

Thermodynamic model for process design, simulation and optimization in the production of biodiesel

N. Cotabarren, P. Hegel, S. Pereda*

Planta Piloto de Ingeniería Química (PLAPIQUI-UNS-CONICET), Camino La Carrindanga Km 7, 8000 Bahía Blanca, Argentina

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ABSTRACT

The separation units of the biodiesel production process require thermodynamic models able to correlate and predict the phase equilibria of mixtures at different stages of the process. Moreover, some units like those in the glycerol washing sector, require high accuracy due to their sensitivity to the components distribution coefficients. In this work, the Group Contribution Equation of State (GCA-EoS) is applied to model several systems of importance in this field. The mixtures evaluated can be highly non-ideal, especially in the last purification steps where polar compounds are infinitely diluted in biodiesel. Experimental VLE and LLE data were satisfactorily correlated and predicted with a single set of interaction parameters, using a simplified version of the association contribution of the model. In this way GCA-EoS can be used for the whole process with a faster convergence of simulated units in comparison with the case of considering the rigorous association model. Furthermore, taking into account that GCA-EoS is a group contribution model, biodiesel production from different raw material, i.e. soy, palm or canola oil, can be predicted without requiring new parameters adjustment. The prediction model can be applied to the design, simulation and optimization of the production and purification sections.

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1. Introduction

With the increasing energy demand and the environmental, economical and political problems arising from the use of fossil fuels, considerable research in renewable fuel sources is being carried out [1]. Biodiesel, which is a blend of methyl or ethyl fatty acid esters (FAAEs), comes up as an alternative to conventional petroleum-based fuels.

A remarkable characteristic of biodiesel is that it can be mixed in all proportions with regular diesel [2]. The conventional method to produce biodiesel is the basic or acid transesterification of vegetable oils and animal fats with an excess of low chain alcohol, particularly methanol or ethanol. The reaction products are fatty acid ester and glycerol [1], having both products commercial value [2]. At the reactor outlet two liquid phases co-exist: one of them rich in glycerol and the other in FAMES. Unreacted alcohol distributes between these two phases. A typical biodiesel production and purification facility contains three main sections: a transesterification unit, a biodiesel purification section and a glycerol recovery section [3]. Purification steps are extremely important in order to produce a fuel in agreement to biodiesel standards [4].

Several thermodynamic models have been developed and upgraded in order to describe phase equilibria of transesterification

products. The UNIFAC model was applied to model LLE of ternary systems with water, acid and short chain esters [5–7]. On the other hand, the NRTL model was used to correlate LLE of ternary mixtures containing water, methanol/propanol and short chain esters [8], [9] and to correlate VLE of binary mixtures with ethanol and methyl esters [10]. Also several cubic equations of state with different mixing rules were applied to CO₂ plus fatty esters or short chain ester mixtures [11–13]. Moreover, the GC-EoS [14] model was extended to fatty esters and applied to predict phase equilibria with supercritical fluids at high pressure [15].

Models which successfully describe polar and highly non-ideal systems in a wide temperature and pressure range like SAFT [16], APACT [17], CPA-EoS [18] and GCA-EoS [19] have been lately developed. Regarding to GCA-EoS, in its first approach to associating mixtures a single (OH) associating group was used to model mixtures of alcohols, water and several inert components as published by Gros et al. [20]. Later, Ferreira et al. [21] extended the model to fatty acids and to deal with cross-association in addition to self-association. Finally, Andreatta et al. [22] presented the application of this version for predicting and correlating phase equilibria from several systems related to biodiesel production.

In this work, GCA-EoS parameters are revised based on binary equilibrium data of FAMES, glycerol, water, methanol and ethanol mixtures. Binary systems involving long chain fatty acids and glycerol are also correlated. The original simplified version of the association contribution will be applied. In this regard, the results of the present work were obtained describing associating compounds

* Corresponding author.

E-mail addresses: spereda@plapiqui.edu.ar, spereda@gmail.com (S. Pereda).

Table 1
GCA-EoS pure-group energy parameters.

