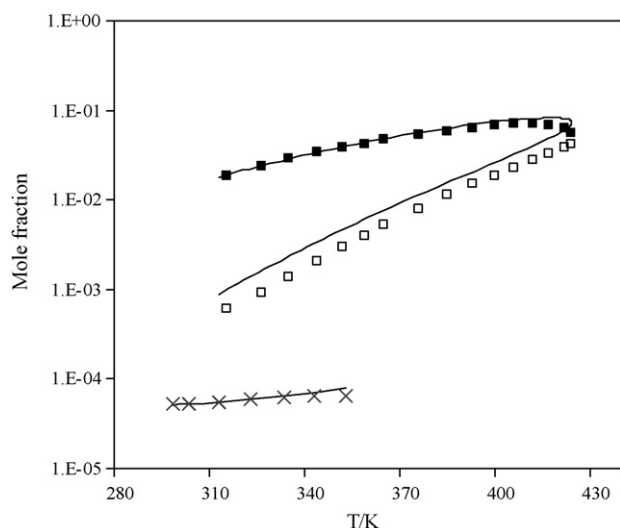


Fig. 10. Vapor–liquid–liquid equilibria of butane + water system. Solid lines: GCA-EoS predictions. Experimental data: (x) butane solubility in the water-rich phase [76], (■) water solubility in the butane-rich phase [77] and (□) water in the vapor phase [77].

alcohol is added to the water + paraffin system. The accuracy of the model in predicting alcohol partition coefficient between water and hydrocarbon is not affected by the use of these parameters.

4. Conclusions

The production of second-generation biofuels requires the development of thermodynamic tools with predictive capacity for mixtures containing a wide variety of organo-oxygenated compounds, water and hydrocarbons. For design purposes, the thermodynamic model should be able to predict qualitatively the phase behavior using a single set of parameters, in order to explore the entire range of potential process conditions. The GCA-EoS model is able to predict vapor–liquid and liquid–liquid equilibria and infinite dilution activity coefficients of mixtures containing water, alcohols and hydrocarbons, using a single set of parameters.

In the case of the binary water + hydrocarbon, the model gives qualitatively good results (good enough for exploratory purposes). However, the accuracy is not similar to the one achieved with the other systems studied. This limitation is consistent with a group-contribution approach, since the environment of a paraffin molecule dissolved in water is completely different to that of a paraffin group within an alcohol molecule dissolved in water. Nevertheless, it is possible to fit a set of parameters specific for the $\text{H}_2\text{O}/\text{CH}_2^\infty$ and $\text{H}_2\text{O}/\text{CH}_3^\infty$ interactions, which can represent the experimental water/hydrocarbon mutual solubility with good accuracy.

List of symbols

AAD	average absolute deviation
ARD	average relative deviations
d_c	hard sphere diameter at the critical temperature (cm mol^{-1})
exp	experimental
calc	calculated
OF	objective function
f^{EQU}	binary equilibrium data residual function
f^{VAP}	pure-component vapor pressure data residual function
g_{ii}^* , g_{ii}' , g_{ii}''	group surface energy ($\text{atm cm}^6 \text{mol}^{-2}$) and temperature dependence
g_{ii}^*	group surface energy at reference temperature T^*

k_{ij} , k'_{ij}	group binary interaction parameters
LLE	liquid–liquid equilibria
P_c	critical pressure (kPa)
q_i	number of surface segments assigned to group i
T_c	critical temperature (K)
T_i^*	reference temperature of the group i (K)
VLE	vapor–liquid equilibria
VLLE	vapor–liquid–liquid equilibria
w_i	weighting factor of the objective function
x_i	mole fraction in liquid phase of the component i
y_i	mole fraction in vapor phase of the component i

Subscripts and superscripts

calc	calculated data
exp	experimental data
L(T,P,x)	property in the liquid phase
NVAP	number of vapor pressure data points
NEQUI	number of binary equilibrium data points
V(T,P,y)	property in the vapor phase

Greek letters

$\Delta z\%$	average relative deviation in variable z
α_{ij} , α_{ji}	non-randomness parameters
ε_{ii}	self-association energy (K)
ε_{ij}	cross-association energy (K)
ϕ	coefficient fugacity
γ^∞	infinite dilution activity coefficient
κ_{ii}	self-association volume ($\text{cm}^3 \text{mol}^{-1}$)
κ_{ij}	cross-association volume ($\text{cm}^3 \text{mol}^{-1}$)

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