Group	q_i	T_i^*	g_{ii}^*	g_{ii}^*	g_{ii}^*	Source
CH ₃	0.848	600.0	316910	−0.9274	0.	[20]
CH ₂	0.540	600.0	356080	−0.8755	0.	[20]
CH ₂ COO	1.420	600.0	831400	−1.0930	0.	[30]
CH ₃ OH	1.432	512.6	816116	−0.3877	0.	[20]
CH ₂ OH	1.124	512.6	787954	−0.3634	0.	[20]
Glycerol	3.060	850.0	510302	−0.3190	0.	[31]
H ₂ O	0.866	647.3	1383953	−0.2493	0.	[20]
COOH	1.224	600.0	999600.5	0.0000	0.	[32]

with a single (OH) associating group. This approach reaches convergence much faster than the rigorous solutions using self and cross association between the different associating groups. The saving of computing time has no significance in the design of one-equilibrium stage equipment. However, when a more complex unit, like a multiple stage column is simulated and optimized, the number of iterations becomes a key parameter.

2. GCA-EoS model

This model was originally proposed by Skjold-Jørgensen [14] as a derivation of combining the van der Waals equation of state, the Carnahan-Starling expression for hard-spheres, the NRTL equation and the group contribution principle. Gros et al. [20] extended the model to represent the association effect of hydrogen bonds in water and alcohols. The inclusion of a single hydroxyl (OH) associating group greatly simplifies the extension of the model to multicomponent mixtures. Ferreira et al. [21] extended the self-association version, by taking into account cross-association effects in mixtures of carboxylic acids with alcohol and water.

The GCA-EoS equation is obtained from the sum of three terms representing the contributions of intermolecular forces: repulsive hard sphere (A^{hs}), dispersive mean field (A^{disp}) and attractive specific (A^{assoc}) interactions. The repulsive and dispersive terms are the same as in the original version of the model [14]. The repulsive term takes into account the size of the molecule through its critical hard sphere diameter (d_c). This value is obtained from the critical properties and vapor pressure data of pure compounds. The attractive contribution has the surface energy (g) as a characteristic parameter, which is calculated by group contribution version of the NRTL model. The groups energy parameters are pure: group parameters (g_{ii}) and binary (k_{ij}) and (α_{ij}) non-random interaction parameters. Finally, the group contribution association term is calculated considering that each associative functional group is characterized by the energy (ε) and volume (κ) of association between bonding-sites as proposed by Wertheim [23,24]. A detail description of each contribution term and an explanation of model equations are given in several works [25–28].

Regarding the group contribution description, methanol and water were described as molecular groups in the attractive term (CH₃OH and H₂O) with one OH associating group. Likewise glycerol (C₃H₈O₃), but in this case with three OH associating groups. All the other compounds included in this work were described by group contribution. Fatty acid methyl ester (FAME) behavior was correlated accurately with methyl oleate (MO) data, which is represented by one ester group (CH₂COO), two CH₃ and 15 CH₂ paraffin groups with the ester group having a negative associating site; therefore, it can cross associate with water and alcohols but do not self-associate. Last, the fatty acids were described by one acid group (COOH), one CH₃ and 10 or 16 CH₂ paraffin group for lauric or stearic acid, respectively. In this case the association follows the scheme proposed by Ferreira et al. [29].

Tables 1 and 2 report the pure group energy parameters and their corresponding binary energy interaction and

Table 2
GCA-EoS binary energy interaction parameters.

Group <i>i</i>	Group <i>j</i>	k_{ij}^*	k_{ij}^*	α_{ij}	α_{ji}	Source
CH ₃ /CH ₂	CH ₂ COO	0.8690	0	0	0	[15]
	CH ₃ OH	1	0	0	0	[22]
CH ₂ COO	CH ₂ OH	0.8500	0	1.620	11.90	[20]
	Glycerol	0.8500	0.0500	25.00	0.590	This work
	H ₂ O	0.7500	0	1.200	1.200	This work
	COOH	0.8520	0	0	0	[29]
	CH ₃ OH	1	0	0	0	[22]
CH ₃ OH	CH ₂ OH	1	0	0	0	[30]
	Glycerol	1.1000	0	0	0	This work
	H ₂ O	1.0657	−0.0369	0	0	[22]
	COOH	1.0300	0	0	0	This work
CH ₂ OH	H ₂ O	1.0300	0	0	0	This work
	COOH	1.0256	0	0	0	[29]
	Glycerol	0.9100	0	0	0	This work
Glycerol	H ₂ O	0.9450	0	0	1.500	This work
	COOH	1.0383	0	0	0	[29]
	COOH	1.0300	0	0	0	This work
COOH	COOH	0.8275	0	20.363	0.645	This work
	H ₂ O	1.0479	0	0	0	[29]

Table 3
GCA-EoS self and cross-association parameters.

<i>i</i>	Self-association		Source	
	ε_{ii} (K)	κ_{ii} (cm ³ mol ^{−1})		
OH	2700.0	0.8621	[20]	
COOH	6300.0	0.0200	[29]	
<i>i</i>	<i>j</i>	Cross-association		Source
		ε_{ij} (K)	κ_{ij} (cm ³ mol ^{−1})	
OH	CH ₂ COO	2105.3	0.9916	[29]
COOH	OH	4500.0	0.1313	[29]

non-randomness parameters, respectively. Table 3 shows parameters for the association contribution (volume and energy of association). Most of the model parameters considered in this work were determined in previous publications, excepted from few binary attractive parameters which were adjusted in the present work to enhanced the prediction accuracy. It is important to highlight that the model is using a single set of parameters not only for different phase equilibria type (VLE, LLE or SLE) but also, due to its group contribution approach, for other compounds not included in the correlation databank. In this work we summarize the model capability to predict phase behavior of compounds that belong to several different organic families, which includes eight functional groups. This may result in a large number of binary interaction parameter, however, as it can be seen in Table 2, only a few parameters are required to correct the attractive energy (g) mixing rule.

3. Results and discussion

This section reports the results achieved in the correlation and prediction of phase equilibria of relevant mixtures for the biodiesel production process. Table 4 summarizes GCA-EoS deviations from VLE and LLE experimental data in temperature and composition of different publications. Source of experimental data, temperature and pressure ranges covered are also reported.

For the vapor–liquid equilibria cases presented earlier it is possible to see that GCA-EoS model accurately predicts the experimental data. Vapor–liquid equilibria for binary systems considered in this work are graphically shown in Figs. 1–3 including experimental data used for its modeling and GCA-EoS performance. It can be seen the good accuracy achieved in the modeling of experimental data with GCA model. Oliveira et al. [33] show that similar accuracy can be achieved by CPA, which is a simpler model, but

Table 4
GCA-EoS modeling results for VLE and LLE of binary systems.

Compounds		T (K)	P (kPa)	$\Delta T\%$ ^c	Data Points	Experimental Data Source
1	2					
Vapor–liquid Equilibria (VLE)						
Biodiesel ^a	Methanol	339–393	101.3	0.48	15	[34]
	Ethanol	354–428	101.3	2.51	15	[34]
Glycerol	Methanol	350–451	101.3	1.17	22	[4]
	Ethanol	363–454	101.3	1.94	19	[4]
	Water	384–481	101.3	1.75	17	[4]
		379–552	101.3	1.90	16	[36]
Liquid–liquid Equilibria (LLE)						
Compounds		T (K)	P (kPa)	Solubility of 2 in 1 ARD % (AAD) ^d	Data Points	Experimental Data Source
1	2					
Biodiesel ^a	Water	322–424	1519.9	7.79 (7.23×10^{-3})	13	[37]
Biodiesel ^b	Glycerol	293–339	506.6	17.8 (5.46×10^{-4})	3	[38]
Biodiesel ^a	Glycerol	333–443	506.6	17.1 (1.17×10^{-3})	12	[37]
Lauric Acid	Glycerol	333–432	506.6	19.1 (1.51×10^{-2})	11	[37]
Stearic Acid	Glycerol	353–397	506.6	25.0 (8.31×10^{-3})	4	[37]

^a Methyl oleate.

^b Palm oil methyl esters.

^c $\Delta T\%$ correspond to average relative deviation (ARD) in temperature for isobaric data.

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

due to its molecular approach, it uses different association and attractive binary interaction parameters for each compound and system, respectively.

Regarding the liquid–liquid equilibria data considered in this work, the GCA-EoS correlations are highly accurate, taking into account that water + biodiesel and glycerol + biodiesel are highly immiscible binary pairs and thus the model predictions become sensitive to the interaction parameters and pure compound critical diameters.

In the case of water solubility in biodiesel, the GCA-EoS binary parameter between water and ester group was correlated using the binary experimental data of water + methyl oleate measured by Korgitzsch [37] and an average deviation of 7.8% was achieved. Oliveira et al. [39,40] also carried out measurements at low temperature, 288 K to 324 K, for this binary. They determined not only water solubility in pure fatty esters (methyl linoleate, methyl oleate and others) but also in synthetic mixtures and biodiesel derived from vegetable oils (biodiesel A, biodiesel B, biodiesel C, biodiesel D,

biodiesel E, biodiesel F, rapeseed, soybean, palm and sunflower). Moreover, the authors also correlated the CPA model with an average deviation between 3.9 and 15.4%. It is important to highlight that, in contrast with GCA-EoS, due to the molecular approach of CPA, a binary interaction parameter had to be fitted for each fatty ester with water.

The data of Oliveira show that water solubility is almost invariant in the different fatty esters considered in their works [39,40]. Table 5 reports the methyl ester composition of the different synthetic mixtures and biodiesels. The GCA-EoS also predicts this invariant behavior. Fig. 4 depicts that there is a small disagreement between the data measured by Korgitzsch [37] and Oliveira et al. [39,40]. These two sets of data were measured in different temperature range; however, it is clear that is not possible to join them with a smooth curve. GCA-EoS prediction of the low temperature data has an average deviation ca. 30%. In this work, the high temperature data was used to correlate the model since this data is more relevant for process simulation

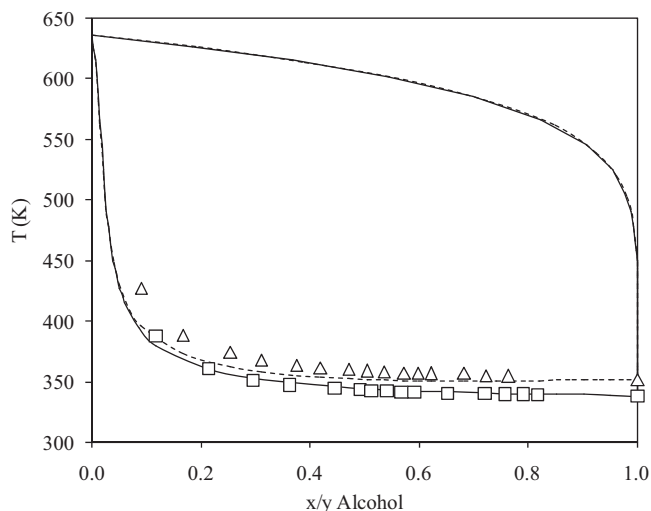


Fig. 1. Vapor–liquid equilibria of methyl oleate + methanol (\square) and methyl oleate + ethanol (Δ) binary systems at atmospheric pressure. GCA-EoS prediction: MO + methanol (solid line) and MO + ethanol (dashed line). Experimental data [34] and pure alcohols normal boiling point [35].

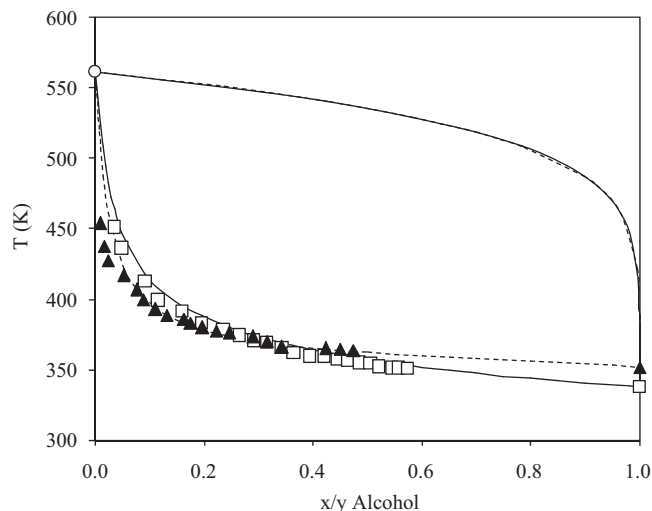


Fig. 2. Vapor–liquid equilibria of glycerol + methanol (\square) and glycerol + ethanol (\blacktriangle) binary systems at atmospheric pressure. GCA-EoS correlation: glycerol + methanol (solid line) and glycerol + ethanol (dashed line). Experimental data [4], pure alcohols and glycerol normal boiling point [35].

Table 5
Compositions of biodiesels studied by Oliveira et al. [39,40].

Methyl ester	Vegetable oil biodiesel [39]				Synthetic biodiesel mixtures [40]					
	Soybean	Rapeseed	Palm	Sunflower	A	B	C	D	E	F
C10		0.01	0.03							
C12		0.04	0.24	0.02						
C14	0.07	0.07	0.57	0.07						
C16	10.76	5.22	42.45	6.4	1.90	10.90		9.80	6.37	6.07
C16:1	0.07	0.2	0.13	0.09						
C18	3.94	1.62	4.02	4.22		0.30		0.10	2.07	1.30
C18:1	22.96	62.11	41.92	23.9	37.80	56.20	86.19	87.40	60.65	63.78
C18:2	53.53	21.07	9.8	64.16	60.30	32.60	13.75	2.20	30.90	22.47
C18:3	7.02	6.95	0.09	0.12						
C20	0.38	0.6	0.36	0.03						
C20:1	0.23	1.35	0.15	0.15						
C22	0.8	0.35	0.09	0.76						
C22:1	0.24	0.19		0.08						
C24		0.22	0.15							

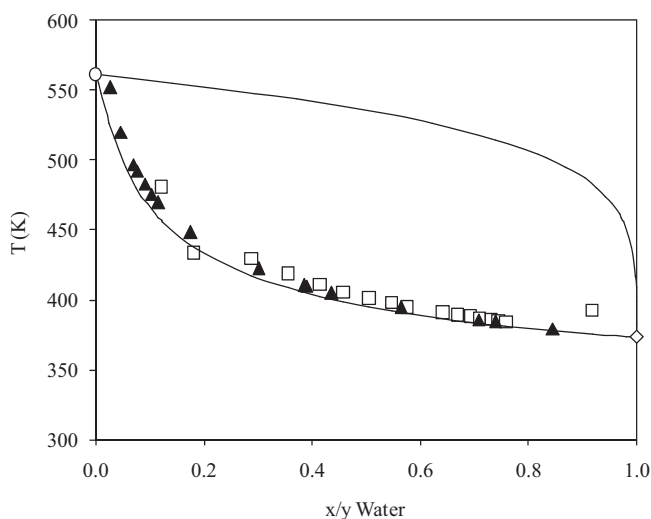


Fig. 3. Vapor–liquid equilibria of glycerol+water binary system at atmospheric pressure. Solid line: GCA-EoS correlation. Experimental data: (□) [4], (▲) [36], glycerol and water boiling point [35].

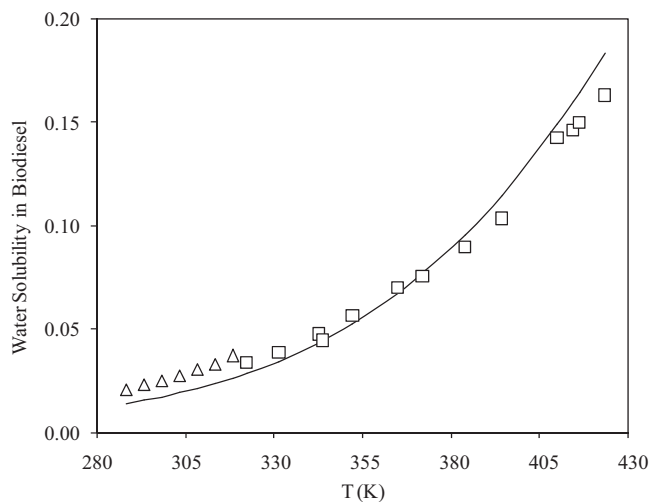


Fig. 4. Water solubility in biodiesel. Solid line: GCA-EoS correlation. Experimental data: Biodiesel F (Δ) [40], methyl oleate (□) [37].

considering the operative temperature range of biodiesel production industry. Fig. 4 also shows GCA-EoS correlation and prediction of the high and low temperature experimental data, respectively.

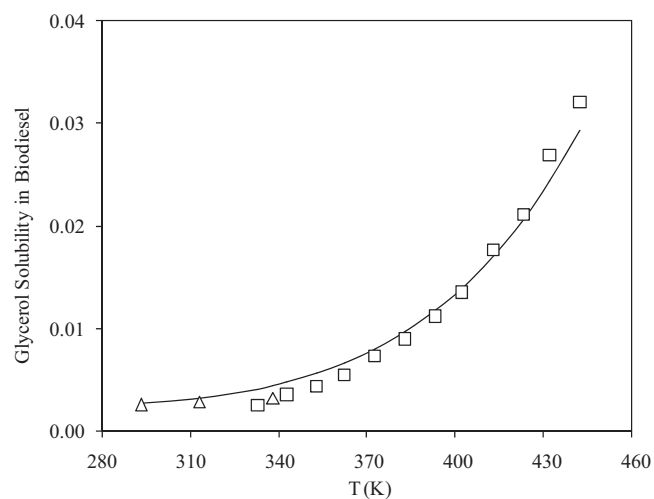


Fig. 5. Glycerol solubility in biodiesel. Solid line: GCA-EoS correlation. Experimental data: Biodiesel (palm oil methyl ester) (Δ) [38], methyl oleate (□) [37].

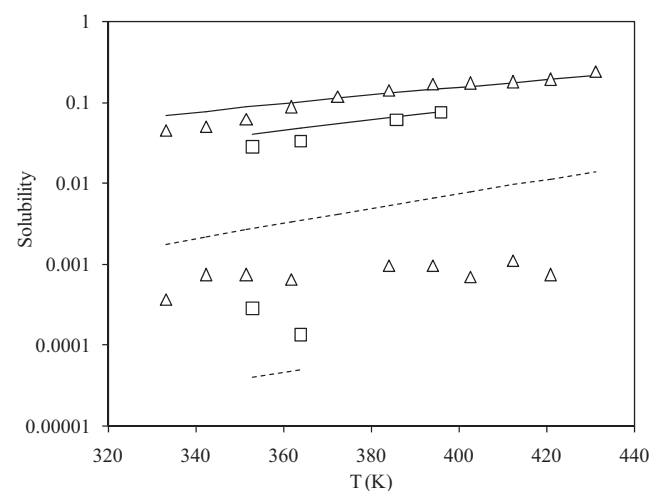


Fig. 6. Temperature dependence of fatty acid + glycerol mutual solubility. Solid and dashed lines GCA-EoS correlation: glycerol solubility in fatty acid (—) and fatty acid solubility in glycerol (---). Experimental data [37]: lauric acid (Δ) and stearic acid (□).

The solubility of water and glycerol in biodiesel become important in the purification units. High accuracy is required in these binaries in order to predict glycerol distribution between water and biodiesel. Figs. 4 and 5 show GCA model correlation of the

water + biodiesel and glycerol + biodiesel binary systems, respectively. The experimental data is reported as molar fraction of water and glycerol in the biodiesel phase. It can be seen the good performance of GCA-EoS for correlating both binaries, which are of importance in the correct design of biodiesel washing units.

Finally, knowledge of fatty acids distribution may become important for alternative technologies that tolerate higher concentration of fatty acids than the conventional biodiesel process [41]. Fig. 6 depicts glycerol + fatty acids (lauric and stearic acid) mutual solubility. GCA-EoS is able to distinguished, by group contribution, the change of glycerol solubility in the acid phase due to the increase in the acid alkyl chain. Moreover, the model also predicts the high immiscibility of the fatty acid in the glycerol

4. Conclusions

The biodiesel production industry requires thermodynamic models able to correlate and predict phase equilibria systems of importance in this field. The accurate description of phase equilibria is necessary in order to get an appropriate design and optimization of production and purification sections.

The GCA-EoS model has been applied to several binary systems of importance in the biodiesel production field. It is important to highlight the fact that GCA-EoS is using the same set of parameters for predicting phase equilibria of all binary systems involved in this work. Moreover, the simplified association description, which considers that water and alcohols association strength is the same, is a good approximation to reduce not only the number of fitting parameters but also the model computing time of non-associated fractions. This assumption did not change the model capacity to accurately correlate experimental data. Considering that GCA-EoS is a group contribution model, esters and derivatives not considered in this work can be predicted without requiring a new adjustment of parameters involved.

List of symbols

A^{assoc}	Helmholtz energy term describing association part
A^{disp}	Helmholtz energy term describing dispersive mean field part
A^{hs}	Helmholtz energy term describing repulsive hard sphere part
AAD	average absolute deviations
ARD	average relative deviations
d_c	hard sphere diameter at the critical temperature (cm mol^{-1})
exp	experimental
calc	calculated
g_{ii}^* , g'_{ii} , g''_{ii}	group surface energy ($\text{atm cm}^6 \text{mol}^{-2}$) and temperature dependence
k_{ij} , k'_{ij}	group binary interaction parameters
q_i	number of surface segments assigned to group i
T_i^*	reference temperature of the group i (K)
LLE	liquid–liquid equilibria
VLE	vapor–liquid equilibria
x_i	mole fraction in liquid phase of the component i
y_i	mole fraction in vapor phase of the component i

Greek letters

α_{ij} , α_{ji}	non-randomness parameters
ε_{ii}	self-association energy (K)
ε_{ij}	cross-association energy (K)
κ_{ii}	self-association volume ($\text{cm}^3 \text{mol}^{-1}$)
κ_{ij}	cross-association volume ($\text{cm}^3 \text{mol}^{-1}$)
$\Delta T\%$	average relative deviation in variable T

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